



Effect of monovalent and divalent cations, anions and fulvic acid on aggregation of citrate-coated silver nanoparticles

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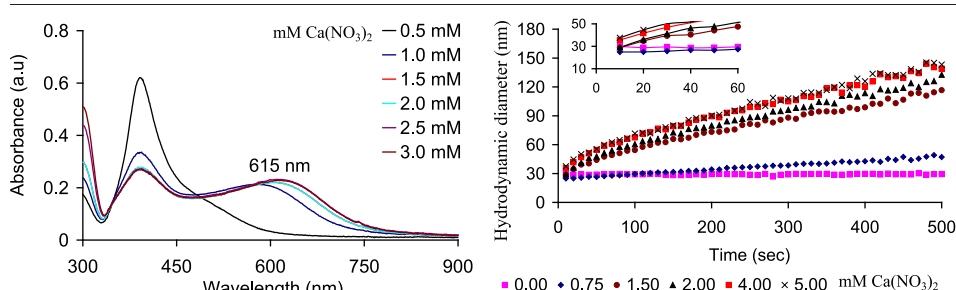
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HIGHLIGHTS

- Potential effect of cations, anions and fulvic acid on aggregation of AgNPs was evaluated.
- Aggregation kinetics was assessed using UV–vis and dynamic light scattering methods.
- Chloride addition enhanced AgNP aggregation.
- Aggregation kinetics appeared additive with mono- and di-valent cations present together.

GRAPHICAL ABSTRACT



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ABSTRACT

The dynamic nature of nanoparticle (NP) aggregation behavior is of paramount interest to many current studies in environmental and toxicological nanoscience. The present study seeks to elucidate the influence that different electrolytes have on the aggregation of citrate-coated silver NPs (cit-AgNPs). The use of both UV–vis spectroscopy and dynamic light scattering (DLS, both z-average hydrodynamic diameter (z-d_h) and size distribution analysis data) allowed improvement in the data quality and interpretation as compared to other studies using only DLS and reporting solely the z-d_h, as the change in the z-d_h can be related to analytical errors and uncertainties rather than only aggregation or dissolution of NPs. Divalent cations (CaCl₂, Ca(NO₃)₂, CaSO₄, MgCl₂ and MgSO₄) have stronger influence (ca. 50–65 fold) on aggregation of cit-AgNPs as compared to monovalent cations (NaCl, NaNO₃, Na₂SO₄), as expected. For electrolytes with monovalent cations, there was no specific ion effect of nitrate and sulfate anions. However, the addition of chloride anions resulted in enhanced apparent aggregation, possibly due to the formation of AgCl NPs that sorb/attach to the surface of cit-AgNPs. Suwannee River fulvic acid enhances the stability of cit-AgNPs and shifts the critical coagulation concentrations to higher electrolyte concentrations for all types of electrolytes. Aggregation kinetics in the presence of mixture of monovalent and divalent cations is additive and controlled by the dominant cations. An empirical formula ($\alpha_{\text{mixture}} = \alpha_{\text{Na}} + (50 \text{ to } 65)\alpha_{\text{Ca}}$) is proposed that reproduces the effect of mixtures of electrolytes in the presence of humic substances and cations that can be used to help predict the aggregation behavior of cit-AgNPs in environmental and ecotoxicological media.

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1. Introduction

Silver nanoparticles (AgNPs) are one of the most widely used nanoparticles (NPs) in the commercial products with applications in cosmetics, fabrics, medical and other consumer products, mainly

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because of their anti-bacterial properties (Fabrega et al., 2011; Woodrow Wilson data base, 2012). The extensive use of AgNPs implies that these NPs are being released to the environment (Mueller and Nowack, 2008; Gottschalk et al., 2010) and recent studies have suggested that there is a potential for AgNPs to enter our waterways (Benn and Westerhoff, 2008; Blaser et al., 2008). Nevertheless, the fate, behavior and effects of AgNPs are, yet, poorly understood. The effect of AgNPs on aquatic environments has received some attention to date (Fabrega et al., 2011). For instance, AgNPs are taken up by rainbow trout, induced expression of *cyp1a2* in the gills, suggesting a possible increase in oxidative metabolism in this tissue (Scown et al., 2010). AgNPs can also inhibit photosynthesis in algae (Navarro et al., 2008). Nevertheless, many questions remain unanswered in regard to their fate, stability and persistence in various environmental compartments or biological test media for ecotoxicology studies (Römer et al., 2011; Tejamaya et al., 2012).

Once released into the environment, the mobility, bioavailability, and toxicity of AgNPs are likely to be largely determined, in addition to NP physico-chemical properties, by their colloidal stability (*i.e.* resistance to aggregation). Numerous toxicological studies have revealed that NPs are much more reactive and toxic than larger particles or aggregates made of the same material (Johnston et al., 2010; Bae et al., 2010). It is therefore of paramount interest to understand and quantify the aggregation behavior of NMs and to develop an approach to predict the behavior of NPs in toxicological media. Colloidal stability of AgNPs has been shown to depend on particle properties such as size, surface charge and capping agent and the water chemistry such as dissolved oxygen level, pH, ionic strength, electrolyte composition and the presence of natural organic macromolecules (Cumberland and Lead, 2009; El Badawy et al., 2010; Li et al., 2010, 2012; Zhang et al., 2011, 2012; Picciapietra et al., 2012; Huynh and Chen, 2011). However, the majority of above-cited studies have ignored the effect of anions on the aggregation behavior of silver NPs as well as the limitations of the dynamic light scattering (DLS). The DLS is the commonly used technique to investigate the aggregation kinetics of NPs in simple salt solutions by measuring the initial rate of change in the *z*-average hydrodynamic diameter (*z*-*d_h*) after mixing with different concentrations of electrolytes (Li et al., 2010, 2012; Huynh and Chen, 2011). However, the *z*-*d_h* measured by DLS is insufficient to interpret the different processes that take place in complex samples such as dissolution and precipitation (*e.g.* formation of new phase) in addition to aggregation. These processes can also bias the aggregation kinetics measured by DLS (Li et al., 2010, 2012).

UV–vis spectroscopy has been used to qualitatively investigate the aggregation behavior of NPs (Kvitek et al., 2008; Chang and Vikesland, 2011), but very little used to quantify the aggregation kinetics of NPs and there is only one study that has used UV–vis to investigate the aggregation kinetics of AgNPs (Moskovits and Vlcová, 2005). Aggregation kinetics can be determined by measuring the rate of loss of the surface plasmon resonance absorption of individual AgNPs in aqueous solution (Moskovits and Vlcová, 2005). By combining UV–vis and DLS, greater information content and certainty in the data quality are produced.

The overall objective of this study is to investigate the colloidal stability and aggregation kinetics of citrate-coated AgNPs (cit-AgNPs) using two complementary techniques (UV–vis and DLS). More specifically, this study aims at investigating the effect on aggregation kinetics of a near-monodisperse cit-AgNPs of (i) single monovalent and divalent electrolytes, (ii) a mixture of electrolytes (iii) Suwannee River fulvic acid and (iv) anions, a parameter largely ignored in previous studies. This study also investigates and compares two different approaches (UV–vis and DLS) for measuring aggregation kinetics of cit-AgNPs. The outcomes of this study can be used to support exposure modeling used to predict the fate of AgNPs in the natural environment, ecotoxicological studies investigating the effect of AgNPs on organisms and to rationalize some of the inconsistent data in the literature on the dissolution/aggregation behavior of AgNPs.

2. Materials and methods

2.1. Synthesis and characterization of silver nanoparticles

Citrate-coated silver NPs (cit-AgNPs) were synthesized and characterized as described in previous publications (Römer et al., 2011; Baalousha and Lead, 2012). Briefly, cit-AgNPs (cit-AgNPs) were prepared by the reduction of silver nitrate in trisodium citrate. A 100 mL of 0.31 mM trisodium citrate, 100 mL of 0.25 mM silver nitrate and 10 mM of sodium borohydride solutions were prepared in high purity water and kept at 4 °C in the dark for 30 min. The silver nitrate and trisodium citrate solutions were mixed together in a conical flask and vigorously stirred. Subsequently, 6 mL of the reducing agent, sodium borohydride, was added in one batch. After 10 min of stirring, the solution was heated slowly to boiling and heated for a further 90 min, left overnight and cooled (4 °C, in the dark). The NPs were cleaned, to remove the excess reagents before use, by ultrafiltration (Amicon, 1 kDa regenerated cellulose membrane, Millipore) using a diafiltration method to prevent NP aggregation and drying. The NPs were redispersed in 0.31 mM trisodium citrate solution to avoid further growth; this process was repeated at least three times.

The concentration of the synthesized AgNPs and the dissolved silver (<1 kDa) in the diluted suspension (3 mL of AgNPs stock suspension in 5 mL ultrahigh purity water) was measured by graphite furnace atomic absorption spectroscopy (AAAnalyst 600 Spectrometer, PerkinElmer). The concentrations of the Ag in the diluted AgNP suspension and of the dissolved silver (<1 kDa) in the stock solution were about 5.58 ± 0.18 and 0.41 ± 0.01 mg L⁻¹, respectively. Thus the concentration of the Ag in the stock AgNP suspension is about 9.3 ± 0.3 mg L⁻¹.

The size and electrophoretic mobility (EPM) were measured by dynamic light scattering and laser Doppler electrophoresis, respectively using a Malvern Zetasizer NanoZS Instrument (Malvern, UK). The Malvern Zeta potential transfer standard consisting of Latex dispersed in pH 9.2 buffer and has an EPM value of -42 mV (DTS1235, Malvern Instrument Limited) was used to verify the performance of the instrument and the zeta potential cell throughout the experiments.

According to the cumulant analysis, the *z*-*d_h*, polydispersity index cit-AgNPs in stock suspension are 29.9 ± 0.6 nm and 0.28 ± 0.026 . According to distribution analysis by DLS, the cit-AgNPs have a bimodal particle size distribution (Fig. S1b) with the first population in the size range of 2–10 nm (represents $5.0 \pm 1.5\%$ of the scattered light intensity) and the second in the range of 20–100 nm (represents $95.0 \pm 5.0\%$ of the scattered light intensity). The EPM of the synthesized AgNPs was $-3.88 \pm 0.2 \times 10^{-8}$ m² s⁻¹. These measurements suggest that the NP suspension is well dispersed. The standard deviation reported here is that of the replicate measurement and not that of the size/EPM distributions. Thus the standard deviation indicated the stability of the replicate measurements rather than the width of the distribution.

The optical absorbance spectrum of the AgNPs were collected by a UV–vis spectrometer (6800 Double-Beam Spectrometer (Jenway, UK)) using a 100 mm path length cuvette, which allowed analysis of AgNPs at relatively low concentrations (370 µg L⁻¹) compared to the large majority of available studies on AgNPs. UV–vis spectra of cit-AgNP suspensions (370 µg L⁻¹) were collected over wavelengths (λ) 300–900 nm. The UV–vis spectra of the cit-AgNPs in MQ water show a single peak centered at 392 nm (Fig. S1a).

The synthesized cit-AgNPs were also characterized in previous studies and can be described as hard spheres (Baalousha and Lead, 2012) with a number average diameter of 17.0 ± 6.0 nm as measured by transmission electron microscopy (Fig. S1c) and weight average hydrodynamic diameter of 20.8 nm as measured by flow-field flow fractionation.

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