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Aggregation kinetics of cerium oxide nanoparticles in monovalent and divalent electrolytes

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ABSTRACT

As a result of the commercial availability and use of nanoparticulate cerium oxide, CeO_2, it is extremely likely that this material will be introduced into the environment requiring knowledge of its fate, transport and bioavailability in natural aquatic systems. To this end, this work probes the physicochemical interactions that govern the aggregation kinetics of cerium oxide nanoparticles using time-resolved dynamic light scattering (TR-DLS) over a range of monovalent, Na^+, and divalent, Ca^{2+}, electrolyte concentrations. Sets of nanoparticles were synthesized by precipitation in aqueous solutions containing varying concentrations of methanol. The point of zero charge (pzc) of these nanoparticles changes as a result of synthesis method. Those produced in the absence of methanol had pzc = 6.5. As predicted by the theories of Derjaguin–Landau–Verwey–Overbeek (DLVO), both reaction-limited and diffusion-limited aggregation were observed in each solution type. The experimental critical coagulation concentrations (CCC) at pH 11.0 was *ca.* 80 mM and *ca.* 16 mM for the monovalent (NaCl) and divalent ($CaCl_2$) salts, respectively. DLVO theory proved to be an adequate predictor for the interactions between cerium oxide nanoparticles albeit the derived Hamaker constant of 1.0×10^{-20} J was somewhat smaller than experimental Hamaker constants determined for other metal oxide nanoparticles. Deviations between experimental data and DLVO theory are discussed.

1. Introduction

Cerium oxide, CeO_2, nanoparticles are known to have multiple commercial applications. The most widely known use for these nanoparticles is as exhaust gas catalysts because they enhance combustion efficiency [1–3]. Additional uses for these nanomaterials are as oxygen ion conductors in solid oxide fuel cells, gas sensors, and as abrasives for polishing [4].

Like transport, the bioavailability, toxicokinetics and toxicodynamics of all nanoparticles are influenced by physicochemical characteristics, including particle size, shape, core composition, and surface chemistry. However, the bioavailability of cerium oxide nanoparticles is poorly understood, primarily because there is a paucity of experimental research focusing on these particles. For example, very little information on the physicochemical interactions between particles or the biophysicochemical interactions of these particles at biological interfaces exists. This is quite surprising in light of the fact that aggregation state of nanoparticles will influence interactions at the nano-bio interface [5]. Regardless, the literature is clear that cerium oxide nanoparticles can be very reactive in biological systems [6–8]. For example, some studies suggest that that they can scavenge reactive oxygen species (ROS) in biological systems thereby attenuating oxidative damage [9] that may accompany ROS formation.

The increased commercial usage of these cerium oxide nanoparticles also increases the probability of their release into the environment, where little is known about their fate in natural aquatic systems. Key characteristics such as aggregation state and favorable conditions for deposition to environmental surfaces have not been studied for cerium oxide nanoparticles to the extent that they have been for other metal oxide nanoparticles [10,11]. In fact, important physiochemical parameters describing cerium oxide such as its point of zero charge (pzc) and its Hamaker constant in aqueous solution are not available in the literature or differ considerably from study to study [12,13].

The purpose of this study is to determine how monovalent and divalent cations control the stability of cerium oxide nanoparticles in aquatic systems, and compare these results to theoretical predictions. To this end we studied the aggregation kinetics of synthetic cerium oxide nanoparticles in aqueous solutions comprised of either Na^+ or Ca^{2+}. The aggregation kinetics of the nanoparticles were studied using time-resolved dynamic light scattering

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(TR-DLS) across a range of solution conditions. The results were compared to predictions based on classic DLVO theory for nanoparticle suspensions [14,15].

2. Materials and methods

2.1. Cerium oxide (CeO_2) synthesis

Cerium oxide nanoparticles were synthesized using a method reported by Chen and Chang [4]. Three different water:methanol solutions of cerium (III) nitrate (Aldrich) were employed at methanol volume percents equal to 0%, 33% and 67%. These solutions were heated to 50 °C before NH_3 (aq) (150 mL, 3.0 M) (Aldrich) was added under constant stirring. Initially we observed the formation of a purple precipitate which later turned yellow indicating the formation of cerium oxide nanoparticles. Particles were aged at 80 °C for 1 week. After aging, the solutions were allowed to cool at room temperature, and then cleaned through a process of centrifugation, decanting of the supernatant, and resuspension in Milli-Q (18.2 MΩ) water until the conductivity of the supernatant was <60 μS. A minimum of five cycles was required to achieve these conditions. Only cleaned nanoparticles were used for all subsequent characterizations and experiments. Particle mass concentrations were determined by gravimetric analysis.

2.2. X-ray diffraction

X-ray powder diffraction was performed using a SCINTAG DMS 2000 equipped with Cu K_α radiation. Dried nanoparticles were ground to a fine powder. Six drops of amyl acetate (Aldrich) and one drop of collodion solution (Aldrich) were added to the powder and mixed. The solution was then transferred to a glass slide using an eyedropper and allowed to dry for more than 1 h. Measurements were taken at a continuous scan rate of 1.20°/min, and the scan was done from 20° to 100° 2θ using filtered Cu radiation and a monochromator. Cu $K_{\alpha 2}$ peaks were corrected for using Scintag software, and the resulting diffraction maxima were determined by Scintag's Peakfinder software and compared to corresponding materials in Scintag's database. The experimental diffraction patterns for each of the three synthesis techniques matched the pattern of synthetic cerium oxide exactly.

2.3. Transmission electron spectroscopy

The size and morphology of the cerium oxide nanoparticles were observed by transmission electron microscopy (TEM). A solution of the 1.0×10^{-9} particles/L CeO_2 nanoparticles was made. One drop (*ca.* 25 μL) containing the solution was deposited on a Formvar- and carbon-coated nickel grid (100 mesh), and the water was immediately removed by absorption onto a filter paper, leaving the nanoparticles on the grid. The grid was air-dried under dust-free conditions and examined in a Tecnai 12 Biotwin electron microscope (FEI) at 100 kV. Images were recorded digitally using a Gatan camera or on film, at magnifications ranging from 68,000× to 98,000×.

2.4. Electrophoretic mobility measurements and zeta potential determination

The electrophoretic mobilities (EPM) of the cerium oxide nanoparticles were measured in 0.01 M NaCl with a Malvern Instruments Zetasizer-ZS. Electrophoretic mobilities were converted to ζ (zeta) potentials using Dispersion Technology Software (v5.10, 2008, Malvern, UK) by employing Smoluchowski's theory (Eq. (1)) for hard particles that are large in comparison to the thickness of the electrical double layer.

$$\mathrm{EPM} = \frac{\varepsilon \zeta}{\eta} \qquad (1)$$

Here ε is the solvent permittivity and η is the solvent viscosity. For determination of the point of zero change, solutions of nanoparticles (*ca.* 20 mg/L) were titrated with NaOH (aq) made from a standardized solution (Aldrich) and filtered through a 0.2 μm syringe filter (Whatman) to remove any dust or particulates that might interfere with these measurements. Titrations were performed using a Malvern Instruments MPT-2 Autotitrator, and measurements were made using a Malvern Instruments folded capillary cell. Titrations covered a range from a pH 4 to pH 12 with measurements made at increments of *ca.* 0.8 pH units. At each pH, the reported zeta potentials and associated uncertainty were determined from six individual measurements of 30 runs each.

2.5. Aggregation kinetics experiments

We employed a single-detector light scattering unit (ALV-CGS-3, Langen, Germany) to make all DLS measurements. The ALV-CGS-3 compact goniometer system employs a 22 mW HeNe Laser (Uniphase) that provided a single-frequency output with a wavelength of 632.8 nm, ALV-proprietary optical fiber based detector, and an Avalanche Photodiode single photon detector. Samples are held in a thermostated index matching quartz vat filled with toluene doubly filtered with 0.02 μm filters (Anotop 25, Whatman). The sample temperature was *ca.* 22 °C, but more importantly never varied by more than 0.5 ° during one run.

Borosilicate culture tubes (Fisher) were used as sample cuvettes for light scattering measurements. Prior to any measurements the cuvettes were soaked in cleaning solution (Extran MA01, Merck KGaA) overnight, rinsed with Milli-Q (18.2 MΩ) water, and dried in an oven before use. A new cuvette was used for each DLS measurement. All sample preparation took place in a class 100 trace metal clean vertical laminar flow hood (Air Clean Products). For sample preparation, the cerium oxide nanoparticle stock solutions were diluted to the appropriate concentration (*ca.* 2 mg/L) with 0.2 μm doubly filtered Milli-Q water and adjusted to the required pH (pH 11.0 ± 0.1) with 0.2 μm filtered NaOH.

To induce aggregation, the appropriate amount of electrolyte stock solution, filtered with 0.1 μm filters (Anotop 25, Whatman), was added to the vial holding 1.0 mL of diluted colloidal sample. The solution was given a brief shake and quickly inserted into the index matching vat. TR-DLS measurements were started immediately. The time to induce aggregation to the beginning of the first DLS measurement was generally less than 15 s and was accounted for during data reduction.

All light scattering measurements were conducted by employing the detector positioned at a scattering angle of 90° from the incident laser beam. The detector signal was fed into the correlator, which accumulated each auto-correlation function for between 7 and 15 s. The intensity-weighted hydrodynamic radius (R_H) of the nanoparticle aggregates was calculated by non-linear least squares fitting of the second order cumulants (ALV software). The measurements were performed over time periods of between 10 min and 12 h because appropriate analysis of time-resolved DLS data requires approximately a 30% increase in the hydrodynamic radius [16]. This provides adequate data to derive the aggregation kinetics of doublet formation since the effective doublet hydrodynamic radius has been reported to be about 1.4 times the primary particle hydrodynamic radius. Time-resolved dynamic light scattering (TR-DLS) was used to measure the intensity of the auto-correlation function of dilute nanoparticle suspensions at varying ionic com-