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The impact of stabilization mechanism on the aggregation kinetics of silver nanoparticles

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ABSTRACT

The use of silver nanoparticles (AgNPs) for various applications is growing drastically. The increase in use will eventually lead to their release into the environment. The tendency of AgNPs to aggregate and the kinetics of aggregation are major factors that govern their fate in the environment. Dynamic light scattering (DLS) was utilized to investigate the electrolyte-induced aggregation kinetics ($NaNO_3$, NaCl and $Ca(NO_3)_2$) of coated and uncoated AgNPs which are electrostatically (H_2-AgNPs and Citrate-AgNPs), sterically (polyvinylpyrrolidone (PVP)-AgNPs) and electrosterically (branched polyethyleneimine (BPEI)-AgNPs) stabilized. The aggregation kinetics of the electrostatically stabilized AgNPs was in agreement with the classical Derjaguin–Landau–Verwey–Overbeek (DLVO) theory and the AgNPs exhibited both reaction-limited and diffusion-limited regimes. The H_2-AgNPs had critical coagulation concentrations (CCC) of 25, 30 and 3 mM in the presence of $NaNO_3$, NaCl and $Ca(NO_3)_2$ salts, respectively. The Citrate-AgNPs had CCC of 70, 70 and 5 mM in the presence of $NaNO_3$, NaCl and $Ca(NO_3)_2$ salts, respectively. The values of the Hamaker constant for the electrostatically stabilized AgNPs were also determined and the values were in agreement with the reported values for metallic particles. The aggregation kinetics for both the sterically and electrosterically stabilized AgNPs (PVP-AgNPs and BPEI-AgNPs) was not in agreement with the DLVO theory and the particles were resistant to aggregation even at high ionic strength and electrolyte valence. The PVP-AgNPs and the BPEI-AgNPs had no critical aggregation concentration value at the investigated ionic strength values.

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1. Introduction

The unique properties of nanoparticles, including nanosilver, allow for their use in a wide spectrum of applications and consumer products (Tolaymat et al., 2010; Rai et al., 2009; Blaser et al., 2008; Silver et al., 2006; Li et al., 2008). There is a potential for release of both engineered and anthropogenic nanominerals into environmental systems where their fate and transport will be influenced by their propensity to aggregate (Chen et al., 2005; Benn and Westerhoff, 2008; Ribeiro et al., 2010; El Badawy et al., 2010; Silva et al., 2011, 2012; Quispe et al., 2012). Research has demonstrated that both the surface properties and the solution chemistry (e.g., pH, ionic strength and the background electrolyte type) influence the aggregation behavior of nanoparticles (El Badawy et al., 2010; Hower et al., 2008; Oliveira et al., 2012).

It is crucial to investigate the aggregation kinetics of nanoparticles under environmental conditions. Several experimental techniques have been employed to evaluate the electrolyte-induced aggregation of colloidal systems. More recently, light scattering techniques have become common place when measuring the extent of colloidal aggregation. Li et al. (2010) used dynamic light scattering (DLS) to measure the aggregation kinetics of bare AgNPs (synthesized by the reduction of the $Ag(NH_3)^{2+}$ with D-maltose) in the presence of monovalent and divalent electrolytes. The critical coagulation concentrations (CCC) for the bare AgNPs in the presence of $NaNO_3$, NaCl and $CaCl_2$ were 30, 40 and 2 mM, respectively. The aggregation results for the AgNPs were found to be consistent with the classical Derjaguin–Landau–Verwey–Overbeek (DLVO) theory. An Huynh and Chen (2011) investigated the aggregation kinetics of citrate and polyvinylpyrrolidone stabilized silver nanoparticles (Citrate-AgNPs and PVP-AgNPs) in monovalent and divalent electrolyte solutions. The CCC of Citrate-AgNPs were 47.6 mM, 2.1 mM and 2.7 mM for NaCl, $CaCl_2$ and $MgCl_2$, respectively. The PVP-AgNPs were more stable and the CCC was 111.5 mM, 4.9 mM and 2.1 mM for NaCl, $CaCl_2$ and $MgCl_2$, respectively.

An extensive number of capping agents are being utilized for the stabilization of AgNPs (Tolaymat et al., 2010). The type of capping agent determines the stabilization mechanism of the AgNPs. The

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current study aims at investigating the impact of the stabilization mechanism on the aggregation kinetics of AgNPs. The aggregation kinetics of electrostatically, sterically and electrosterically stabilized AgNPs were investigated in monovalent and divalent electrolytes. Even though few studies have investigated the aggregation kinetics of some types of AgNPs, the current study is unique in a number of aspects related to the preparation and the selection criteria for the AgNPs. The AgNP suspensions utilized herein were coated with the stabilizing agents during the synthesis process that guaranteed the complete coating of the AgNPs with the stabilizing agent. The synthesized AgNPs were purified using ultrafiltration membranes to remove any residual chemicals remaining in the suspensions in order to assure that the results are not impacted by these impurities. Furthermore, the selected AgNPs do not only represent nanoparticles stabilized through the common stabilization mechanisms but also represent AgNPs exhibiting the various surface charging scenarios (positive, neutral and negative).

2. Experimental section

2.1. AgNP suspension synthesis and purification

Silver nanoparticles with three different capping agents as well as one uncoated AgNP were investigated. The nanoparticles were synthesized using procedures reported in the literature with slight modifications in order to generate nanoparticles with specific morphologies. The details of the synthesis of the investigated AgNP suspensions are presented in supporting information (SI). The AgNPs were, 1) uncoated hydrogen reduced AgNPs (H_2-AgNPs), 2) citrate coated AgNPs (Citrate AgNPs), 3) polyvinylpyrrolidone coated AgNPs (PVP-AgNPs) and 4) branched polyethyleneimine coated AgNPs (BPEI-AgNPs).

The purification (removal of residual impurities) of the synthesized AgNPs was performed using 10 kDa polyethersulfone (PES) membrane (Spectrum Labs MidiKros Hollow Fiber Module (P-X3-010E-300-02N)) (El Badawy et al., 2011). A schematic of the purification system is provided in Fig. S1 (SI). The purification procedure encompassed an initial process of concentrating the AgNP suspensions followed by a Milli-Q water (0.67 μs cm^{-1} conductivity) exchange process in order to remove free Ag^+ ions as well as other impurities from the AgNP suspensions. A conductivity of the purified AgNP suspensions of <5 μs cm^{-1} was used as an indicator for satisfactory purification.

2.2. Determination of AgNP aggregation kinetics

The change in hydrodynamic diameter (HDD) with time of the AgNPs was examined at pH 7.0 (adjusted using 0.01 M solutions of NaOH and/or HNO_3) as a function of ionic strength using three different background electrolytes (NaCl, $NaNO_3$ and $Ca(NO_3)_2$). The AgNP concentration was held constant at 2E11 particles mL^{-1} (mass concentrations are presented in Table 1). After AgNP synthesis and purification, the aggregation experiments were performed as follows: 1) the pH of the AgNP stock suspensions (2E11 particles mL^{-1} concentration) was adjusted to 7.0, 2) the amount of salt corresponding to the target ionic strength was weighed out and placed in 15 mL centrifuge tubes, 3) 10 mL of AgNP suspensions was added to the previously weighed out salt and 4) the measurement of the HDD as a function of time was immediately initiated after the salt was rapidly mixed with the AgNP suspensions. The HDD data were collected for 10 min with a rate of 1 reading every 10 s.

The HDD and zeta potential (ζ) of the AgNPs were determined by DLS using a Zetasizer Nanoseries (Malvern Instruments) with a 633 nm laser source and a detection angle of 173° (the HDD detection ranges from 1 nm to 10 μm). The total Ag mass concentration was measured using a PerkinElmer AAnalyst 800 atomic absorption spectrometer after microwave acid digestion following the EPA method 3015.

The rate of change in the hydrodynamic radius of a colloidal particle at a fixed scattering angle can be used to determine the aggregation rate constant (k_{11}) using the following relationship (Chen et al., 2006; Kleimann et al., 2005):

$$\frac{1}{r_{h\ (0,q)}}\left(\frac{dr_{h(t,q)}}{dt}\right)_{t\to 0} = k_{11}\ N_0\left[1+\frac{\sin(2aq)}{2aq}\right]\left(1-\frac{1}{\delta}\right) \quad (1)$$

where q is the scattering vector ($q = \left({}^{4\pi n}/_{\lambda}\right)\sin(\theta/2)$), n is the refractive index of the medium, r_h (t, q) is the hydrodynamic radius as a function of time, λ is the wavelength of light, θ is the scattering angle, k_{11} is the absolute aggregation rate constant, N_0 is the initial primary particle concentration, a is the primary particle radius and δ is the relative hydrodynamic radius of the doublet which is approximately 1.38 (Holthoff et al., 1996; Chen et al., 2006).

The value of dr_h/dt for both the slow and fast aggregation regimes can be determined from the slope of the best fit of the increase in hydrodynamic radius with time. Providing the same initial particle concentration of AgNPs for both aggregation regimes, the value of the attachment efficiency α (the probability of an irreversible attachment from the collision of two colloidal particles) could be obtained by dividing the slope dr_h/dt for the slow aggregation regime at a given ionic strength over the slope $(dr_h/dt)_{fast}$ of the fast aggregation regime. Thus, the attachment efficiency could be obtained from the following relationship (Liu et al., 2009; Chen and Elimelech, 2007):

$$\propto = \frac{1}{W} = \frac{k_{11}}{(k_{11})_{fast}} = \frac{\frac{1}{N_0}\left(\frac{d_{rh(t,q)}}{dt}\right)_{t\to 0}}{\left(\frac{1}{(N_0)_{fast}}\left(\frac{d_{rh(t,q)}}{dt}\right)_{t\to 0}\right)_{fast}} \quad (2)$$

where $(k_{11})_{fast}$ is the fast aggregation rate constant determined under favorable aggregation conditions (diffusion-limited aggregation regime) and W is the stability ratio (inverse of the attachment efficiency).

2.3. Determination of the Hamaker constant

The attractive interactions between two colloidal particles can be characterized by the Hamaker constant (A) (Bastos and de las Nieves, 1994). As presented by Reerink and Overbeek (Bastos and de las Nieves, 1994; Reerink and Overbeek, 1954), considering the DLVO theory, the value of the Hamaker constant can be obtained by

Table 1
Characteristics of the purified AgNP suspensions.

AgNPs	Stabilization mechanism	Mass concentration[a] (mg L^{-1})	Hydrodynamic diameter (HDD)					Zeta potential (ζ) (mV)
			Size (nm)	% volume	Size	% volume	Z-ave (nm)	
H_2-AgNPs	Electrostatic	19.3	13	97	94	3%	67	−22
Citrate-AgNPs	Electrostatic	8.8	10	98	82	2%	58	−39
PVP-AgNPs	Steric	15.2	12	96	84	4%	72	−10
BPEI-AgNPs	Electrosteric	8.8	10	95	123	5%	95	+40

[a] Corresponds to a particle concentration of 2E11 mL^{-1}.