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Stable cluster formation in aqueous suspensions of iron oxyhydroxide nanoparticles

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Abstract

Metal oxide and oxyhydroxide nanoparticles are important components of natural aqueous systems and have application in photocatalysis. Uncoated (oxyhydr)oxide nanoparticles can form charge-stabilized colloids in water, but the precise regimes of dispersion and aggregation have been determined for very few nanomaterials. We studied the colloidal behavior of ∼6 nm nanoparticles of iron oxyhydroxide (FeOOH), a common natural nanoscale colloid, and found that these nanoparticles formed stable suspended clusters under a range of aqueous conditions. Light and X-ray scattering methods show that suspended fractal nanoclusters are formed between pH 5 and 6.6 with well-defined maximum diameters that can be varied from 25 nm to approximately 1000 nm. The nanoclusters retain a very high surface area, and persist in suspension for at least 10 weeks in solution. The process is partially reversible because optically transparent suspensions are regained when nanoparticles that aggregated and settled at pH >7 are adjusted to pH 4 without stirring. However, completely redispersed nanoparticles are not obtained even after one month. Because nanocluster formation is controlled predominantly by surface charge, we anticipate that many metal oxide and other inorganic nanoparticles will exhibit equivalent cluster-forming behavior. Our results indicate that natural nanoparticles could form stable nanoclusters in groundwater that are likely to be highly mobile, with implications for the long-range transport of surface sorbed contaminants.

Keywords: Nanoparticles; Clusters; Aggregation; Colloid transport; Small-angle X-ray scattering; Dynamic light scattering; Photon correlation spectroscopy

1. Introduction

Colloids are of widespread importance in numerous areas of science, medicine, and engineering [1,2], and of enduring theoretical interest due to the rich behavior that can emerge from apparently simple systems. The conceptual basis of the colloidal behavior of particle suspensions is well established for micron and submicron particles, although quantitative discrepancies persist [3], and surprising behavior, such as colloid jamming [4], has been recently observed. Quantitative experimental tests of the regimes of colloid stability and of aggregation behavior have clarified the validity and limitations of the classical descriptions of colloids. However, nanoparticle suspensions represent an increasingly common colloid because nanomaterials can be produced that possess modified mechanical, optical and electronic properties relative to the bulk. While considerable effort has been directed at making nanoparticles with narrow size distributions that are dispersible in water or in organic media, there have been very few studies of the colloidal behavior of such systems. Moreover, there is now considerable evidence that mineral nanoparticles are common components of natural aqueous systems. Numerous natural inorganic and biologically mediated processes produce mineral nanoparticles such as metal sulfides and metal oxides that can be exceedingly small (<10 nm) [5,6]. Nanoscale iron (oxy)hydroxide phases are among the most common natural mineral nanoparticles [7,8], formed by precipitation from solution following oxidation of aqueous ferrous iron.

Natural nanoparticles exhibit size dependent trends in structure and reactivity that are analogous to those found in synthetic materials [9]. Because the chemistry of these materials involves surface processes, the dispersion behavior of nanoparticles is an important aspect of their effective reactivity in both environ-

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mental and technological settings. Moreover, aggregation is a major factor determining the transport of environmental particles [10], which can move material between redox zones and facilitate or inhibit contaminant transport. Although environmental colloidal particles frequently aggregate in circumneutral water, studies have indicated that certain nanoscale colloids have the ability to travel unexpectedly large distances in the environment [11–13]. Despite numerous observations that nanoscale minerals represent an important fraction of environmental colloids [5–9,11], the fundamental aggregation and transport properties of nanoparticles have not yet been established. We addressed these topics with a study of the colloidal properties of iron oxyhydroxide (α-FeOOH) nanoparticles with diameters of approximately 6 nm.

2. Materials and methods

2.1. Nanoparticle synthesis and characterization

The synthesis method chosen for this work has been used for several independent studies of FeOOH nanoparticle adsorption properties and reactivity [14–16]. Dispersed iron oxyhydroxide nanoparticles were synthesized as follows. 10 mL of 2.4 M $NaCO_3$ was added dropwise to 25 mL of 0.2 M $Fe(III)(NO_3)_3$ during rapid stirring to reach pH 2. Rapid hydrolysis and precipitation was induced by microwave heating at approximately 35 s intervals until the solution had just reached a full boil. Further reaction and particle growth was immediately quenched by plunging the flask into iced water. This procedure was repeated an additional 3 times. The resulting suspension was dialyzed in 1000 MWCO membranes (SpectrumLabs) for at least 3 days against a solution of HNO_3 in ultrapure water at pH 4, replacing the dialysis bath solution regularly. All water used in these experiments was purified to greater than 18 MΩ (Elga UHQ 2) and filtered through 0.1 µm pore membranes. The synthesis method produced a suspension of FeOOH nanoparticles at a concentration of 6.5 g/L. The surface area was determined by the BET method to be $306 \pm 1\ m^2/g$. The crystal phase was investigated by X-ray diffraction, and found to be consistent with a nanoscale and/or highly disordered goethite (α-FeOOH) phase (supplementary Fig. S1). The particle size was determined to be 6 ± 1 nm by high-resolution transmission electron microscopy (Fig. S2).

2.2. Potentiometric titrations

We performed potentiometric (acid–base) titrations of solutions of FeOOH nanoparticles at three ionic strengths to determine the point of zero net surface charge (pH_{znsc}) and the variation of surface charge as a function of pH. We followed standard procedures [17,18], with the exception that CO_2 was not excluded from the nanoparticle suspension prior to the titration. (The consequences of the presence of CO_2 are shown by an aqueous speciation calculation given in Fig. S3.) Specifically, 39 mL of a dialyzed nanoparticle suspension at pH 4 and FeOOH concentration of 6.5 g/L was titrated in a Mettler–Toledo DL50 autotitrator against a freshly prepared solution of 0.0059 M NaOH in ultra pure water. The solution ionic strength was determined by $NaNO_3$ addition, and titrations were performed at 10^{-3}, 10^{-2} and 10^{-1} M $NaNO_3$. The pH was recorded with a Mettler–Toledo combination glass pH electrode that was calibrated with buffers at pH 4, 7 and 10 between each measurement. Each titration took approximately 20 min with a step size of approximately 8 mV. A measurement was recorded once the drift was less than 0.1 mV/s. Separately, background titrations of pH 4 HNO_3 solutions at the same $NaNO_3$ concentrations were performed. The surface charge density was calculated from the titration results by subtracting the blank titration curve from the data and converting the adsorbed proton quantities into charge density using the surface area determined by BET analysis.

2.3. Small-angle X-ray scattering analysis

We acquired small-angle X-ray scattering data from solutions containing FeOOH nanoparticles as a function of pH from pH 4–10 at a temperature range of 21–23 °C. In order to avoid dilution when the solution conditions were altered, the pH was varied by dialyzing nanoparticle solutions against 3 L baths at successively higher pH. The SAXS data were acquired from Stanford Synchrotron Radiation Laboratory (SSRL) beamline 1–4 at 8.333 keV using a configuration that maximized the accessible q-range, attaining almost two orders of magnitude in q. Approximately 0.4 mL of solution was drawn into a SAXS liquid cell with kapton windows and a 1 mm X-ray path length. 2D scattering patterns were collected on a CCD based area detector (Roper) from the sample mounted in one of two positions for acquisition times of 4 min (high-q position) or 8 min (low-q position). The CCD data was binned into 1D intensity data on a calibrated q-axis using macros written in the Image-Pro Plus software by John Pople.

All SAXS data were first processed by subtracting a CCD background (obtained from an X-ray free exposure). Subsequent subtraction of the blank solvent scattering pattern resulted in SAXS data associated with the nanoparticles alone. The measured intensity of the SAXS data from the two positions differed by a geometrical scaling factor that was fitted from the overlapping portion of the data. Data reduction and further analysis was performed with routines written in the Igor-Pro software (Wavemetrics). The mean diameter and fractal dimension of the nanoparticle clusters were estimated by fitting an analytical expression for the SAXS scattering intensity from fractal aggregates to the treated data [20,21]. The SAXS structure factor for fractal aggregates of spherical particles of radius a and fractal dimension, d_f, is calculated from:

$$S(q) = 1 + \frac{1}{(qa)^{d_f}} \frac{2a\Gamma(a-1)}{(a-1)} \sin\left[(a-1)\tan^{-1}(q\xi)\right] \times \left(1 + \frac{1}{(q\xi)^2}\right), \tag{1}$$

where $\Gamma(a-1)$ is the gamma function and ξ is the large-size cut-off in the aggregate density distribution function. A finite size distribution of particle sizes (obtained from a fit to SAXS