Aggregation Kinetics of Citrate and Polyvinylpyrrolidone Coated Silver Nanoparticles in Monovalent and Divalent Electrolyte Solutions

Khanh An Huynh and Kai Loon Chen

Department of Geography and Environmental Engineering, Johns Hopkins University, Baltimore, Maryland 21218-2686

Corresponding author: Kai Loon Chen, Email: kailoon.chen@jhu.edu, Phone: (410) 516-7095

Abstract

The aggregation kinetics of silver nanoparticles (AgNPs) that were coated with two commonly use agents—citrate and polyvinylpyrrolidone (PVP)—were investigated. Time-resolved dynamic light (DLS) was employed to measure the aggregation kinetics of the AgNPs over a range of monovalent electrolyte concentrations. The aggregation behavior of citrate-coated AgNPs in NaCl was in excel with the predictions based on Derjaguin–Landau–Verwey–Overbeek (DLVO) theory, and the Ham of citrate-coated AgNPs in aqueous solutions was derived to be $3.7 \times 10^{-20}$ J. Divalent electrolytes efficient in destabilizing the citrate-coated AgNPs, as indicated by the considerably lower critical concentrations (2.1 mM CaCl$_2$ and 2.7 mM MgCl$_2$ vs. 47.6 mM NaCl). The PVP-coated AgNPs were significantly more stable than citrate-coated AgNPs in both NaCl and CaCl$_2$, which is likely due to repulsion imparted by the large, non-charged polymers. The addition of humic acid resulted in the adsorption of humic acid induce electrosteric repulsion that elevated the stability of both nanoparticles in suspensions containing NaCl concentrations of CaCl$_2$. Conversely, enhanced aggregation occurred for both nanoparticles at high concentrations due to interparticle bridging by humic acid clusters.

Introduction

Because of the optical and antimicrobial properties and electrical conductivity of silver nanoparticl 4), these nanomaterials are already finding applications in a wide variety of fields, which includes chemical, and electrical engineering. The combination of their antimicrobial activity and relative l likely the key reason for nanosilver-containing products to presently comprise more than 50% of t consumer products that contain engineered nanoparticles (5). For example, AgNPs are being incor
clothes, bandages, and food containers as deodorizers and disinfectants (6). In addition, studies have conducted to explore the use of AgNPs for drinking water treatment applications (7).

With AgNPs increasingly being manufactured and utilized in consumer products, AgNPs are likely to enter surface waters and the subsurface. Recent studies have shown that AgNPs can exert toxic effects on mammalian cells (8, 9) and microorganisms (4, 10), even though the mechanisms for cytotoxicity are not yet well understood. Thus, the potential release of these engineered nanomaterials into the environment raises concerns on their impacts on the ecosystem and human health.

Currently, the most commonly used method to synthesize spherical, reasonably monodisperse AgNPs is the reduction of silver salts (3). In addition, AgNPs are often modified with capping agents. Since these agents are usually negatively charged species or relatively large, hydrophilic polymers, the adsorption of capping agents will impart colloidal stability to AgNPs by either enhancing their surface charge or introducing electrosteric repulsion (11). This enhancement in colloidal stability is especially critical for applications that require the dispersion of AgNPs in aqueous solutions, such as the high ionic strength solutions typically encountered in biomedical applications.

The environmental impact of AgNPs is greatly dependent on their mobility and aggregation behavior in the natural and engineered environment. Recently, Li et al. (12) investigated the influence of solution chemistry on the aggregation kinetics of unmodified AgNPs and obtained the critical coagulation concentrations of these nanoparticles through time-resolved dynamic light scattering (DLS). Since the CCC represents the minimum amount of electrolyte needed to completely destabilize the suspension (13), it provides a measure of colloidal stability for AgNPs and hence can be used to predict the fate and transport of AgNPs in natural and engineered systems. To date, no study has been conducted to derive the CCCs of AgNPs that have been modified with capping agents. Furthermore, the impact of natural organic matter (NOM), which is ubiquitous in aquatic systems, on the colloidal stability of modified AgNPs is still not well understood.

The objective of this study is to quantify and compare the aggregation kinetics and colloidal stability of AgNPs that were synthesized through the reduction of a Tollens’ reagent and modified with two common capping agents—citrate and polyvinylpyrrolidone (PVP). Time-resolved DLS measurements were conducted to study the aggregation kinetics of both modified AgNPs over a range of monovalent (NaCl) and divalent (MgCl2) electrolyte concentrations. The Derjaguin–Landau–Verwey–Overbeek (DLVO) theory was used to model the experimental data in order to derive the Hamaker constant of citrate-coated AgNPs. In addition, the impact of humic acid on the colloidal stability of both citrate- and PVP-coated AgNPs was investigated.

Materials and Methods

Silver Nanoparticle Synthesis and Characterization

All reagents used for the preparation of the citrate- and PVP-coated AgNPs were purchased from Sigma-Aldrich. Unmodified AgNPs were first synthesized through the reduction of a Tollens’ reaction using glucose. Details for the preparation of the unmodified AgNP suspension are provided in the Supporting Information. This suspension will be referred to as the original AgNP stock suspension. Measurements using inductively coupled plasma mass spectroscopy (ICP-MS) showed that the total and dissolved silver concentrations of the freshly prepared stock suspension were 10.360 mg/L and 0.002 mg/L, respectively. These measurements indicated that the yield of AgNP formation was nearly 100%.
The citrate-coated and PVP-coated AgNP stock suspensions used in this study were prepared by cl
original AgNP stock suspension and re-suspending the nanoparticles in citrate and PVP solutions.
Preparation of these stock suspensions are provided in the SI. According to the supplier (Sigma), the
stock coat the AgNPs has an average MW of 10 kDa. The stock suspensions were contained in tightly
sealed glass bottles and stored in the dark at 4°C. Through ICP-MS analysis, the AgNP and dissolved silver
concentrations in the citrate-coated AgNP stock suspension used for the aggregation experiments
were determined to be 8.467 mg/L and 0.112 mg/L, respectively. The AgNP and dissolved silver concen-
PVP-coated AgNP stock suspension used for the aggregation experiments were 8.247 mg/L and 0.
respectively. The total citrate and PVP concentrations in the citrate- and PVP-coated AgNP stock sus-
spensions were 1 µM and 6.6 mg/L total organic carbon (TOC), respectively.

The absorbance spectra of citrate-and PVP-coated AgNP suspensions were obtained over a range of
from 300 to 900 nm by using a UV-Vis spectrophotometer (UV-1800, Shimadzu). In addition, the
PVP-coated AgNPs were examined using a transmission electron microscope (TEM) (Philips CM-
220 drop of AgNP stock suspension was deposited and dried on a specimen copper TEM grid, which
w a Lacey carbon film (SPI Supplies, PA), before being observed under the TEM at 300 kV. The ele-
composition and crystalline structure of the AgNPs were obtained through energy dispersive X-ray
(EDS) and selected area electron diffraction (SAED) analysis, respectively, with the employment of
The electron diffraction pattern of PVP-coated AgNPs was obtained by using a Philips EM 420 TE

**Determination of Silver Nanoparticle and Dissolved Silver Concentrations**

The AgNP and dissolved silver concentrations of the AgNP stock and diluted suspensions used in
the study were obtained through centrifugal ultrafiltration (using 3-kDa centrifugal membrane filters) and ICP-MS
provided in the SI.

**Solution Chemistry**

ACS-grade electrolyte (NaCl, CaCl₂, and MgCl₂) stock solutions were prepared and filtered using
alumina syringe filters (Anotop 25, Whatman) before use. Humic acid stock solution was prepared
Suwanee River humic acid (Standard II, International Humic Substances Society) in DI water. De-
provided in the SI. All experiments and measurements were performed at pH 7.0 ± 0.1 (buffered w
NaHCO₃).

**Electrophoretic Mobility Measurements**

A ZetaPALS analyzer (Brookhaven, NY) was used to measure the electrophoretic mobilities (EPMs)
and PVP-coated AgNPs over a range of electrolyte concentrations at 25°C. For each solution chem-
measurements were conducted for each of at least 3 samples. The zeta (ζ) potentials were convert-
average EPMs by using the tabulated values that were provided by Ottewill and Shaw (15).

**Time-Resolved Dynamic Light Scattering**

Time-resolved DLS measurements of aggregating AgNP suspensions were performed using a light
unit. This unit comprises an argon laser (Lexel 95, Cambridge laser, CA) with a wavelength of 488
photomultiplier tube mounted on a goniometer (BI-200SM, Brookhaven, NY), a digital correlator (Brookhaven, NY), and a thermostated vat filled with an index-matching cis- and trans-mixture of
decahydronaphthalene which was maintained at 25°C for all our measurements. The detailed proce

http://www.ncbi.nlm.nih.gov/pmc/articles/PMC3137917/
DLS measurements is provided in the SI. For all aggregation experiments, the AgNP suspensions had a total volume of 1 mL and a AgNP concentration of 1.129 mg/L of citrate-coated AgNPs, 1.010 mg/L of PVP-coated AgNPs (7.5 times dilution from citrate- or PVP-coated AgNP stock suspensions, respectively). The total citrate and PVP concentrations of the final citrate- and PVP-coated AgNP suspensions were 0.13 μM and 0.88 mg/L TOC, respectively.

All DLS measurements were conducted at a scattering angle of 90°. Each autocorrelation function accumulated over 15 s and the intensity-weighted hydrodynamic diameter was then derived using cumulant analysis (Brookhaven software). Time-resolved DLS measurements were performed over a period of between 12 min and 3 h in order to achieve a large enough increase in hydrodynamic diameter for derivation of aggregation kinetics.

**Determination of Aggregation Kinetics**

The early-stage aggregation kinetics of AgNPs can be obtained from the initial rate of change of hydrodynamic diameter, \(D_h\), with time, \(t\), as measured by time-resolved DLS. In the early aggregation stage, the aggregation rate constant, \(k\), is proportional to the initial rate of increase in \(D_h\) and inversely proportional to the initial primary AgNP concentration in the suspension, \(N_0\) \((16, 17)\):

\[
k \propto 1N_0(dD_h(t)dt)t \to 0
\]

A linear least squares regression analysis of the initial increase in \(D_h\) was conducted to obtain \(k\). For chemistries, this analysis was performed over the time period in which the hydrodynamic diameter was 1.3 times the initial hydrodynamic diameter, \(D_{h,0}\). At low electrolyte concentrations, however, the hydrodynamic diameter failed to reach 1.3 \(D_{h,0}\). Under such conditions, the linear regression was performed over a prolonged time period (> 90 min). For all solution chemistries, the \(y\)-intercept of the fitted line defined in excess of \(D_{h,0}\).

The attachment efficiency, \(\alpha\), is used to quantify the aggregation kinetics of AgNPs. It is calculated by normalizing the aggregation rate constant obtained in the solution of interest to the rate constant of favorable (non-repulsive) aggregation conditions, \(k_{fast}\) \((16-18)\):

\[
\alpha = k/k_{fast} = 1N_0(dD_h(t)dt)t \to 0/(N_0)_{fast}(dD_h(t)dt)t \to 0,_{fast}
\]

The terms with subscript “fast” refer to favorable conditions. To calculate \(\alpha\) in the presence of humic acid, was determined using \((dD_h(t)dt)t \to 0,_{fast}\) obtained for the same type of AgNPs in the absence of the same electrolyte of interest. In such cases, \(\alpha\) values exceeding unity indicates that interparticle bridging is taking place \((19)\).

**Detection of AgNP Dissolution**

The degree of nanoparticle dissolution taking place in our systems was determined since dissolution can influence the mechanism of AgNP aggregation. Specifically, the precipitation of AgCl resulting from the dissolution of AgNPs may lead to interparticle bridging between AgNPs and in turn enhance the nanoparticle aggregation kinetics \((12)\). In this study, dissolution experimenter conducted by measuring the dissolved silver concentrations of the citrate- and PVP-coated AgNP suspensions.
prepared at the highest electrolyte concentrations which were used for the aggregation experiments measurements were conducted using ICP-MS and the details are provided in the SI.

## Results and Discussion

### Physicochemical Properties of Citrate- and PVP-Coated AgNPs

The size distribution of the citrate-coated AgNPs (Figure 1a) was determined by using the Digital software (Gatan, CA) to measure the diameters of 210 nanoparticles randomly selected from a TEM representative TEM image of the AgNPs is presented in the insert. The nanoparticles were observed spherical with slight angular features. The number average diameter of the citrate-coated AgNPs was 18.9 nm. Through 20 DLS measurements, the average intensity-weighted hydrodynamic diameter of stable citrate-coated AgNPs prepared in DI water was determined to be which is very similar to the number average diameter of the nanoparticles. The average intensity-weighted hydrodynamic diameter of PVP-coated AgNPs obtained from 20 DLS measurements was 66.9 nm.

![FIGURE 1](image.png)

(a) Size distribution of 210 citrate-coated AgNPs. The inset presents a representative TEM image of the citrate-coated AgNPs. The scale bar represents 100 nm. (b) Electrophoretic mobilities (EPMs) of citrate- and PVP-coated AgNPs as a function of electrolyte ... 

Absorbance peaks for citrate- and PVP-coated AgNP suspensions were at 431 nm and 418 nm, respectively (Figure S1 in SI). These values are within the reported range for AgNPs with the size of 57–87 nm resolution TEM imaging of both AgNPs revealed lattice fringes with different alignments within a nanoparticle, which are indicative of the polycrystalline nature of AgNPs synthesized through the method (Figure S2).

SAED analysis was performed on citrate- and PVP-coated AgNP clusters and the distances between planes (d-spacing) were determined by measuring the diameters of the first four rings on the diffraction patterns (Figure S3a and Figure S4a). The similarity in the first four d-spacing values between the AgNPs (1.42 Å, 1.23 Å for citrate-coated AgNPs and 2.40 Å, 2.08 Å, 1.50 Å, 1.23 Å for PVP-coated AgNPs) confirmed that the nanoparticles have the same crystal lattice as bulk silver.

The elements and their relative abundance of citrate- and PVP-coated AgNPs were obtained by pet EDS on AgNP samples which were freshly dried on TEM grids. The EDS spectra of randomly selected PVP-coated AgNP clusters (Figure S3b and Figure S4b) showed that the nanoparticles were composed of silver and the amount of oxygen of the whole cluster was relatively small. Therefore, from both SAED and EDS analyses confirmed that our synthesis method resulted in the production of AgNPs.
Electrokinetic Properties of Citrate- and PVP-Coated AgNPs

Figure 1b presents the EPMs of citrate-coated AgNPs measured over a range of monovalent (NaCl, CaCl\textsubscript{2} and MgCl\textsubscript{2}) electrolyte concentrations. The measurements showed that citrate-coated AgNPs are negatively charged over the entire range of monovalent and divalent electrolyte concentrations used. Since the pK\textsubscript{a} values of citric acid are 3.13, 4.72, and 6.33 (22), the carboxylic acid groups of citrate are mostly deprotonated at pH 7 and will thus contribute to the surface charge of citrate-coated AgNPs. Addition of electrolyte concentrations, the EPMs of citrate-coated AgNPs are negative due to an increase in charge screening (for NaCl) or charge neutralization (for CaCl\textsubscript{2} and MgCl\textsubscript{2}).

Figure 1b also presents the EPMs of PVP-coated AgNPs over a range of NaCl concentrations. It was observed that PVP-coated AgNPs had similar EPMs as citrate-coated AgNPs. Since PVP polymers are neutral, the increase in PVP concentration in the suspension was relatively low (0.88 mg/L TOC), the AgNPs may not be coated with PVP and the negative surface charge is likely due to the residual side products which were observed on the nanoparticle surface.

Dissolution of Citrate- and PVP-Coated AgNPs at High Electrolyte Concentrations

Because the precipitation of silver salts may enhance the aggregation kinetics of AgNPs, we performed dissolution experiments at the highest electrolyte concentrations that were used in our aggregation experiments to establish the dissolved silver concentrations under these solution chemistries. These dissolution experiments were performed at 455 mM NaCl, 27 mM CaCl\textsubscript{2}, and 27 mM MgCl\textsubscript{2} for citrate-coated AgNPs and at 45 and 27 mM CaCl\textsubscript{2} for PVP-coated AgNPs. These are the electrolyte concentrations at which the nanoparticles underwent diffusion-limited aggregation (to be discussed in the following section). Control experiments were performed in the absence of electrolytes. For these experiments, the samples were prepared in the same manner as for the DLS experiments by diluting the citrate- or PVP-coated AgNP stock suspension 7.5 times by the addition of either the electrolyte solution of interest or DI water (for control experiments).

The dissolved silver concentrations of the citrate- and PVP-coated AgNP suspensions prepared in different electrolyte solutions are presented in Figure 2. It should be noted that the initial AgNP and dissolved silver concentrations of citrate- and PVP-coated AgNP suspensions were different because the citrate- and PVP-coated AgNP stock suspensions were prepared separately. The slight increase in dissolved silver concentration in citrate- and PVP-coated AgNP suspensions prepared in DI water after 30 min indicated that some dissolution have occurred. The increase in temperature (from 4 to 25°C) and dissolved oxygen concentration, a decrease in citrate and PVP concentrations, are expected to lead to the slight dissolution of both AgNPs diluted in DI water (23-25).

Also shown in Figure 2, citrate- and PVP-coated AgNPs were generally observed to undergo a higher dissolution in all electrolyte solutions than in DI water. These results are consistent to other observations where an increase in ionic strength can enhance AgNP dissolution (12). The presence of chloride ions in the...
solutions will lead to the formation of soluble silver chloride complexes, such as AgCl$_2^-$ and AgCl can accelerate the dissolution of AgNPs. The measured dissolved silver concentrations in solutions NaCl, 27 mM CaCl$_2$, and 27 mM MgCl$_2$ were used as input parameters for the conservative estimations of dissolved silver species in our aggregation experiments at the same solution chemistry (MINTEQ, Version 3.0). Due to the considerably low dissolved silver concentrations, the simulations that no precipitation of any silver species (including AgCl) would occur at equilibrium. This result the minor dissolution of either citrate- or PVP-coated AgNPs in our systems did not lead to interparticle bridging of AgNPs over the range of NaCl, CaCl$_2$, and MgCl$_2$ concentrations employed.

**Aggregation Kinetics of Citrate-Coated AgNPs in Monovalent Electrolyte Solution**

The attachment efficiencies of citrate-coated AgNPs are presented as a function of NaCl concentrations. Representative aggregation profiles are presented in Figure S5. The aggregation behavior of citrate-coated AgNPs in NaCl solutions is consistent with the DLVO theory. At low concentrations of NaCl, in NaCl concentration will elevate the degree of charge screening and hence allow for an increase in aggregation kinetics, as reflected by the rise in attachment efficiency. This regime is known as the reaction-limited regime ($\alpha < 1$). At high NaCl concentrations, the charge of citrate-coated AgNPs is completely screened and charged barrier between AgNPs is eliminated. Under such conditions, the nanoparticles undergo diffusion-limited aggregation ($\alpha = 1$). In the diffusion-limited regime, the kinetics of aggregation has reached a maximum independent of the NaCl concentration. The CCC, which delineates the reaction- and diffusion-limited regimes was derived by determining the intersection of the extrapolations through both regimes (17). In NaCl concentrations, the CCC of citrate-coated AgNPs was 47.6 mM.

![FIGURE 3](attachment_url)

**FIGURE 3**

Attachment efficiencies of citrate-coated AgNPs as functions of (a) NaCl and (b) CaCl$_2$ and MgCl$_2$ concentrations at pH 7.0. The solid line in a represents DLVO prediction using a Hamaker constant of $3.7 \times 10^{-20}$ J. For all experiments, the citrate...
Comparing Citrate-Coated AgNP Aggregation Kinetics with DLVO Theory

The aggregation kinetics of citrate-coated AgNPs obtained through time-resolved DLS was compared with DLVO theory. The attachment efficiency of aggregating spherical colloidal particles can be calculated using the following expression which accounts for colloidal and hydrodynamic interactions (17, 26):

\[
\alpha = \int_0^\infty \beta(h) \exp\left[\frac{VA(h)}{(kT)}\right](2a+h)^2 dh
\]

\[
\int_0^\infty \beta(h) \exp\left[\frac{VT(h)}{(kT)}\right](2a+h)^2 dh
\]

where \( h \) is the separation distance between two particles, \( a \) is the particle radius (35.65 nm, based on the average diameter of the citrate-coated AgNPs), \( k \) is the Boltzmann constant, and \( T \) is the absolute temperature (298.15 K). The van der Waals attraction, \( V_A(h) \), was calculated using the expression proposed by Derjaguin and co-workers (17, 26). The superposition approximation expression was used to calculate the electrical double layer interaction, \( V_R(h) \). The function \( \beta(h) \) is used to correct for the hydrodynamic interactions between two approaching particles. Details on the calculation of DLVO interactions can be found in the SI.

In this study, ζ potentials, which were converted from the EPMs, were used instead of surface potential calculation of \( V_R(h) \) (30). Logarithmic regression analysis was performed on the ζ potentials to determine the relationship between ζ potential and NaCl concentration. This relationship was then used for the calculation of the experimental attachment efficiencies as the single fitting parameter, the experimentally obtained attachment efficiencies were in remarkable agreement with DLVO predictions (eq 3).

The solid line in Figure 3a represents the best-fitting theoretical attachment efficiencies derived using a constant of \( 3.7 \times 10^{-20} \) J for citrate-coated AgNPs in aqueous solutions. This value falls within the range of the values suggested by Fornasiero and Grieser (31). Furthermore, Figure 3a shows that the agreement between the experimental results and theoretical predictions had been observed for the first time in this study, may be due to the uniform charge distribution on the citrate-coated AgNP surface.

Aggregation Kinetics of Citrate-Coated AgNPs in Divalent Electrolyte Solutions

The aggregation kinetics of citrate-coated AgNPs in CaCl₂ and MgCl₂ electrolytes are presented in Figure 3a. Similar to the inverse stability profile obtained in the presence of NaCl (Figure 3a), the presence of CaCl₂ and MgCl₂ ions in the electrolytes is controlled by electrostatic interactions. The CCCs of citrate-coated AgNPs in the presence of CaCl₂ and MgCl₂ were determined to be 2.1 mM and 2.7 mM, respectively. These values are much smaller than the one determined in NaCl, since Ca²⁺ and Mg²⁺ ions can neutralize the surface charge of citrate-coated AgNPs through interactions with the carboxyl groups of the adsorbed citrate molecules. The results from the aggregation experiments corroborate with the EPM measurements which showed that mobilities of citrate-coated nanoparticles were considerably less negative in the presence of CaCl₂ and MgCl₂ than in NaCl (E). This disparity in the magnitude of the CCC of citrate-coated AgNPs in CaCl₂ is lower than that in MgCl₂. This disparity is due to Ca²⁺ ions having a higher propensity to form complexes with citrate compared with Mg²⁺ ions.
from the higher stability constant of monodentate Ca-citrate complexes compared to monodentate Mg complexes at 0 mM ionic strength and 25°C (10.4 vs. 10.0) (32). Therefore, Ca^{2+} ions are expected to be more efficient than Mg^{2+} ions in neutralizing the surface charge of citrate-coated AgNPs.

**Comparing Aggregation Kinetics of PVP-Coated AgNPs with Citrate-Coated AgNPs**

*Figure 4* presents the inverse stability profiles of PVP- and citrate-coated AgNPs in NaCl and CaCl. The total PVP concentration in the PVP-coated AgNP suspensions was 0.88 mg/L TOC, which is equivalent to 0.14 μM PVP by using a PVP MW of 10 kDa. Therefore, the molar concentration of suspensions is comparable to that of citrate in the citrate-coated AgNP suspensions (0.13 μM). When concentrations of capping agents were used, the PVP-coated AgNPs were more stable than citrate-coated AgNPs, as indicated by the considerably higher CCCs of PVP-coated AgNPs. In the presence of CaCl, the CCC of PVP-coated AgNPs was 111.5 mM, compared to 47.6 mM for the citrate-coated AgNPs. In the presence of CaCl, the CCCs of PVP- and citrate-coated AgNPs were 4.9 mM and 2.1 mM, respectively. For citrate-coated AgNPs, the inverse stability profiles in both NaCl and CaCl indicated that electrostatic interaction still played a significant role in controlling the stability of PVP-coated AgNPs. Trace amount of residual side products from the production process on the nanoparticle surface are likely the origin of the negative surface charge of the PVP-coated AgNPs. At higher PVP concentrations, the PVP coverage will be increased and significant sections of adsorbed PVP polymers will be expected to extend into the bulk solution (33), thus leading to steric repulsion to be the major contributor to the stability of PVP-coated AgNPs. In the study of Badawy et al. (11), the authors found that the ζ potential, which was close to neutral (ca. −7 mV), and the diameter of PVP-coated AgNPs remained constant over a wide range of pH conditions. Their observation confirmed that steric repulsion was the dominant contributor to the high stability of the AgNPs and that the contribution by electrostatic interactions was minor at elevated PVP concentrations.

**Influence of Humic Acid on Aggregation Kinetics of Citrate- and PVP-Coated AgNPs**

The aggregation kinetics of citrate-coated AgNPs in the absence and presence of humic acid are presented as functions of NaCl concentrations in *Figure 5a*. The presence of humic acid (1 mg/L TOC) increased the CCC from 47.6 mM to 72.1 mM NaCl. The adsorption of humic acid macromolecules, which contains n
charged carboxyl groups, on the surface of citrate-coated AgNPs is very likely to result in electrostatic interactions and thus increase the stability of the citrate-coated AgNPs. Although both citrate-coated AgNPs are negatively charged at pH 7.0, humic acid may still adsorb on the modified nanoparticles through electrostatic interactions. It is also possible that the nanoparticles were not completely coated with citrate and thus available surface sites for humic acid adsorption to take place.

**FIGURE 5**

Attachment efficiencies of citrate-coated AgNPs in the absence and in the presence of humic acid (1 mg/L TOC) as functions of (a) NaCl and (b) CaCl$_2$ concentrations at pH 7.0. The attachment efficiencies of citrate-coated AgNPs in the absence of humic ...

The aggregation behavior of citrate-coated AgNPs in the presence of humic acid and CaCl$_2$ is dissimilar to that observed in NaCl, as shown in Figure 5b. Specifically, no distinct reaction- and diffusion-limited regimes were observed, suggesting an inverse stability profile. When the concentration of CaCl$_2$ was smaller than 9 mM, the citrate-coated AgNPs were more stable in the presence than in the absence of humic acid due to electrosteric stabilization. Above 9 mM CaCl$_2$, the attachment efficiencies were higher than unity and increased with CaCl$_2$ concentration. Similarly, enhanced aggregation of fullerene (19), gold (34), and silicon (35) was previously observed in the presence of humic acid at high CaCl$_2$ concentrations. Chen and Ellis hypothesized that the enhanced aggregation was due to interparticle bridging of nanoparticles by humic acid aggregates which were created from the complex formation between humic acid macromolecules and nanoparticles.

PVP-coated AgNPs exhibited similar aggregation behavior in the presence of humic acid as that of citrate-coated AgNPs in both NaCl and CaCl$_2$ electrolytes (Figure S6). In NaCl solutions, the presence of humic acid elevated the colloidal stability of both citrate- and PVP-coated AgNPs. In the presence of CaCl$_2$, the PVP-coated AgNPs were more stable in the presence than in the absence of humic acid below 18 mM. At CaCl$_2$ concentrations above 18 mM, enhanced aggregation of PVP-coated AgNPs occurred in the presence of humic acid. How the highest CaCl$_2$ concentration employed (30 mM), the enhancement in aggregation kinetics of PVP-coated AgNPs ($\alpha = 1.6$) was not as dramatic as that of citrate-coated AgNPs ($\alpha = 3.7$ at 19 mM CaCl$_2$). This enhancement in aggregation kinetics may be an indication that the adsorbed PVP can cause steric interparticle bridging by the humic acid clusters.

**Environmental Implications**

The aggregation kinetics of citrate-coated AgNPs is shown to be in excellent agreement with DLV Hamaker constant of citrate-coated AgNPs derived from this study is a critical parameter for the prediction of the fate and transport of these nanoparticles in aquatic systems (36). PVP-coated AgNPs are significantly more stable than citrate-coated AgNPs, likely due to the steric repulsion imparted by PVP molecules. Since the CCCs for both AgNPs are much higher than typical monovalent and divalent cation concentrations in freshwater systems, both AgNPs are expected to be highly mobile in these environments. Humic acid elevates the colloidal stability of both citrate- and PVP-coated AgNPs in NaCl and at lower concentrations of CaCl$_2$, it enhances the aggregation kinetics at high CaCl$_2$ concentrations. Similar experiments need to be conducted to establish the effects of other key components of NOM, such as fulvic acids and polyelectrolytes.
on the aggregation kinetics of modified AgNPs. In addition, further research is required to assess the reversibility of the adsorption of citrate and PVP on AgNPs, which will have important implications on aggregation behavior and persistence of these nanoparticles in aquatic systems.

### Supplementary Material

[1_si_001](#)

Click here to view. ([469K, pdf](#))

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### Footnotes

Supporting Information Available

Additional figures and details for Materials and Methods and Results and Discussion are presented. This material is free of charge via the Internet at [http://pubs.acs.org](http://pubs.acs.org).

### Literature Cited


