Effect of nanomaterial and media physicochemical parameters on nanomaterial aggregation kinetics

Mohammed Baalousha*

¹ Center for Environmental Nanoscience and Risk, Arnold School of Public Health, University South Carolina, Columbia, South Carolina 29208.

² Department of Environmental Health Sciences, Arnold School of Public Health, University South Carolina, Columbia, South Carolina 29208.

* Corresponding author: mbaalous@mailbox.sc.edu

Abstract

Understanding nanomaterial (NM) stability is required for an adequate interpretation of ecotoxicological test outcomes, fate and behavior studies, to generate parameters (such as critical coagulation concentration, CCC; and attachment efficiency, α) for environmental fate models, and for comparison among different studies. Numerous studies measured CCC and α for different types of NMs with a major focus on investigating the effect of ionic strength, ion valency and natural organic matter, with fewer studies investigating the effect of NM and other medium properties. Consequently, wide discrepancies can be found in the literature among the reported CCC and α values, even for NMs of the same composition and properties. In this context, the aim of this review is to investigate the dependence of NM aggregation kinetic parameters (*e.g.* CCC and α) on NM and medium physicochemical properties and to rationalize the differences observed among different studies, where possible.

We found that various material and medium physicochemical properties need to be considered to predict NM aggregation behavior. Some trends were observed and rationalized based on theoretical studies and data available in the literature. For charge stabilized NMs with constant zeta potential, NM stability (CCC) decreases with the increase in Hamaker constant, increase in NM size, increase in buffer (carbonate and phosphate) concentration, increase in temperature, and light irradiation. The CCC increase with counterion complexation. For sterically stabilized NMs, the CCC increases with the increased surface coverage by the capping agent molecules and completely coated NMs do not aggregate even in high ions strength medium (*e.g.* seawater). These results highlight the significant role of NM and medium properties in influencing the environmental stability and fate of NMs, and will help refine NM fate models and improve our understanding of NM uptake and toxicity.

1. Introduction

The stability of engineered nanomaterials (NMs) has been studied over the past two decades, since the evolution of nanotechnology. However, the stability of colloidal dispersions has been studied for over a century^{1,2}. A substantial progress in the understanding of the stability phenomena has been made since the introduction of the DLVO theory, which attributed the interaction between two identical particles to van der Waals attraction and the electrical double layer repulsion^{1,2}. Additionally, numerous studies have shown the importance of other interaction forces such as steric forces, and hydration forces on NM aggregation and aggregation kinetics³.

Quantitative assessment of NM stability can be achieved by estimating the attachment efficiency (α) - the inverse of the stability ratio (W) - and the critical coagulation concentration (CCC), which is the minimum counterion concentration required to fully destabilize the dispersion (see details in section 2)⁴. The aggregation kinetics parameters (α , W , and CCC) of a specific counterion can be calculated theoretically using the classical DLVO theory on the basis of a static force balance. The aggregation kinetic parameters also can be measured experimentally from a kinetic point of view by studying the process of colloidal aggregation⁵. This can be achieved by monitoring the growth in NM size, or the loss of UV-vis absorbance for plasmonic NMs (*e.g.* Au and Ag NMs) at early stage of aggregation⁶.

Numerous aggregation kinetics' experimental studies have focused on investigating the effect of ionic strength, ion valency, pH and natural organic matter (NOM) concentration on NM kinetic stability (CCC and α)⁶⁻¹⁰. However, wide discrepancies can be found in the literature among the reported CCC and α values. These discrepancies are likely to be attributed to differences in the experimental conditions among the different studies such as: **1)** method employed to investigate NM aggregation kinetics (*e.g.* DLS, and UV-vis)⁶, **2)** physicochemical properties of the NMs (*e.g.* size, shape, surface coating, *etc.*)^{11,12}, and **3)** media chemistry (*e.g.* buffer type and concentration, and ligand type and concentration)¹³, and **4)** environmental factors (*e.g.* temperature, and irradiation)^{7,8,12}.

There is currently a limited knowledge on the effect of intrinsic properties of NMs (*e.g.* particle size, morphology, crystal structure, surface heterogeneity, and dopants) and intrinsic properties of the medium (*e.g.* buffer type and concentration, interaction of NM with medium constituents, and dissolved oxygen) and environmental factors (*e.g.* light, and temperature) on NM aggregation^{7,8,12}. For instance, recent studies reported contradictory results on the dependence of CCC on NM size including a decrease with the decrease in NM size (*e.g.* hematite¹⁴, TiO₂¹²), an increase with the decrease in NM size (*e.g.* CdSe¹⁵) or independence of CCC of NM size (*e.g.* Au and Ag NMs^{16,17}). In addition, whereas some studies reported a linear correlation between the CCC and NM primary particle size (*e.g.* anatase TiO₂¹²), other found that the CCC correlated better with NM specific surface area (*e.g.* anatase TiO₂¹², CdSe¹⁵). Other studies reported an important role of stabilizing agent¹⁵, impurities introduced during synthesis process¹⁸, *etc.* on NM stability. These studies suggest that material properties such as particle size, capping ligand, and impurities are important parameters affecting NMs' aqueous stability. However, a systematic review on the role of NM, and medium intrinsic properties on NM aggregation kinetics is lacking.

Several studies also reported deviations in NM aggregation behavior from classical DLVO behavior. Such deviations have been attributed to a wide selection of causes including discreteness of surface charge¹⁹, steric and relaxation effects²⁰, the presence of nanobubbles on particles²¹⁻²³, and the

inherent surface roughness of the particles themselves²⁴⁻²⁷. The deviation of NM aggregation behavior from the classical DLVO theory and the corrections proposed in the literature to the DLVO theory is discussed where relevant in the manuscript.

In this context, this article aims to investigate the relationship between the CCC values and the parameters affecting NM aggregation behavior and kinetics, in particular NM and media properties. This review focuses on studies reporting NM aggregation kinetics measurement and is organized as follows: **1)** a brief review of the key concepts in NM stability (*e.g.* DLVO theory, Schulze-Hardy rule, α and CCC), **2)** a brief discussion of the methods used to measure NM aggregation kinetics (*e.g.* DLS and UV-vis), **3)** a critical discussion on the factors affecting NM aggregation kinetics, together with a rationale for the variability in the reported CCC values for the same type of NM based on NM and media physicochemical properties, and **4)** critical discussion on deviations from DLVO theory due to NM specific properties, which is integrated throughout the manuscript.

Understanding of the fate and behavior of NMs in environmental and toxicological media is crucial to allow for comprehensive environmental risk assessment of NMs²⁸. Aggregation is one of the key processes, among others, determining their environmental fate, behavior, uptake, effects, etc²⁹. Furthermore, understanding the interplay of NM and media physicochemical properties and their aggregation behavior under conditions of ecotoxicological and environmental media is required for an adequate interpretation of ecotoxicological test outcomes, fate and behavior studies, to generate parameters (*e.g.* α and CCC)³⁰ for environmental fate models³¹⁻³³, and for comparison among different studies.

In this paper, we gathered data from research articles reporting NM aggregation kinetics' experiments and deriving CCC values (**Table S1 and S2**). Data on NM properties (size, zeta potential, coating type and concentration, and NM concentration), water properties (pH, buffer concentration, ion type and concentration, concentration and type of NOM) and CCC were extracted and tabulated (**Table S1 and 2**). Therefore, this review will act as a repository for CCC values for different types of NMs.

2. Theoretical background

This section briefly summarizes the scientific theories of stability and interactions of NM suspensions to underpin the discussion presented later on in the article. For more details on colloidal science theories and interaction forces between particles, the reader is referred elsewhere^{1-3,25,34-37}.

2.1. DLVO theory

DLVO theory is a fundamental colloidal science theory that was developed by Derjaguin, Landau, Verwey, Overbeek (DLVO) to explain the interaction between colloidal particles. Classical DLVO theory assumes that the total interaction potential (V_T) of two colloidal particles is determined by the sum of the electric double layer repulsions (V_{EL}) and the van der Waals attractions (V_A) (Eqs. 1-4)^{4,35}.

$$V_T = V_A + V_{EL} \quad (\text{Eq. 1})$$

$$V_A = -\frac{rA}{12h} \quad (\text{Eq. 2})$$

Where r is particle radius, A is Hamaker constant of particles in water, h is particle-particle separation

$$V_{EL} = 32\pi\epsilon r \left(\frac{k_B T}{ze}\right)^2 \gamma^2 \exp(-\kappa h) \quad (\text{Eq. 3})$$

Where ε is the dielectric constant of water, K_B is Boltzmann constant, T is temperature, γ is the reduced surface potential, κ is the Debye-Hückel parameter, Z is the valence of ions and e is the elementary charge.

The reduced surface potential, γ , can be calculated using the equation

$$\gamma = \tanh\left(\frac{Ze\phi}{4k_B T}\right) \quad (\text{Eq. 4})$$

Where ϕ is the surface potential

On approach of NMs, the electric double layer results in repulsion that is determined by the magnitude of the surface or zeta potential and electrolyte concentration and valency. The combination of these two forces results in an energy-distance profile (**Figure 1**), which can be used to calculate the aggregation rate of two colloidal particles. In agreement with experiment, DLVO theory predicts that charged particle suspensions are kinetically stable at low counterion concentrations and become unstable at higher counterion concentrations^{38,39}. The transition between these two regimes is rather sudden and is referred to as the critical coagulation concentration (CCC), which is the minimum counterion concentration required to fully destabilize the dispersion⁴.

Figure 1. Energy-distance curve for electrostatically stabilized dispersions

Figure 1 explains the kinetic stability of colloidal dispersions. For particles to undergo aggregation into the primary minimum, they need to overcome the energy barrier (V_{max}). The higher the value of this energy barrier, the lower is the probability of aggregation, *i.e.* the aggregation rate will be slow. Hence the aggregation process can be considered as a rate (kinetic) phenomenon, also known as reaction limited aggregation (RLA) regime. When the aggregation rate is low enough, the system can remain kinetically stable for months or years, depending on the magnitude of the energy barrier. The aggregation rate increases with the reduction of the energy barrier (due to the reduction in double layer repulsion) and becomes very fast in the absence of the energy barrier. This is also known as diffusion limited aggregation (DLA) regime.

The secondary minimum at long separation distances (**Figure 1**) may become deep enough depending on electrolyte concentration, particle size and shape and the Hamaker constant, reaching several $k_B T$ units. Under these conditions, the system becomes weakly flocculated⁴. Aggregation in

secondary minimum – when a secondary minimum is of the order of *ca.* $1-5 k_B T$ - is reversible in nature and some disaggregation may occur, *e.g.* under shear force⁴.

The DLVO theory achieved great success in explaining the stability of colloids in electrolyte solutions. Many recent studies have begun applying colloid science principles such as DLVO theory to NMs. However, the novel properties of NMs (*e.g.* small size, shape, structure, composition, roughness, surface coating and functionalization, *etc.*) challenged the assumptions of the DLVO theory^{7,40-42}. Assumptions of DLVO theory are summarized below, but the reader is referred elsewhere⁴⁰⁻⁴² for extensive discussion of these assumptions:

- 1- Dispersion is dilute,
- 2- Perfect sphere: the surface is molecularly smooth, solid and spherical,
- 3- The electric charge and other properties are uniformly distributed over the solid surface,
- 4- Only two forces act on the dispersed particles; van der Waals force and electrostatic force. These forces are treated independently and assumed additive,
- 5- Additivity: the net interaction energy between a molecule and planer surface made up of like molecules will be the sum of the interaction energy between the molecule and every molecule in the surface body,
- 6- The ions are point charges, *i.e.* without any particle size,
- 7- The distribution of ions is determined by the electrostatic force, Brownian motion and entropic dispersion,
- 8- The intervening medium is a structureless continuum, characterized only by its dielectric constant,
- 9- Electrical permittivity is constant through the double layer,
- 10- The solvent is uniform at the atomic level,
- 11- Derjaguin approximation $\kappa r \gg 1$ and $h \gg r$; that is the thickness of the diffuse double layer is much smaller than the particle radius and the separation distance between the particles is much greater than the particle radius.

These assumptions, clearly not all fulfilled in practical colloidal interactions, work quite well for large surface separations $h > \kappa^{-1}$ and large particles, but start to break down at smaller h and r , where an accurate description of the interaction forces should resort to numerical solution of the Poisson Boltzmann equation⁴⁰. Further discussion of these limitations is provided in the manuscript where relevant.

2.2. Stability ratio, attachment efficiency, and critical coagulation concentration

Depending on counterion concentration, aggregation occurs in reaction limited or diffusion limited regimes (RLA and DLA, respectively). These two aggregation processes are differentiated by the attachment efficiency (α); ranging from 0 to 1, which defines the probability that two colliding particles attach successfully or irreversibly. In RLA regime, an increase in electrolyte concentration screens the surface charge and reduces the energy barrier (see DLVO theory below) to aggregation, which leads to faster aggregation. At electrolyte concentrations above the CCC, the energy barrier is eliminated resulting in DLA. The CCC is the transition point between the two aggregation regimes. For DLA regime, particles attach to each other after first collision ($\alpha = 1$) and form large open fractal aggregates. For RLA regime, particles attach to each other following several collisions ($\alpha < 1$) and form denser aggregates⁴³.

Theoretically, the DLVO theory can be used to calculate the aggregation kinetic parameters (stability ratio (W), α , and CCC). Under unfavorable conditions (*e.g.* high zeta potential and low ionic strength), NM aggregation is “slow” or “reaction limited”. The W and α for spherical NMs of equal sizes is given by Fuchs equation⁴⁴

$$W = \frac{1}{\alpha} = 2r \int_0^\infty \frac{\exp\left(\frac{V_{max}}{k_B T}\right)}{(2r+h)^2} dh \quad (\text{Eq. 5})$$

A simple approximation of this equation is given in Eq.6³⁷

$$\alpha = 2\kappa r \exp\left(-\frac{V_{max}}{k_B T}\right) \quad (\text{Eq. 6})$$

$$\kappa = \sqrt{\frac{\epsilon k_B T}{2N_A e^2 I}} \quad (\text{Eq. 7})$$

Where I is the ionic strength of the electrolyte, N_A is Avogadro number, and e is the elementary charge.

Equation 6 predicts very low attachment efficiencies for energy barrier above few $k_B T$ because of the exponential dependence of α on the energy barrier (V_{max}). Equations 6 and 7 also predict that small changes in electrolyte concentration can have a dramatic effect on the aggregation rate because κ decrease with the increase in electrolyte concentration.

Experimentally, the stability of any dispersion can be assessed quantitatively by measuring the attachment efficiency (α) - the inverse of the stability ratio (W) - and the critical coagulation concentration (CCC). W (Eq. 8) is the ratio between the rate of fast aggregation (k_f , in the absence of energy barrier) to that of slow aggregation (k_s , in the presence of energy barrier). CCC is the minimum counterion concentration required to fully destabilize the dispersion; that is to induce rapid NM aggregation⁴. In general, W , α , and CCC are experimentally determined from the dependence of the aggregation rate on counterion concentration (C_E).

$$\alpha = \frac{1}{W} = \frac{k_s}{k_f} \quad (\text{Eq. 8})$$

There are a few approaches for determining CCC experimentally including: **(1)** approaches based on measuring the aggregation rate constant and the attachment efficiency (α) including direct counting of aggregates with ultramicroscope or particle counter⁴⁵⁻⁴⁹, turbidity measurements⁵⁰⁻⁵⁴, NM aggregate diffusion coefficient (size) measurement by static light scattering⁵⁵⁻⁵⁸, dynamic light scattering (DLS)⁵⁹⁻⁶², fluorescence correlation spectroscopy (FCS), and absorbance of primary particles by UV-vis⁶. DLS is by far the most commonly used method for monitoring NM aggregation. However, these methods still have their own limitations⁶³. **(2)** Approaches based on measuring the sedimentation rate which can be obtained from the determination of the percent transmittance of the supernatant after 24 h sedimentation⁶⁴⁻⁶⁷. The gravitational sedimentation methods have now been recognized to be complicated, cumbersome, and unreliable, and therefore have been recently replaced by the DLS measurements. Full discussion of these approaches is beyond the scope of this article, however extensive discussion of these approaches can be found elsewhere⁶³.

2.3. The Schulze-Hardy rule

The Schulze-Hardy rule is an empirical rule stating that: the CCC of hydrophobic sols is extremely sensitive of the valence of the counterion, and decreases very strongly with the increased valence of the counterion^{68,69}. The Schulze-Hardy rule suggests that the destabilizing power of an electrolyte is

principally due to the valence of its ion that has charge opposite to NM surface (counterion), whereas the nature and valence of its ionic species with the same sign (co-ions) have relatively little effect. For this reason trivalent salts of aluminum and iron are the most widely used inorganic coagulants in water clarification and wastewater treatment⁷⁰.

The theoretical explanation of this rule had to wait the development of the DLVO theory. Verwey and Overbeek introduced the following criteria for transition between stability and instability⁷¹:

$$V_T = V_{El} + V_A = 0$$

$$\frac{dV_T}{dh} = 0$$

Solving Eq. 5 for these boundary conditions results in

$$CCC \propto \frac{1}{A^2 Z^6} \tanh^4 \left(\frac{Ze\zeta}{4K_B T} \right) \quad (\text{Eq. 9})$$

Equation 9 shows that the CCC increase with the increase in zeta potential (ζ), and decrease with increasing A (the Hamaker constant) or van der Waals attraction and it also decreases with increase in counterion valency, Z. This equation shows that for large ζ and symmetric Z:Z electrolyte (*i.e.* $Ze\zeta/4K_B T \gg 1, \tanh^4 \left(\frac{Ze\zeta}{4K_B T} \right) \rightarrow 1$), the CCC is proportional to Z^6 . However, for low ζ and symmetric Z:Z electrolyte (*i.e.* $Ze\zeta/4K_B T \ll 1, \tanh^4 \left(\frac{Ze\zeta}{4K_B T} \right) \rightarrow \left(\frac{Ze\zeta}{4K_B T} \right)^4$), which are common for NMs, the CCC is proportional to Z^2 . In practice, the CCC dependence on Z for a wide range of NMs should be between Z^6 and Z^2 .³⁵ Therefore, for the majority of NMs, the $CCC_{divalent}/CCC_{monovalent}$ ratio lies between 4 and 64.

Several studies verified the applicability of Schulze-Hardy rule. For instance, Au NMs have been shown to follow the Schulze-Hardy rule for monovalent, divalent and trivalent electrolytes⁷⁰. Hematite NMs were shown to follow the Schulze-Hardy rule for monovalent, divalent and trivalent electrolytes; whereas humate-coated hematite NMs followed the Schulze-Hardy rule for monovalent and divalent electrolytes only and deviated for trivalent electrolytes. This behavior was attributed to the relatively strong complexation of humate⁷².

2.4. Stabilization mechanisms and criteria

NMs are typically stabilized by either an electrostatic (*i.e.* charge-based) repulsion or a steric repulsion by surface coating (*i.e.* engineered or incidental), or a combination of both (*i.e.* electrosteric), in which case surface coating can further stabilize NM by steric stabilization in addition to charge repulsion^{73,74}.

Electrostatic stabilization

Electrostatically-stabilized NMs owe their stability to particle charge, which results in the formation of diffuse double layer around NMs. Any constituent which influences the surface charge will also change NM stability. The most profound effect is exercised by ions of charge opposite to that of NMs, which result in charge screening and shrinkage of the diffuse double layer thickness. The condition of colloid stability of charge stabilized NMs is to have an energy barrier that is much greater than the thermal energy of the particles (which is of the order of $k_B T$). As a rule of thumb, the energy barrier should be typically $> 25 k_B T$. This can be achieved by having a high zeta potential (*ca.* typically $|\zeta| > 40$ mV) and low electrolyte concentration (*ca.* typically < 100 mM 1:1 electrolyte).

Steric stabilization

Steric stabilization refers to the stabilization of colloidal particles against aggregation by nonionic macromolecules *e.g.* polymers⁷⁵. When two particles having an adsorbed polymer layer with a hydrodynamic thickness δ_h approach each other to a surface-surface separation distance h that is smaller than $2\delta_h$, the polymer layers from the two particles interact resulting in two main situations; either the polymer chains may overlap or the polymer layer may undergo some compression. In both cases, there will be an increase in the local segment density of the polymer chains in the interaction zone. This local increase in segment density in the interaction zone will result in strong repulsion as a result of two main effects⁷⁶:

- 1- Restriction of adsorbed polymer chain motion, which causes a decrease in entropy and thus an increase in free energy. This entropy reduction results from the decrease in the volume available for the polymer chains whether these chains are overlapped or compressed.
- 2- Increase in the osmotic pressure as the solvent will reestablish the equilibrium by diluting the polymer chains and thus separating the particles.

The criteria for effective steric stabilization are⁴:

- The particles should be fully covered by the polymer. Any bare patches may cause aggregation either by van der Waals attraction between the bare patches or by bridging. The latter occurs when polymer becomes simultaneously adsorbed on two or more particles.
- The polymer should be strongly adsorbed to the particle surface. Desorption or replacement of the surface coating by molecules/ligands with high affinity to particle surface could compromise NM stability⁷⁷.
- The stabilizing chain should be highly soluble in the medium and strongly solvated by its molecules.
- The adsorbed layer thickness should be sufficiently large to maintain shallow minimum. This is particularly the case when a colloidal stable dispersion without any weak aggregation is required.⁴

Electrosteric stabilization

Electrostatic and steric stabilization can be combined to maintain the NM stability, which is also referred to as electrosteric stabilization. This kind of stabilization is generally provided by means of ionic surfactants. These compounds bear a polar head group able to generate an electric double layer and a lyophobic side chain able to provide steric stabilization. The adsorption of charged, high molecular weight molecules such as NOM also provides electrosteric stabilization^{6,9,10}.

2.5. Destabilization mechanisms

The destabilization of colloidal suspension can be accomplished by two different mechanisms: **1)** processes that induce a reduction in the total potential energy of interaction between the electrical double layers of two similar particles and **2)** processes that aggregate colloidal particles by the formation of chemical bridges⁷⁸. The first mechanism can be achieved by surface charge screening by a counterion, or by surface coating replacement (*e.g.* a charged coating by a neutral coating)⁷⁹. The second mechanism can be achieved by chemical sorption of organic compounds, formation of inorganic

complexes, and precipitation of inorganic salts. These interactions can significantly impact NM surface charge and aggregation kinetics and results in significant changes in CCC and α .

So far, a significant attention has been giving to investigating the impact of water physicochemical parameters such as ionic strength, cation type, and valency, pH, and NOM concentration and type on NM aggregation kinetics (**Table S1 and 2**)^{9,10}. However, little attention has been giving to chemical interactions that may affect NM aggregation kinetics. Natural waters, cell growth media as well as toxicological media are rich in other constituents than those listed above such as anions (*e.g.* PO_4^{3-} , CO_3^{2-} , Cl^-), and biomolecules (*e.g.* cysteine, cystine, glutathione, proteins, enzymes, vitamins, glucose, *etc.*)⁸⁰, and pH buffers (*e.g.* carbonate, phosphates, Tris, HEPES, *etc.*). Chemical interaction between NM surfaces and medium constituents leads to the formation of ligand-metal complexes, core-shell NMs and chemical sorption of macromolecules, which will alter NM surface charge and thus overall stability. For instance, taking silver as example, this includes, but not limited to, formation of AgCl , Ag_2CO_3 , Ag_3PO_4 , and Ag-cysteine complexes.

3. A note on Variability of Experimental Conditions

Crucial to improving the understanding of the factors controlling NM aggregation kinetics is to establish meaningful comparison between results obtained by different research groups. A survey of recent research articles in the field reveals substantial variation in experimental conditions (**Table S1 and S2**). Variations include NM size, dispersity, morphology, surface area, surface roughness, composition, crystal structure, concentration, surface coating type and concentration, buffer concentration, electrolyte type and concentration, dissolved oxygen (DO), light, and temperature, and consequently CCC values. Ag NMs are the most widely studied NMs in the literature with the largest number of articles reporting CCC values under variable NM and media properties (Table S1), and full statistical analysis of these data is provided elsewhere⁸¹. pH was generally around neutral conditions (*ca.* 6.0-8.0), except few studies^{38,82}. Citrate was the most investigated capping agent among others such as SDS, alginate, PVP, casein, dextrin, tween, branched polyethyleneimine (BPEI), and Gum Arabic (Table S1 and S2). Parameters such as NM size, buffer concentration have rarely been investigated^{17,83}. Below we rationalize the differences in the CCC values based on the variability in the experimental conditions, which includes NM and medium physicochemical properties.

4. Effect of Medium and Environmental Physicochemical Properties on NM stability

4.1. Counterion, pH and natural organic matter

The large majority of NM aggregation kinetics investigated the effects of counterion valence, pH and NOM on NM aggregation kinetics (**see Table S1 and S2**). There is currently a consensus that divalent counterions are more effective in screening NM surface charge than monovalent counterions, in agreement with Schulze-Hardy rule^{70,72,84}. For electrostatically stabilized NM, the CCC of an electrolyte depends strictly on the counterion valence, as long as the adsorption of the co-ion or the counterions on the surface is negligible. Under this condition, the Schulze-Hardy rule is obeyed. If an ion adsorbs sufficiently strongly on the surface of NMs at concentrations lower than the CCC, the Schulze-Hardy rule does not apply⁶⁸. This is because specific sorption of ions on the surface of NM will alter their surface

potential. The majority of studies on electrostatically stabilized NMs reported CCC values for monovalent and divalent electrolytes (**Table S1 and S2**) within the boundaries of the Schulze-Hardy rule; that is the ratio of the CCC of monovalent to that of divalent counterions varies within the range 4 to 64.

NOM (typically Suwannee River fulvic and humic acids) sorb on the surface of NMs, increase their zeta potential, impart NM electrosteric stabilization, and increases the CCC by *ca.* 1-5 folds (**Table S1 and S2**). Additionally, several studies have demonstrated that NOM results in a reduction in the Hamaker constant^{6,85,86}.

pH plays an important role in controlling NM aggregation kinetics by determining NM zeta potential. For instance, the CCC of ZnO⁸ and TiO₂⁸⁷ NMs increases as the pH was further away from the point of zero charge (pH_{PZC}). Nonlinear monotonic relationships were found between the CCC and either pH-pH_{PZC} or electrophoretic mobility (EPM)⁸. This is because, further away from the pH_{PZC}, ZnO NMs possess a larger zeta potential; therefore, higher ionic strength is needed to screen the surface charge and reduce the electrostatic repulsion between NMs.

4.2. Buffer concentration

Buffers are usually used to maintain a constant pH during a reaction, but their presence can result in substantial changes in NM surface chemistry (*e.g.* formation of a core-shell particles, or alteration of zeta potential)⁸⁸ and therefore NM stability^{13,89}. For instance, goethite NMs aggregate size increased with increased MOPS (3-Morpholinopropanesulfonic acid) buffer concentration. This behavior was attributed to sorption of MOPS molecules on the surface of goethite NMs accompanied by a decrease in zeta potential¹³. Furthermore, the buffer composition greatly affects goethite NMs aggregation state. Goethite NMs suspended in solution containing 1 mM Fe²⁺ and HEPES buffer were the most dispersed, and the aggregate sizes were 3-5 times larger for goethite NMs suspended in MOPS and Triethanolamine (TEA) buffers compared to those suspended in HEPES buffer¹³. The stability of hematite particles decrease in the presence of phosphate anions⁸⁹. Furthermore, the CCC values for electrostatically stabilized Ag NMs decrease with the increase in carbonate buffer concentration⁸¹ and phosphate buffer⁸³. This behavior was attributed to the formation of Ag₂CO₃, or Ag₃PO₄ layer on the surface of Ag NMs, altering NM surface charge⁸³. For a constant Ag NM concentration (5.4 mg L⁻¹), zeta potential increased from -42 mV to -29 mV with the increase in phosphate buffer concentration from (0 to 2.5 mM potassium phosphate monobasic)⁸³. Another study demonstrated that, at pH 7, the zeta potential of Ag NMs increases (become less negative) with the decrease in NM concentration (1 to 100 μM) in 10 mM carbonate concentration⁹⁰. Concurrently, Ag NM aggregate size increases with the decrease in NM concentration. This behavior can be attributed to the increased sorption of CO₃⁻² on the surface of Ag NMs at lower NM concentrations due to the increased abundance of CO₃⁻² anions compared to the NM total surface area.

4.3. Dissolved oxygen

Dissolved oxygen (DO) in aqueous environments tends to oxidize metallic NMs such as Ag NMs and QDs⁹¹⁻⁹⁴ resulting in the formation of surface oxide layer (*e.g.* AgO⁹⁵), release of metallic cations^{92,95,96}, and NM aggregation^{91,92,97}. For instance, the aggregation rate of Ag NMs is much faster (*e.g.*, 3–8 times depending on the primary particle size) in the presence of DO than those in the absence of DO⁹¹.

The increased aggregation of Ag NMs in the presence of DO was attributed to surface oxidation and sorption of Ag^+ on Ag NM surface⁹¹. These processes could lead to increase (become less negative) Ag NM zeta potential, hence the increased aggregation rate⁹⁸. Furthermore, NM aggregation can be attributed to the degradation/detachment of surface coating in the presence of oxygen. For instance, the destabilization of Ag NMs, CdS NMs and QDs was found to be related to the detachment/degradation of surface coating in the presence of oxygen, compression of EDL and surface energy changes^{92,97,99}. In contrast, anoxic and anaerobic conditions exert low redox potentials, which inhibit oxidation and consequently lead to different aggregation kinetics^{92,97}.

4.4. Light

Light irradiation including UV, sunlight and even fluorescent light has been shown to promote NM surface oxidation, dissolution and aggregation¹⁰⁰⁻¹⁰². The CCC of NaNO_3 was found to be lower for citrate-Ag NMs following 3-day exposure to UVA and UVB radiation ($\text{ccc} = 37.8$ and 21.4 mM NaNO_3) compared with unexposed cit-Ag NMs ($\text{ccc} = 161.4 \text{ mM NaNO}_3$). This decrease in the CCC was concurrent with the increase in the ζ potential (become less negative) after exposure to UVA and UVB¹⁰⁰. The aggregation rate of bare-, citrate-, and PVP-Ag NMs followed the order UV-365 > xenon lamp light > UV-254 > dark for the same type of Ag NMs, which indicated that the wavelength and photo-energy of the light irradiation influence Ag NM aggregation kinetics⁹⁷. The aggregation rate was highest for bare-Ag NMs followed by citrate Ag NMs and PVP Ag NMs.

UV irradiation of a TiO_2 NM suspension accelerated NM aggregation, which was dependent on the irradiation duration. The aggregation rate increased from $< 0.001 \text{ nm s}^{-1}$ before irradiation to 0.027 nm s^{-1} after 50 h irradiation, resulting in aggregates with a hydrodynamic diameter of 623 nm. The isoelectric point of the suspension was lowered from 7.0 to 6.4 after irradiation. ATR-FTIR spectra displayed successive growth of surface hydroxyl groups (OH^-) with UV irradiation which is likely to be responsible for the decreased surface charge and increased aggregation rate. Further explanations of the light-induced ζ potential reduction is described in Sun et al (2014)¹⁰³.

On the other hand, irradiation could result in breakage of NM aggregates (disaggregation). For instance, sunlight partially disaggregated metal oxide (*e.g.* CeO_2 and ZnO) aggregates, but primary particles bonded by solid state necks remained intact¹⁰⁴. Localized heating of NM agglomerates, due to exposure to natural or artificial light, provides sufficient thermodynamic energy for the clusters to disagglomerate¹⁰⁴. Similarly, Bennett and coworkers found that different light sources (*e.g.* sunlight or Xenon lamp light) exposure can partially disaggregate TiO_2 NMs aggregates; TiO_2 NM aggregate size decreased from about 280 nm to about 230 nm after few minutes' exposure to light, and returned to 280 nm in the dark¹⁰⁵. The photo-induced disaggregation was more pronounced (aggregate size decreased from 253 nm to 159 nm after 30 minutes exposure) under natural sunlight conditions. The absorption of light provides enough energy to partially disaggregate TiO_2 NMs in aqueous media, releasing small particles from the larger aggregates. Concurrently, the dermal transport of NMs was higher (200 mg kg^{-1}) under light conditions compared to dark conditions (75 mg kg^{-1}), suggesting that photo-induced disaggregation may have important health implications¹⁰⁵.

4.5. Temperature

Understanding the temperature effect on NM aggregation kinetics is important to understand NM behavior in environmental and biological media and to understand NM behavior within the context of climate change. Both natural water and human body fluids can be at temperatures that are remarkably different from the typically studied room temperature. For example, water temperature may vary substantially from freezing point to near boiling depending on the type of water body, depth, season, latitude and the surrounding environment. Temperature of human body fluids is around 37 °C.

The aggregation rate of CeO₂ NMs in KCl and CaCl₂ increased as the temperature increased. The CCC decreased from 100 to 10 mM in KCl and from 10 to 2 mM in CaCl₂ with temperature increase from 4 to 37 °C (**Figure 2**)¹⁰⁶. The decrease in CCC in KCl shows a linear correlation with the increase in temperature; whereas in CaCl₂, the CCC remained constant at 10 mM until the temperature reached 25 °C and then decreased to 3 mM at 37 °C. Similarly, the increase in temperature from 25 to 70 °C resulted in a decrease (67%, 50%, and 33% for Na⁺, Mg²⁺, and Ca²⁺, respectively) of the CCC for silica NMs (25 nm), which was attributed to the increased collision frequency of the colloidal particles at higher temperatures, which promotes successful particle collision and aggregation¹⁰⁷. However, increased NM collision frequency does not explain the reduction in CCC. Additionally, according to equation 9, for low ζ which are common for NMs and symmetric Z:Z electrolyte (*i.e.* $\frac{Ze\zeta}{4K_B T} \ll 1, \tanh^4\left(\frac{Ze\zeta}{4K_B T}\right) \rightarrow \left(\frac{Ze\zeta}{4K_B T}\right)^4$). This implies that if all other parameters are constant, the CCC is proportional to T^{-4} . The dependence of CCC on medium temperature does not fully explain the reduction in CCC with the increase in temperature as observed above. The reduction in CCC is likely to be also influenced by the reduction in zeta potential of silica NMs, which unfortunately was not reported by the authors for the different temperatures. Other studies reported decreased stability and increased in NM aggregate size (e.g. CuO¹⁰⁸, ZnO¹⁰⁹, and single wall carbon nanotubes¹¹⁰) with the increase in temperature.

Figure 2. Effect of temperature on the CCC of CeO₂ NMs. Taken from ¹⁰⁶.

The increased NM aggregation with the increase in water temperature is likely to be due to the decrease in the magnitude of the zeta potential with the increase in temperature, which was reported for different types of NMs such as ZnO¹⁰⁹, CuO¹⁰⁸, TiO₂¹⁰⁴, single wall carbon nanotubes¹¹⁰, α -Al₂O₃¹¹¹, mineral particles (*e.g.* quartz, kaolinite and calcite)¹¹². The surface charge of NPs in aqueous medium is mainly determined by two phenomena, protonation/de-protonation of surface functional groups, and adsorption of electrolyte ions on the surface¹¹³. The temperature-dependent decrease in zeta potential is attributed to the changes in NM surface speciation (*e.g.* protonation or deprotonation of functional groups) with temperature. For instance, increasing temperature favors proton desorption from the α -Al₂O₃ surface, resulting in a shift in the pH_{pzc} of α -Al₂O₃ from 9.6 to 8.1 as the temperature increases from 10 to 40 °C¹¹¹.

On the other hand, high temperatures may increase the potential disaggregation or detachment of NMs, because increased Brownian motion of water molecules could increase the hydrodynamic shear on the particle surface and possibly break the weakly attached aggregates^{104,114,115}. This behavior was previously reported for metal oxide NMs such as CuO¹⁰⁸, CeO₂^{104,115,116}, iron (III) oxyhydroxide¹¹⁷, TiO₂ and ZnO NMs¹⁰⁴. For instance, a cyclic temperature increase from 25 °C to 65 °C and then decrease back was found to disaggregate the NM aggregates in the heating phase and re-aggregate them as more open fractal structures during the cooling phase¹⁰⁴.

4.6. Chemical interactions of NMs with water constituents

Despite its importance in determining NM surface charge, chemical sorption of macromolecules and ligands (*e.g.* PO₄³⁻, CO₃²⁻, Cl⁻) has been somewhat widely ignored in studying NM aggregation kinetics as the large majority of these studies focused on the physical interactions between NMs. However, emerging studies have reported the importance of chemical interactions in addition to physical interactions in controlling NM aggregation kinetics¹¹⁸⁻¹²⁵. For instance, the CCC for citrate-Ag NMs decreases with the increased concentration of carbonate and phosphate anions in the medium, which was ascribed to the sorption of phosphate and carbonate anions on the surface of citrate-Ag NMs, and the concurrent reduction in the magnitude of Ag NM zeta potential^{81,83}. Addition of cystine to citrate-Ag NMs results in NM concentration-dependent shift in the CCC, where the CCC of cystine decreases with the decrease in Ag NM concentration⁷⁷. At lower Ag NM concentrations, lower concentration of cystine is required to fully cover and destabilize Ag NMs⁷⁷. Organic compounds containing both thiol and amine groups strongly promote the aggregation of citrate-Au NMs due to their cooperative functionalities¹²³. Three features of organic compounds could influence citrate-Au NMs (and similarly Ag NMs) aggregation kinetics including: the presence of a sulfur atom, which can form covalent bonds with gold atoms, the presence of ionizable functional groups, and the sign (+ or -) of ionizable functional groups, which determines the Au NM zeta potential¹²³. Specific sorption of Ca²⁺ and Mg²⁺ on the surface of TiO₂ NMs results in surface charge inversion¹²⁶, which was found to increase the destabilization of TiO₂ NMs¹²⁷.

Furthermore, complexation of the counterion in complex aqueous media may result in an increase in the measured CCC values. For instance, the CCC of aluminum for negatively charged silver iodide sols was found to increase if the sol was acidified by sulfuric acid; whereas this behavior was not observed when the sol was acidified by nitric acid or perchloric acids¹²⁸. This behavior was attributed to the formation of AlSO₄⁺ complexes in the presence of sulfuric acid, resulting in the reduction in the concentration of trivalent counterion (Al³⁺) and the formation of monovalent counter ion (AlSO₄⁺)¹²⁹.

Monovalent counterions are orders of magnitude less potent than trivalent counterions in inducing particle aggregation according to Schulze-Hardy rule. This study reveals the importance of considering counterion speciation in interpreting the discrepancies in CCC.

Clearly, focusing only on the physical interactions (*e.g.* attraction and repulsion) of NM when taking into account water chemistry in modeling NM environmental fate and behavior¹³⁰ might lead to erroneous conclusions as many other parameters can play a major role in determining NM aggregation kinetics - such as anions, buffers, small organic compounds, salt precipitation, *etc.* - and thus fate and behavior. Therefore, the chemical speciation of counterions and the chemical interaction between NMs and the medium constituent should be fully taken into account to improve our understanding of NM fate and behavior.

5. Effect of NM Physicochemical Properties on their Stability

5.1. NM Composition

Chemical composition affects NM aggregation as it determines the Hamaker constant;⁷ a material specific constants, typically on the order of 10^{-21} - 10^{-19} J (**Table 1**),¹³¹ that is used to calculate the van der Waals attraction forces between small particles (**see section 1.2**). The increase in the Hamaker constant results in an increase in the van der Waals attraction force and therefore the tendency of NM to form aggregates at the same solution and surface chemistry. Therefore, the increase in the Hamaker constant results in a decrease in the CCC and in a steeper slope of the α -electrolyte concentration profile under RLA regime (**Figure 3a and b**). According to Eq. 9, for a constant zeta potential, the CCC is inversely proportional to the squared Hamaker constant, $CCC \propto \frac{1}{A^2}$. Therefore, the CCC of different types of NMs of the same physicochemical properties and in the same medium will follow the order Au < TiO₂ < Ag < Fe₂O₃ < ZnO < SiO₂ (**Figure 3a**). Due to the variability in the experimental conditions and the dependence of the CCC on other material and media properties⁸¹, it is not possible to verify this order of CCC for all types of NMs. However, this trend can be observed clearly for some NMs; in particular, the CCC of monovalent electrolyte at nearly similar zeta potential values for SiO₂ (450-700 mM) > B (200 mM) > Ag (25-200 mM) (**Tables S1-S2**).

The Hamaker constant is long thought to be size-independent. However, recent theoretical calculations demonstrate that the Hamaker constant of 1 nm Ag- and Au NMs increases by approximately 15% compared with 100 nm Ag and Au NMs^{131,132}. Another theoretical study demonstrated that the Hamaker constant of a 13 nm diameter Au NMs increases by up to 50% compared with that of bulk gold, causing such small NMs to exhibit larger van der Waals attractive interactions and aggregate more readily than larger particles¹³³. The increased aggregation of smaller NM would occur if no other properties (*e.g.* surface charge, crystallographic phase, surface facets, dissolution, *etc.*) are affected by particle size¹³³.

Table 1. Hamaker constant of different materials

Material	A (x 10 ⁻²⁰ J)	References
Gold	9-30	133-135
TiO ₂	9.1	136,137
CeO ₂	5.57	138

Cit-Ag NMs	3.7	6,85
Al ₂ O ₃	3.67	138
iron oxides	3.3-3.9	136,137,139
ZnO	1.9	136,137
Boron	0.88	140
SiO ₂	0.83-1.2	54,136,137

Figure 3. Effect of material composition (Hamaker constant) on their aggregation kinetics according to classical DLVO theory: (a) attachment efficiency as a function of ionic strength, and (b) CCC as a function of Hamaker constant. Calculations were performed assuming a particle diameter of 20 nm and a constant zeta potential of -50 mV. These calculations are only illustrative.

5.2. Crystal structure

Crystal structure such as crystal phase, surface facets and defects can alter surface charge, and thus NM aggregation kinetics¹⁴¹. The surface charge of different polymorph of the same NM may be different. For example, TiO₂, with three phases of crystallinity, has surface charge of -35 mV for rutile and -20 mV for anatase and brookite at pH 7.5. The origin of charge heterogeneities is commonly attributed to the existence of different crystallographic planes within each particle, which is reported to affect aggregation and deposition rates^{142,143}. This is because different crystallographic planes, each with a different atomic density, are interfacing with the aqueous phase and forming different extent of EDL and surface energy. For instance, the point of zero charge of goethite particles having 70% and 30% of the 001 face were 9.0 and 9.1 respectively, which was attributed to the differences in the point of zero charge of the 001 and 101 facets, which was calculated theoretically to be 8.9 and 9.2, respectively¹⁴³. Crystal structure also affects the Hamaker constant, and thus the attractive van der Waals forces¹⁴⁴. For instance, the magnitude of van der Waals interactions varies significantly between iron oxide phases and follow the order magnetite < maghemite < hematite¹³⁹. This is because the Hamaker constant depend on the phase and follows the order magnetite (3.3×10^{-20} J) < maghemite (3.6×10^{-20} J) < hematite (3.9×10^{-20} J).¹³⁹

5.3. Morphology

There are only few studies that investigated the effect of NM morphology on their aggregation kinetics with inconclusive general conclusions. Whereas some studies demonstrated strong effect on NM morphology on their aggregation kinetics (*e.g.* ZnO⁸), others reported no effect (*e.g.* TiO₂¹⁸). For

instance, the aggregation kinetics of nearly spherical ZnO exhibited strong dependence on the ionic strength of the solution; whereas minimal influence of ionic strength was observed on the irregularly shaped (mixtures of slab-like and rod-shaped) ZnO NMs⁸. The CCC for nearly spherical ZnO was approximately 25 mM; whereas the CCC for irregularly shaped ZnO was below 1 mM. This behavior was attributed to lower energy barrier for irregularly shaped NMs compared to spherical NMs. Vold (1954) estimated that plates and rods would have greater van der Waals attractions compared with spheres at small separation distances¹⁴⁵, resulting in a lower energy barrier against aggregation.

However, another study suggested that the CCC for TiO₂ NMs (5, and 50 nm spherical anatase and 10 x40 nm rutile rods) is independent of particle morphology and crystal structure¹⁸ as the CCC (10 mM NaCl and 0.5 mM CaCl₂) value for 10 x 40 nm rutile rods was between those of the 5 nm (5 mM NaCl and 0.3 mM CaCl₂) and 50 nm (18 mM NaCl and 1.0 mM CaCl₂) spherical anatase. The differences in the conclusions drawn by Lie et al¹⁸ and Vold et al¹⁴⁵ were attributed to the difference in the aspect ratios of the studied rods.

Morphology is likely to play an important role in controlling NM aggregation kinetics, as morphology determines NM zeta potential and isoelectric point (pH_{iep}). This is because different surface facets possess different zeta potentials and pH_{iep}. For instance, the pH_{iep} of TiO₂ surface facets follows the order (100) surface 3.2-3.7 < (110) surface 4.8-5.6 < (001) surface 5.6-5.8. Polycrystalline surfaces of both rutile and anatase forms of TiO₂ possess the same pH_{iep} of $\approx$ 6, resulting from the weighted average of the PZC of the single crystal facets¹⁴⁶. Similarly, the double-layer properties of (110)-oriented CaF₂¹⁴⁷ indicated a sharp contrast between the pH_{iep} of that surface and the previously measured (111) orientation^{148,149}. Other works have noted anisotropy among hematite surfaces¹⁵⁰ and distinctions between numerous surface chemistries¹⁵¹, and differences in various orientations of sapphire surfaces have also been investigated¹⁵². Therefore, the variability in the reported NM pH_{iep} can be partially attributed to the relative contribution of surface facets to each type of NM.

5.4. Size

There is a contradictory evidence on the dependence of CCC on NM size including a decrease with the decrease in NM size (*e.g.* hematite¹⁴, TiO₂¹²), an increase with the decrease in NM size (*e.g.* CdSe¹⁵, Au NMs¹⁵³, Ag NMs⁸¹ or independence of CCC of NM size (*e.g.* Au NMs¹⁶). Similarly, earlier studies on colloid stability reported contradictory results including a decrease^{45,154,155}, an increase¹⁴, an increase followed by a decrease^{50,156}, as well as an independence of colloid stability¹⁵⁷ on particle size. The discrepancies reported in the literature on size-dependence of CCC are closely related to the size-dependence of zeta potential⁸¹. An increase in CCC with decrease in NM size is generally observed when NMs of different sizes possess a constant surface charge, whereas an increase in the CCC with the increase in particle size is observed when the zeta potential increases with particle size. Full discussion of the rational of the effect of NM size on CCC is provided elsewhere⁸¹.

5.5. NM dispersity

Currently, no studies have investigated the effect of NM dispersity on the CCC. However, given that the CCC of NM at constant surface potential decrease with the increase in NM size⁸¹, size dispersity is likely to significantly influence the CCC for NM suspension. That is in a polydispersed NM suspension, at a given counterion concentration, larger NMs are likely to aggregate in DLA regime whereas small

NMs may remain stable or aggregate in RLA regime. For instance, Frens (1972) used this phenomenon to fractionate a mixture of citrate-Au NMs (7.5 and 80 nm) according to particle size by coagulating the larger particles by addition of 30 mM NaNO_3 ¹⁵³. Therefore, small NMs may remain stable for longer times compared to larger NMs with the same surface potential.

5.6. Surface area

Only few studies investigated the correlation between the CCC and NM specific surface area (SSA). For instance, Zhou *et al.* reported that the CCC of rutile rods correlated positively with the SSA; that is samples with higher SSA exhibited higher stability¹². In contrast, the CCC of anatase spheres correlated linearly with NM size; that is the CCC increased with the increase in NM size. Nonetheless, the authors also reported a decrease in the CCC with the decrease in rutile rod length, where the CCC tends to a stable value around a length of 50 nm, which is a similar size where the CCC of cit-Ag NMs approaches a constant value⁸¹. Interestingly, the electrophoretic mobility of the different rutile rods varied in a narrower range compared to the zeta potential of the anatase spheres, which might explain the differences in the behavior of the two types of TiO_2 NMs. The electrophoretic mobility, and thus zeta potential, of anatase sphere decreases by approximately two folds from the largest to the smallest anatase spheres, which contributes significantly to the reduction in the stability of the small anatase spheres.

Mulvihill reported that the CCC of four different CdSe NMs were found to be linearly correlated to their SSA (**Figure 4a**)¹⁵. Reevaluating the data reported in this study for spherical CdSe NMs suggests that the CCC decrease with the increase in NM size (**Figure 4b**). Similarly, the CCC of all CdSe correlates linearly with the particle size calculated from the specific surface area (**Figure 4c**)¹⁵⁸. It is worth noting that the zeta potential of the spherical CdSe used in this study varies within a narrow range (*ca.* -33 ± 3 to -35 ± 3 mV). These results are in good agreement with the data observed for cit-Ag NMs (**Figure 4a, and c**).

Figure 4. CCC of CdSe NMs as a function of (a) specific surface area, and (b) primary NM size, and (c) NM diameter calculated from specific surface area. Re-drawn from¹⁵

5.7. Heterogeneity of chemical composition and surface structure

NM might purposefully contain (*e.g.* dopants) or acquire (*e.g.* during synthesis process or as a result of sorption processes in natural waters) some impurities, which might play an important role in controlling the electrokinetic properties and colloidal stability of NMs. For instance, The CCC for TiO₂ NMs depends on the concentration of chemical impurities (*e.g.* silicon and phosphorous) introduced during the synthesis process¹⁸. This was attributed to the decrease in the pH_{PZC} of TiO₂ with the increase in the concentration of impurities (Si+P)¹⁸.

Furthermore, at the atomic level, NM surfaces are heterogeneous in term of chemical composition and structure (*e.g.* surface roughness and ligand composition and organization)¹⁵⁹, making it a challenge to quantitatively evaluate and predict surface properties and interfacial processes¹⁶⁰. For instance, NMs nearly always have a certain degree of surface roughness on the scale of the Debye length, which under aggregation conditions is on the order of 1 nm in the surrounding electrolyte²⁴. For instance, reasonable agreement between theoretical attachment efficiencies calculated by DLVO theory and experimentally measured attachment efficiencies could only be obtained if an effective interaction radius, corresponding to surface asperities on TiO₂ particles, was used in the calculations⁸⁷. High resolution TEM images suggested that the effective interaction radius corresponds to the size of surface crystallites formed during synthesis. Additionally, surface roughness influences the dependence of CCC on particle size. For fine roughness, the CCC decreases with increasing particle size¹⁶¹; whereas, in the case of coarse surface irregularities, the CCC depends on the average configuration of the surface irregularities in the surface area where two double layers overlap. For big particles, this can, in some cases make the CCC increase with the particle size²⁴. Additionally, the repulsion energy due to the electrical double layer is always larger for rough than for smooth surfaces²⁶. This should not be confused with the increased particle stability as the particle stability is not only influenced by the repulsion energy, but rather by the total interaction energy and, more specifically, by the height of the energy barrier. In calculating this energy barrier, the influence of surface roughness on van der Waals forces must also be taken into account²⁶.

Heterogeneity in chemical composition and organization of capping ligands on NM surfaces also plays an important role in controlling NM electrokinetic properties and colloidal stability¹⁶⁰. For instance, Au NMs with randomly distributed polar and nonpolar groups have less negative zeta potential values

and smaller CCC compared to that of homogeneously charged groups, which agree with DLVO prediction. However, when the ligand composition on the surface of Au NMs is the same, particles with nanoscale striates have less negative zeta potential, but much larger CCC compared to particles with disordered surface. The inconsistency of particles with nanoscale striates in their EPM and CCC reflects the complex EDL structure developed in the vicinity of a surface¹⁶⁰.

5.8. NM Concentration

Several studies have demonstrated the increased NM aggregation rate and the increased aggregate size with the increase in NM concentrations *e.g.* ZnO⁸, iron oxides^{10,14}, AuNMs¹⁶², etc. However, it has been reported that NM concentration does not affect the attachment efficiency for spherical ZnO NMs (10-100 mg L⁻¹)⁸. Indeed, this observation is true when NM aggregation is controlled by their physical interactions (*e.g.* van der Waals and electrostatic repulsion). However, several NMs have high affinity to media constituents such as anions^{62,89} and small organic compounds⁷⁷. In such circumstances, the attachment efficiency and the CCC values are strongly dependent on NM concentration, in particular at low, environmentally relevant NM concentrations⁷⁷. This is because at lower NM concentrations, less total surface area is available, and thus chemical sorption of anions, and bio- and geo-molecules on the surface of NMs is more significant. These chemical sorption processes can result in a significant shift in the surface charge and thus NM aggregation. For instance, Afshinnia et al, reported a concentration-dependent attachment efficiency and CCC values of citrate-Ag NMs in the presence of cystine, which was attributed to the chemical sorption of cystine to the surface of Ag NMs, resulting in a significant shift in Ag NM surface charge⁷⁷. Similarly, carbonate and phosphate anions have high affinity to Ag NMs, sorb to the surface of Ag NMs and reduce the CCC values with the decrease in NM concentration^{81,83}.

5.9. Surface coating composition and coverage

The capping agent is the factor that determines NM stabilization mechanism (see section 1.4). Physicochemical properties of the capping agent have a greater influence on the aggregation behavior of functionalized Ag NMs than either core composition or their size (Table S1 and 2)¹⁶. Some capping agents such as citrate, SDS, and alginate stabilize NM by electrostatic mechanism^{6,85,163-165}; whereas other capping agents such as PVP, casein, dextrin, tween, branched polyethyleneimine (BPEI), and Gum Arabic stabilize NMs by steric mechanisms¹⁶⁴⁻¹⁶⁶. For instance, the CCC values of Ag NMs with different capping agents follow the trend citrate ~ alginate ~ SDS < casein < dextrin < PVP < tween < BPEI ~ gum Arabic (Table S1 and 2).

Additionally, surface coverage by capping agent plays an important role in determining the stability of NMs. For instance, the CCC of monovalent counterions for PVP-Ag NMs increase with the increase in PVP molecules available to coat the surface of Ag NMs. High capping agent concentrations result in complete coverage of NM surface and thus full steric stabilization, whereas lower capping agent concentrations may result in partial surface coverage and thus electrosteric stabilization (*e.g.* partial steric stabilization of Ag NMs)⁸¹. Increased concentration of human serum albumin (HSA) protein resulted in a reduced attachment efficiency of citrate-Ag NM in K₂SO₄ electrolyte. The attachment efficiency decreased with increasing HSA concentration until the attachment efficiency reached zero which coincided with the HSA concentration required to form a monolayer on the surface of Ag NMs,

providing full steric stabilization¹²⁴. Similarly, increased concentration of guar gum (a natural, neutrally charged, nonionic, water-soluble polysaccharide; 0 to 4.0 g L⁻¹) enhanced the stability of zero valent iron NMs (1.5 g L⁻¹); that is resulted in decreased aggregate size (*ca.* from 500 to 200 nm)¹⁶⁷.

Some studies reported CCC for PVP-coated Ag NMs approaching those of electrostatically stabilized Ag NMs^{85,163,164}, which can be attributed to the partial surface coverage of Ag NMs by PVP molecules⁸¹. These observations highlight the importance of characterizing the surface coverage of NMs by the capping agent.

6. Concluding Remarks

This review highlights the role of NM and medium physicochemical properties in controlling NM aggregation kinetics (*e.g.* α and CCC). These factors are interdependent, rendering it complex to disentangle the correlation between an individual property and NM aggregation kinetics. We found that no single material or media property was a determining factor that control NM aggregation; rather a combination of various material and media physicochemical properties needs to be considered to predict NM aggregation behavior. Correlations between CCC and NM or media property are observed only when all other properties remain constant. Some trends are outlined below for electrostatically-stabilized:

- The CCC increase with the decrease in Hamaker constant, if all other NM properties and media properties are kept constant; Hamaker constant is determined by NM composition and generally follow the order Au > TiO₂ > CeO₂ > Ag $\approx$ Al₂O₃ $\approx$ iron oxides > ZnO > B $\approx$ SiO₂. Nonetheless, surface functionalization (*ca.* by citrate, PVP, and humic substances) decreases the Hamaker constant, and thus increases, the CCC of NMs, if all other NM and media properties are kept constant. Yet, surface functionalization of NMs could increase, or decrease their surface charge and therefore might increase, or decrease the CCC irrespective of the influence of surface coating on the Hamaker constant.
- Crystal structure affects NM stability by determining NM Hamaker constant and surface charge (zeta potential).
- The CCC of Ag and Au NMs increases with the decrease in NM size at a fixed surface (zeta) potential. This trend is likely to apply for other types of NMs, but no data is currently available to generalize this conclusion for all types of NMs. For variable NM surface (zeta) potential, the CCC might increase with the increase in NM size, or might be independent of NM size, depending on the change in NM surface charge as a function of their size.
- For a polydispersed NM suspensions (*ca.* Ag and Au), larger NMs aggregate in DLA regime at lower electrolyte concentration compared with smaller NMs, if all size fractions have the same surface charge (zeta potential).
- Counterion complexation can result in an antagonistic effect *e.g.* increased CCC values due to reduction in the counterion valence (*e.g.* Al³⁺ to AlSO₄⁺),
- The CCC is independent of NM concentration for pure electrostatic interactions. However, in the presence of chemical constituents of high affinity to NMs (*e.g.* Ag NMs in the presence of cystine, carbonate and phosphate anions) that chemisorb on the surface of NMs, the CCC is NM concentration-dependent.

- The CCC of Ag NM increases with the decrease in buffer (*e.g.* phosphate and carbonate) concentration. This trend is likely to apply for other NMs with high affinity to buffers/ligands due to specific sorption of these buffers/ligands on the surface of NMs and thus alteration of surface (zeta) potential.
- The CCC for Ag NM decreases with light irradiation due to degradation of surface coating and reduction of the magnitude of surface charge.
- The CCC (*ca.* for CeO₂) increase with the decrease in temperature due to decrease in the magnitude of zeta potential.
- Other NM and media physicochemical properties such as surface area, surface roughness, morphology and surface facets, heterogeneity of chemical composition and surface structure, impurities, dissolved oxygen, also affect the CCC, but, based on the available data in the literature, no general trend can be stated at this stage.

Fully coated, sterically stabilized NMs do not aggregate even in high ionic strength solutions. However, the stability (or CCC) of partially coated NMs decreases with the decrease in surface coverage by the capping agent. Also, sterically stabilized NMs can be destabilized by surface coating replacement, rendering such particles subject to aggregation.

Clearly, the stability of NMs is a complex issue that cannot be described by an individual parameter such as ionic strength, or concentration of NOM, that has been the focus of a significant number of studies in the literature. NM stability is rather determined by a combination of NM and medium physicochemical properties. Chemical interactions of NMs with water constituents such as buffer, anions, cysteine, *etc.* play an equally important role in controlling the stability of NMs, especially at environmentally relevant NM concentrations (*ca.* ng to $\mu\text{g L}^{-1}$ range).

Although a significant progress has been made in the understanding NM stability, there is still a need for systematic experimental studies especially on the effect of NM and medium physicochemical properties, and the interplay between these factors in order to develop more comprehensive predictive models to estimate NM aggregation kinetics (CCC and α) based on water chemistry and NM physicochemical properties and to further validate the trends summarized above.

7. Abbreviations

NMs	nanomaterials
CCC	critical coagulation concentration
α	attachment efficiency
W	stability ratio
PVP	polyvinylpyrrolidone
BPEI	branched polyethyleneimine
EPM	electrophoretic mobility
MOPS	3-Morpholinopropanesulfonic acid
TEA	Triethanolamine
DO	Dissolved oxygen
SSA	specific surface area

HSA human serum albumin
GA gum Arabic
RLA reaction limited aggregation
DLA diffusion limited aggregation
pH_{pzc} point of zero charge

8. Acknowledgement

We acknowledge funding support from the National Science Foundation (NSF, 1437307, 1553909), the SmartState Centre for Environmental Nanoscience and Risk, and the Arnold School of Public Health at the University of South Carolina.

References

- (1) Verwey, E. J. W.; Overbeek, J. Th. G. *Theory of the Stability of Lyophobic Colloids*; Elsevier: Amsterdam, 1948.
- (2) Derjaguin, B. V.; Landau, L. D. Theory of the Stability of Strongly Charged Lyophobic Sols and of the Adhesion of Strongly Charged Particles in Solutions of Electrolytes. *Acta physicochim. U. R. S. S.* **1941**, *14* (633-662.
- (3) Baalousha, M.; Lead, J. R.; Ju-Nam, Y. 3.05 - Natural Colloids and Manufactured Nanoparticles in Aquatic and Terrestrial Systems. In *Treatise on Water Science*; Wilderer, P., Ed.; Elsevier: Oxford, 2011.
- (4) Tadros, T. General Principles of Colloid Stability and the Role of Surface Forces. *Colloid stability part I. Viley-VCH Verlag GmbH, Weinheim* **2007**.
- (5) Liu, L.; Moreno, L.; Neretnieks, I. A Novel Approach to Determine the Critical Coagulation Concentration of a Colloidal Dispersion With Plate-Like Particles. *Langmuir* **2009**, *25* (2), 688-697.
- (6) Baalousha, M.; Nur, Y.; Römer, I.; Tejamaya, M.; Lead, J. R. Effect of Monovalent and Divalent Cations, Anions and Fulvic Acid on Aggregation of Citrate-Coated Silver Nanoparticles. *Sci. Tot. Environ.* **2013**, *454-455* (0), 119-131.
- (7) Hotze, E. M.; Phenrat, T.; Lowry, G. V. Nanoparticle Aggregation: Challenges to Understanding Transport and Reactivity in the Environment. *J. Environ. Qual.* **2010**, *39* (6), 1909-1924.
- (8) Zhou, D.; Keller, A. A. Role of Morphology in the Aggregation Kinetics of ZnO Nanoparticles. *Wat. Res.* **2010**, *44* (9), 2948-2956.
- (9) Baalousha, M.; Manciu, A.; Cumberland, S.; Kendall, K.; Lead, J. R. Aggregation and Surface Properties of Iron Oxide Nanoparticles; Influence of PH and Natural Organic Matter. *Environ. Toxicol. Chem.* **2008**, *27* (9), 1875-1882.
- (10) Baalousha, M. Aggregation and Disaggregation of Iron Oxide Nanoparticles: Influence of Particle Concentration, PH and Natural Organic Matter. *Sci. Tot. Environ.* **2009**, *407* (6), 2093-2101.
- (11) Penners, N. H. G.; Koopal, L. K. The Effect of Particle Size on the Stability of Haematite (α -Fe₂O₃) Hydrosols. *Colloid Surf.* **1987**, *28* (67-83.
- (12) Zhou, D.; Ji, Z.; Jiang, X.; Dunphy, D. R.; Brinker, J.; Keller, A. A. Influence of Material Properties on TiO₂ Nanoparticle Agglomeration. *PLoS ONE* **2013**, *8* (11), e81239.
- (13) Stemig, A. M.; Do, T. A.; Yuwono, V. M.; Arnold, W. A.; Penn, R. L. Goethite Nanoparticle Aggregation: Effects of Buffers, Metal Ions, and 4-Chloronitrobenzene Reduction. *Environ. Sci. Nano.* **2014**, *1* (5), 478-487.

- (14) He, Y. T.; Wan, J.; Tokunaga, T. Kinetic Stability of Hematite Nanoparticles: the Effect of Particle Sizes. *J. Nanopart. Res.* **2008**, *10* (321-332.
- (15) Mulvihill, M. J.; Habas, S. E.; Jen-La Plante, I.; Wan, J.; Mokari, T. Influence of Size, Shape, and Surface Coating on the Stability of Aqueous Suspensions of CdSe Nanoparticles. *Chem. Mater.* **2010**, *22* (18), 5251-5257.
- (16) Liu, J.; Legros, S.; Ma, G.; Veinot, J. G. C.; von der Kammer, F.; Hofmann, T. Influence of Surface Functionalization and Particle Size on the Aggregation Kinetics of Engineered Nanoparticles. *Chemosphere* **2012**, *87* (8), 918-924.
- (17) Afshinnia, K.; Sikder, M.; Cai, B.; Baalousha, M. Effect of Nanomaterial and Media Physicochemical Properties on Ag NM Aggregation Kinetics. *J. Colloid Interf. Sci.* **2016**, *487* (192-200.
- (18) Liu, X.; Chen, G.; Su, C. Effects of Material Properties on Sedimentation and Aggregation of Titanium Dioxide Nanoparticles of Anatase and Rutile in the Aqueous Phase. *J. Colloid Interf. Sci.* **2011**, *363* (1), 84-91.
- (19) Schudel, M.; Behrens, S. H.; Holthoff, H.; Kretzschmar, R.; Borkovec, M. Absolute Aggregation Rate Constants of Hematite Particles in Aqueous Suspensions: A Comparison of Two Different Surface Morphologies. *J. Colloid Interf. Sci.* **1997**, *196* (2), 241-253.
- (20) Ortega-Vinuesa, J. L.; Martín-Rodríguez, A.; Hidalgo-Alvarez, R. Colloidal Stability of Polymer Colloids With Different Interfacial Properties: Mechanisms. *Journal of Colloid and Interface Science* **1996**, *184* (1), 259-267.
- (21) Mahnke, J.; Stearnes, J.; Hayes, A.; Fornasiero, D.; Ralston, J. The Influence of Dissolved Gas on the Interactions Between Surfaces of Different Hydrophobicity in Aqueous Media Part I. Measurement of Interaction Forces. *Phys. Chem. Chem. Phys.* **1999**, *1* (11), 2793-2798.
- (22) Parker, J. L.; Claesson, P. M.; Attard, P. Bubbles, Cavities, and the Long-Ranged Attraction Between Hydrophobic Surfaces. *J. Phys. Chem.* **1994**, *98* (34), 8468-8480.
- (23) Yakubov, G. E.; Butt, H. J.; Vinogradova, O. I. Interaction Forces Between Hydrophobic Surfaces. Attractive Jump As an Indication of Formation of "Stable" Submicrocavities. *J. Phys. Chem. B.* **2000**, *104* (15), 3407-3410.
- (24) Shulepov, S. Yu.; Frens, G. Surface Roughness and Particle Size Effect on the Rate of Perikinetic Coagulation: Experimental. *J. Colloid Interf. Sci.* **1996**, *182* (2), 388-394.
- (25) Bhattacharjee, S.; Ko, C. H.; Elimelech, M. DLVO Interaction Between Rough Surfaces. *Langmuir* **1998**, *14* (12), 3365-3375.
- (26) Kostoglou, M.; Karabelas, A. J. Effect of Roughness on Energy of Repulsion Between Colloidal Surfaces. *J. Colloid Interf. Sci.* **1995**, *171* (1), 187-199.
- (27) Sun, N.; Walz, J. Y. A Model for Calculating Electrostatic Interactions Between Colloidal Particles of Arbitrary Surface Topology. *J. Colloid Interf. Sci.* **2001**, *234* (1), 90-105.

- (28) Klaine, S. J.; Alvarez, P. J. J.; Batley, G. E.; Fernandes, T. F.; Handy, R. D.; Lyon, D. Y.; Mahendra, S.; McLaughlin, M. J.; Lead, J. L. Nanomaterials in the Environment : Behaviour, Fate, Bioavailability and Effects. *Environ. Toxicol. Chem.* **2008**, *27* (9), 1825-1851.
- (29) Peijnenburg, W. J.; Baalousha, M.; Chen, J.; Chaudry, Q.; von der Kammer, F.; Kuhlbusch, T. A.; Lead, J.; Nickel, C.; Quik, J. T.; Renker, M. A Review of the Properties and Processes Determining the Fate of Engineered Nanomaterials in the Aquatic Environment. *Crit. Rev. Environ. Sci. Technol.* **2015**, *45* (19), 2084-2134.
- (30) Dale, A. L.; Lowry, G. V.; Casman, E. A. Much Ado About α : Reframing the Debate Over Appropriate Fate Descriptors in Nanoparticle Environmental Risk Modeling. *Environmental Science: Nano* **2015**, *2* (27-32).
- (31) Dale, A. L.; Lowry, G. V.; Casman, E. A. Modeling Nanosilver Transformations in Freshwater Sediments. *Environ. Sci. Technol.* **2013**, *47* (22), 12920-12928.
- (32) Baalousha, M.; Cornelis, G.; Kuhlbusch, T. A. J.; Lynch, I.; Nickel, C.; Peijnenburg, W.; van den Brink, N. W. Modeling Nanomaterial Fate and Uptake in the Environment: Current Knowledge and Future Trends. *Environ. Sci. Nano.* **2016**, *3* (2), 323-345.
- (33) Dale, A. L.; Casman, E. A.; Lowry, G. V.; Lead, J. R.; Viparelli, E.; Baalousha, M. Modeling Nanomaterial Environmental Fate in Aquatic Systems. *Environ. Sci. Technol.* **2015**, *49* (5), 2587-2593.
- (34) Baalousha, M.; Lead, J. R.; Ju-Nam, Y. Natural Colloids and Manufactured Nanoparticles in Aquatic and Terrestrial Systems. In *Treatise on Water Science*; Peter, W., Ed.; Elsevier: Oxford, 2011.
- (35) Petosa, A. R.; Jaisi, D. P.; Quevedo, I. R.; Elimelech, M.; Tufenkji, N. Aggregation and Deposition of Engineered Nanomaterials in Aquatic Environments: Role of Physicochemical Interactions. *Environ. Sci. Technol.* **2010**, *44* (17), 6532-6549.
- (36) Elimelech, M.; Gregory, J.; Jia, G.; Williams, R. A. Surface Interaction Potentials. In *Particle Deposition and Aggregation: Measurement, Modelling and Simulation*; Elimelech, M., Gregory, J., Jia, G., Williams, R. A., Eds.; Butterworth-Heinemann: Woburn, MA, USA, 1995.
- (37) Elimelech, M.; Gregory, J.; Jia, X.; Williams, R. A. *Particle Deposition and Aggregation: Measurement, Modeling and Simulation.*; Butterworth-Heinemann: Oxford, 1995.
- (38) Chen, K. L.; Mylon, S. E.; Elimelech, M. Aggregation Kinetics of Alginate-Coated Hematite Nanoparticles in Monovalent and Divalent Electrolytes. *Environ. Sci. Technol.* **2006**, *40* (5), 1516-1523.
- (39) Chen, K. L.; Mylon, S. E.; Elimelech, M. Enhanced Aggregation of Alginate-Coated Iron Oxide (Hematite) Nanoparticles in the Presence of Calcium, Strontium, and Barium Cations. *Langmuir* **2007**, *23* (11), 5920-5928.
- (40) Cosgrove, T. *Colloid Science: Principles, Methods and Applications*; Blackwell : Oxford, 2005.

- (41) Ninham, B. W. On Progress in Forces Since the DLVO Theory. *Adv. Colloid Interf. Sci.* **1999**, *83* (1-3), 1-17.
- (42) Masliyah, J. H.; Bhattacharjee, S. *Electrokinetic and Colloid Transport Phenomena*; John Wiley & Sons: 2006.
- (43) Waite, T. D.; Cleaver, J. K.; Beattie, J. K. Aggregation Kinetics and Fractal Structure of Γ -Alumina Assemblages. *J. Colloid Interf. Sci.* **2001**, *241* (2), 333-339.
- (44) Fuchs, v. N. Über Die Stabilität Und Aufladung Der Aerosole. *Zeitschrift für Physik* **1934**, *89* (11-12), 736-743.
- (45) Matthews, B. A.; Rhodes, C. T. The Use of the Coulter Counter for Investigating the Coagulation Kinetics of Mixed Monodisperse Particulate Systems. *J. Colloid Interf. Sci.* **1968**, *28* (1), 71-81.
- (46) Gedan, H.; Lichtenfeld, H.; Sonntag, H.; Krug, H. J. Rapid Coagulation of Polystyrene Particles Investigated by Single-Particle Laser Light Scattering. *Colloid Surf.* **1984**, *11* (1), 199-207.
- (47) Cahill, J.; Cummins, P. G.; Staples, E. J.; Thompson, L. Aggregate Size Distribution in Flocculating Dispersions. *Colloid Surf.* **1986**, *18* (2), 189-205.
- (48) Pelssers, E. G. M.; Stuart, M. C.; Fleer, G. J. Single Particle Optical Sizing (SPOS): II. Hydrodynamic Forces and Application to Aggregating Dispersions. *J. Colloid Interf. Sci.* **1990**, *137* (2), 362-372.
- (49) Broide, M. L.; Cohen, R. J. Measurements of Cluster-Size Distributions Arising in Salt-Induced Aggregation of Polystyrene Microspheres. *J. Colloid Interf. Sci.* **1992**, *153* (2), 493-508.
- (50) Ottewill, R. H.; Shaw, J. N. Stability of Monodisperse Polystyrene Latex Dispersions of Various Sizes. *Discussions of the Faraday Society* **1966**, *42* (0), 154-163.
- (51) Reerink, H.; Overbeek, J. T. The Rate of Coagulation As a Measure of the Stability of Silver Iodide Sols. *Discuss. Faraday Soc.* **1954**, *18* (0), 74-84.
- (52) Lichtenbelt, J. T.; Pathmamanoharan, C.; Wiersema, P. H. Rapid Coagulation of Polystyrene Latex in a Stopped-Flow Spectrophotometer. *J. Colloid Interf. Sci.* **1974**, *49* (2), 281-285.
- (53) Lichtenbelt, J. T.; Ras, H. J. M. C.; Wiersema, P. H. Turbidity of Coagulating Lyophobic Sols. *J. Colloid Interf. Sci.* **1974**, *46* (3), 522-527.
- (54) Trompette, J. L.; Meireles, M. Ion-Specific Effect on the Gelation Kinetics of Concentrated Colloidal Silica Suspensions. *Journal of Colloid and Interface Science* **2003**, *263* (2), 522-527.
- (55) Lips, A.; Smart, C.; Willis, E. Light Scattering Studies on a Coagulating Polystyrene Latex. *Trans. Faraday Soc.* **1971**, *67* (2979-2988).
- (56) Lips, A.; Willis, E. Low Angle Light Scattering Technique for the Study of Coagulation. *J. Chem. Soc. Faraday Trans. 1: Phys. Chem. Condensed Phases* **1973**, *69* (1226-1236).

- (57) Giles, D.; Lips, A. Light Scattering Method for the Study of Close Range Structure in Coagulating Dispersions of Equal Sized Spherical Particles. *Journal of the Chemical Society, Faraday Transactions 1: Physical Chemistry in Condensed Phases* **1978**, 74 (733-744.
- (58) Zeichner, G. R.; Schowalter, W. R. Effects of Hydrodynamic and Colloidal Forces on the Coagulation of Dispersions. *J. Colloid Interf. Sci.* **1979**, 71 (2), 237-253.
- (59) Virden, J. W.; Berg, J. C. The Use of Photon Correlation Spectroscopy for Estimating the Rate Constant for Doublet Formation in an Aggregating Colloidal Dispersion. *J. Colloid Interf. Sci.* **1992**, 149 (2), 528-535.
- (60) Novich, B. E.; Ring, T. A. Photon Correlation Spectroscopy of a Coagulating Suspension of Illite Platelets. *Journal of the Chemical Society, Faraday Transactions 1: Physical Chemistry in Condensed Phases* **1985**, 81 (6), 1455-1457.
- (61) Einarson, M. B.; Berg, J. C. Electrosteric Stabilization of Colloidal Latex Dispersions. *J. Colloid Interf. Sci.* **1993**, 155 (1), 165-172.
- (62) Nur, Y.; Lead, J. R.; Baalousha, M. Evaluation of Charge and Agglomeration Behavior of TiO₂ Nanoparticles in Ecotoxicological Media. *Sci. Tot. Environ.* **2015**, 535 (45-53.
- (63) Gregory, J. Monitoring Particle Aggregation Processes. *Adv. Colloid Interf. Sci.* **2009**, 147–148 (109-123.
- (64) Burns, J. L.; Yan, Y. d.; Jameson, G. J.; Biggs, S. A Light Scattering Study of the Fractal Aggregation Behavior of a Model Colloidal System. *Langmuir* **1997**, 13 (24), 6413-6420.
- (65) Saejiew, A.; Grunberger, O.; Arunin, S.; Favre, F.; Tessier, D.; Boivin, P. Critical Coagulation Concentration of Paddy Soil Clays in Sodium-Ferrous Iron Electrolyte. *Soil Sci. Soc. Am. J.* **2004**, 68 (3), 789-794.
- (66) Frenkel, H.; Levy, G. J.; Fey, M. V. Organic and Inorganic Anion Effects on Reference and Soil Clay Critical Flocculation Concentration. *Soil Sci. Soc. Am. J.* **1992**, 56 (6), 1762-1766.
- (67) Hesterberg, D.; Page, A. L. Flocculation Series Test Yielding Time-Invariant Critical Coagulation Concentrations of Sodium Illite. *Soil Sci. Soc. Am. J.* **1990**, 54 (3), 729-735.
- (68) Matijevic, E.; Allen, L. H. Interactions of Colloidal Dispersions With Electrolytes. *Environ. Sci. Technol.* **1969**, 3 (3), 264-268.
- (69) Vincent, B. Early (Pre-DLVO) Studies of Particle Aggregation. *Adv. Colloid Interf. Sci.* **2012**, 170 (1–2), 56-67.
- (70) Nowicki, W.; Nowicka, G. Verification of the Schulze-Hardy Rule: A Colloid Chemistry Experiment. *J. Chem. Ed.* **1994**, 71 (7), 624.
- (71) Tadros, T. F. *Interfacial Phenomena and Colloid Stability: Industrial Applications*; Walter de Gruyter GmbH & Co KG: 2015.

- (72) Verrall, K. E.; Warwick, P.; Fairhurst, A. J. Application of the Schulze-Hardy Rule to Haematite and Haematite/Humate Colloid Stability. *Colloids Surf. A: Physicochem. Eng. Aspects.* **1999**, *150* (1-3), 261-273.
- (73) Fritz, G.; Schadler, V.; Willenbacher, N.; Wagner, N. J. Electrosteric Stabilization of Colloidal Dispersions. *Langmuir* **2002**, *18* (16), 6381-6390.
- (74) Roucoux, A.; Schulz, J. +.; Patin, H. Reduced Transition Metal Colloids:ΓÇē A Novel Family of Reusable Catalysts? *Chem. Rev.* **2002**, *102* (10), 3757-3778.
- (75) Napper, D. H. Steric Stabilization. *Journal of Colloid and Interface Science* **1977**, *58* (2), 390-407.
- (76) Hiemenz, P. C.; Rajagopalan, R. *Principles of Colloid and Surface Chemistry*; CRC Press: New York, USA, 1997.
- (77) Afshinnia, K.; Gibson, I.; Merrifield, R.; Baalousha, M. The Concentration-Dependent Aggregation of Ag NPs Induced by Cystine. *Sci. Tot. Environ.* **2016**, *557-558* (395-403).
- (78) Stumm, W.; O'Melia, C. R. Stoichiometry of Coagulation. *Journal (American Water Works Association)* **1968**, *60* (5), 514-539.
- (79) Moskovits, M.; Vlc ková, B. Adsorbate-Induced Silver Nanoparticle Aggregation Kinetics. *J. Phys. Chem. B.* **2005**, *109* (31), 14755-14758.
- (80) Metreveli, G.; Frombold, B.; Seitz, F.; Grün, A.; Philippe, A.; Rosenfeldt, R. R.; Bundschuh, M.; Schulz, R.; Manz, W.; Schaumann, G. E. Impact of Chemical Composition of Ecotoxicological Test Media on the Stability and Aggregation Status of Silver Nanoparticles. *Environ. Sci. Nano.* **2016**.
- (81) Afshinnia, K.; Sikder, M.; Cai, B.; Baalousha, M. Effect of Nanomaterial and Media Physicochemical Properties on Ag NM Aggregation Kinetics. *J. Colloid Interf. Sci.* **2017**, *487* (192-200).
- (82) Liu, X.; Wazne, M.; Han, Y.; Christodoulatos, C.; Jasinkiewicz, K. L. Effects of Natural Organic Matter on Aggregation Kinetics of Boron Nanoparticles in Monovalent and Divalent Electrolytes. *J. Colloid Interf. Sci.* **2010**, *348* (1), 101-107.
- (83) Afshinnia, K.; Baalousha, M. Effect of Phosphate Buffer on Aggregation Kinetics of Citrate-Coated Silver Nanoparticles. *NanoImpact. (Submitted)* **2016**.
- (84) Hall, S. B.; Duffield, J. R.; Williams, D. R. A Reassessment of the Applicability of the DLVO Theory As an Explanation for the Schulze-Hardy Rule for Colloid Aggregation. *J. Colloid Interf. Sci.* **1991**, *143* (2), 411-415.
- (85) Huynh, K. A.; Chen, K. L. Aggregation Kinetics of Citrate and Polyvinylpyrrolidone Coated Silver Nanoparticles in Monovalent and Divalent Electrolyte Solutions. *Environ. Sci. Technol.* **2011**, *45* (13), 5564-5571.

- (86) Amal, R.; Raper, J. A.; Waite, T. D. Effect of Fulvic Acid Adsorption on the Aggregation Kinetics and Structure of Hematite Particles. *J. Colloid Interf. Sci.* **1992**, *151* (1), 244-257.
- (87) Snoswell, D. R. E.; Duan, J.; Fornasiero, D.; Ralston, J. Colloid Stability of Synthetic Titania and the Influence of Surface Roughness. *J. Colloid Interf. Sci.* **2005**, *286* (2), 526-535.
- (88) Buchholz, A.; Laskov, C.; Haderlein, S. B. Effects of Zwitterionic Buffers on Sorption of Ferrous Iron at Goethite and Its Oxidation by CCl_4 . *Environ. Sci. Technol.* **2011**, *45* (8), 3355-3360.
- (89) Liang, L. Effects of Surface Hemistry on Kinetics of Coagulation of Submicron Iron-Oxide Particles (Alpha-Iron-Oxide) in Water. **1988**.
- (90) Piccapietra, F.; Sigg, L.; Behra, R. Colloidal Stability of Carbonate Coated Silver Nanoparticles in Synthetic and Natural Freshwater. *Environ. Sci. Technol.* **2012**, *46* (2), 818-825.
- (91) Zhang, W.; Yao, Y.; Li, K.; Huang, Y.; Chen, Y. Influence of Dissolved Oxygen on Aggregation Kinetics of Citrate-Coated Silver Nanoparticles. *Environ. Pollut.* **2011**, *159* (12), 3757-3762.
- (92) Li, Y.; Zhang, W.; Li, K.; Yao, Y.; Niu, J.; Chen, Y. Oxidative Dissolution of Polymer-Coated CdSe/ZnS Quantum Dots Under UV Irradiation: Mechanisms and Kinetics. *Environ. Pollut.* **2012**, *164* (2), 259-266.
- (93) Zhang, W.; Yao, Y.; Sullivan, N.; Chen, Y. Modeling the Primary Size Effects of Citrate-Coated Silver Nanoparticles on Their Ion Release Kinetics. *Environ. Sci. Technol.* **2011**, *45* (10), 4422-4428.
- (94) Liu, J.; Hurt, R. H. Ion Release Kinetics and Particle Persistence in Aqueous Nano-Silver Colloids. *Environ. Sci. Technol.* **2010**, *44* (6), 2169-2175.
- (95) Römer, I.; Wang, Z. W.; Merrifield, R. C.; Palmer, R. E.; Lead, J. High Resolution STEM-EELS Study of Silver Nanoparticles Exposed to Light and Humic Substances. *Environ. Sci. Technol.* **2016**, *50* (5), 2183-2190.
- (96) Ho, C. M.; Yau, S. K.-W.; Lok, C. N.; So, M. H.; Che, C. M. Oxidative Dissolution of Silver Nanoparticles by Biologically Relevant Oxidants: A Kinetic and Mechanistic Study. *Chem. Asian J.* **2010**, *5* (2), 285-293.
- (97) Li, Y.; Zhang, W.; Niu, J.; Chen, Y. Surface-Coating-Dependent Dissolution, Aggregation, and Reactive Oxygen Species (ROS) Generation of Silver Nanoparticles Under Different Irradiation Conditions. *Environ. Sci. Technol.* **2013**.
- (98) Misra, N.; Kumar, V.; Borde, L.; Varshney, L. Localized Surface Plasmon Resonance-Optical Sensors Based on Radiolytically Synthesized Silver Nanoparticles for Estimation of Uric Acid. *Sens. Actuat. B: Chem.* **2013**, *178* (2), 371-378.
- (99) Correa-Duarte, M. A.; Giersig, M.; Liz-Marzán, L. M. Stabilization of CdS Semiconductor Nanoparticles Against Photodegradation by a Silica Coating Procedure. *Chem. Phys. Lett.* **1998**, *286* (5/6), 497-501.

- (100) Mittelman, A. M.; Fortner, J. D.; Pennell, K. D. Effects of Ultraviolet Light on Silver Nanoparticle Mobility and Dissolution. *Environ. Sci. Nano.* **2015**, 2 (6), 683-691.
- (101) Gorham, J. M.; MacCuspie, R. I.; Klein, K. L.; Fairbrother, D. H.; Holbrook, D. UV-Induced Photochemical Transformations of Citrate-Capped Silver Nanoparticle Suspensions. *J. Nanopart. Res.* **2012**, 14 (10).
- (102) Shi, J.; Xu, B.; Sun, X.; Ma, C.; Yu, C.; Zhang, H. Light Induced Toxicity Reduction of Silver Nanoparticles to *Tetrahymena Pyriformis*: Effect of Particle Size. *Aquat. Toxicol.* **2013**, 132-133 (53-60).
- (103) Sun, J.; Guo, L. H.; Zhang, H.; Zhao, L. UV Irradiation Induced Transformation of TiO₂ Nanoparticles in Water: Aggregation and Photoreactivity. *Environ. Sci. Technol.* **2014**, 48 (20), 11962-11968.
- (104) Zhou, D.; Bennett, S. W.; Keller, A. A. Increased Mobility of Metal Oxide Nanoparticles Due to Photo and Thermal Induced Disagglomeration. *PLoS ONE* **2012**, 7 (5), e37363.
- (105) Bennett, S. W.; Zhou, D.; Mielke, R.; Keller, A. A. Photoinduced Disaggregation of TiO₂ Nanoparticles Enables Transdermal Penetration. *PLoS ONE* **2012**, 7 (11), e48719.
- (106) Chen, Y.; Huang, Y.; Li, K. Temperature Effect on the Aggregation Kinetics of CeO₂ Nanoparticles in Monovalent and Divalent Electrolytes. *J. Environ. Anal. Toxicol.* **2012**, 2 (7), 1000158-1-1000158-5.
- (107) Metin, C. O.; Lake, L. W.; Miranda, C. R.; Nguyen, Q. P. Stability of Aqueous Silica Nanoparticle Dispersions Under Subsurface Conditions. *J. Nanotech.* **2010**, 3 (627-630).
- (108) Misra, S. K.; Dybowska, A.; Berhanu, D.; Croteau, M. N.; Luoma, S. N.; Boccaccini, A. R.; Valsami-Jones, E. Isotopically Modified Nanoparticles for Enhanced Detection in Bioaccumulation Studies. *Environ. Sci. Technol.* **2011**, 46 (2), 1216-1222.
- (109) Majedi, S. M.; Kelly, B. C.; Lee, H. K. Combined Effects of Water Temperature and Chemistry on the Environmental Fate and Behavior of Nanosized Zinc Oxide. *Sci. Tot. Environ.* **2014**, 496 (585-593).
- (110) Adeleye, A. S.; Keller, A. A. Long-Term Colloidal Stability and Metal Leaching of Single Wall Carbon Nanotubes: Effect of Temperature and Extracellular Polymeric Substances. *Wat. Res.* **2014**, 49 (236-250).
- (111) Valdivieso, A. L.; Bahena, J. R.; Song, S.; Urbina, R. H. Temperature Effect on the Zeta Potential and Fluoride Adsorption at the α -Al₂O₃/Aqueous Solution Interface. *J. Colloid Interf. Sci.* **2006**, 298 (1), 1-5.
- (112) Rodríguez, K.; Araujo, M. Temperature and Pressure Effects on Zeta Potential Values of Reservoir Minerals. *J. Colloid Interf. Sci.* **2006**, 300 (2), 788-794.
- (113) Borghi, F.; Vyas, V.; Podest+á, A.; Milani, P. Nanoscale Roughness and Morphology Affect the Isoelectric Point of Titania Surfaces. *PLoS ONE* **2013**, 8 (7), e68655.

- (114) Ryan, J. N.; Elimelech, M. Colloid Mobilization and Transport in Groundwater. *Colloid Surf. A: Physicochem. Eng. Aspects*. **1996**, *107* (1-56.
- (115) Zhang, W.; Crittenden, J.; Li, K.; Chen, Y. Attachment Efficiency of Nanoparticle Aggregation in Aqueous Dispersions: Modeling and Experimental Validation. *Environ. Sci. Technol.* **2012**, *46* (13), 7054-7062.
- (116) Li, K.; Zhang, W.; Huang, Y.; Chen, Y. Aggregation Kinetics of CeO₂ Nanoparticles in KCl and CaCl₂ Solutions: Measurements and Modeling. *J. Nanopart. Res.* **2011**, *13* (12), 6483-6491.
- (117) Gilbert, B.; Ono, R. K.; Ching, K. A.; Kim, C. S. The Effects of Nanoparticle Aggregation Processes on Aggregate Structure and Metal Uptake. *J. Colloid Interf. Sci.* **2009**, *339* (2), 285-295.
- (118) Metreveli, G.; Frombold, B.; Seitz, F.; Grun, A.; Philippe, A.; Rosenfeldt, R. R.; Bundschuh, M.; Schulz, R.; Manz, W.; Schaumann, G. E. Impact of Chemical Composition of Ecotoxicological Test Media on the Stability and Aggregation Status of Silver Nanoparticles. *Environ. Sci. Nano*. **2016**.
- (119) Pokhrel, L. R.; Dubey, B.; Scheuerman, P. R. Impacts of Select Organic Ligands on the Colloidal Stability, Dissolution Dynamics, and Toxicity of Silver Nanoparticles. *Environ. Sci. Technol.* **2013**, *47* (22), 12877-12885.
- (120) Wang, F.; Liu, X.; Lu, C. H.; Willner, I. Cysteine-Mediated Aggregation of Au Nanoparticles: The Development of a H₂O₂ Sensor and Oxidase-Based Biosensors. *ACS Nano* **2013**, *7* (8), 7278-7286.
- (121) Zakaria, H. M.; Shah, A.; Konieczny, M.; Hoffmann, J. A.; Nijdam, A. J.; Reeves, M. E. Small Molecule- and Amino Acid-Induced Aggregation of Gold Nanoparticles. *Langmuir* **2013**, *29* (25), 7661-7673.
- (122) Doyen, M.; Goole, J.; Bartik, K.; Bruylants, G. Amino Acid Induced Fractal Aggregation of Gold Nanoparticles: Why and How. *J. Colloid Interf. Sci.* **2016**, *464* (160-166.
- (123) Chegel, V.; Rachkov, O.; Lopatynskyi, A.; Ishihara, S.; Yanchuk, I.; Nemoto, Y.; Hill, J. P.; Ariga, K. Gold Nanoparticles Aggregation: Drastic Effect of Cooperative Functionalities in a Single Molecular Conjugate. *J. Phys. Chem. C*. **2012**, *116* (4), 2683-2690.
- (124) Gebauer, J. S.; Malissek, M.; Simon, S.; Knauer, S. K.; Maskos, M.; Stauber, R. H.; Peukert, W.; Treuel, L. Impact of the Nanoparticle–Protein Corona on Colloidal Stability and Protein Structure. *Langmuir* **2012**, *28* (25), 9673-9679.
- (125) Lesniak, A.; Salvati, A.; Santos-Martinez, M. J.; Radomski, M. W.; Dawson, K. A.; +àberg, C. Nanoparticle Adhesion to the Cell Membrane and Its Effect on Nanoparticle Uptake Efficiency. *J. Am. Chem. Soc.* **2013**, *135* (4), 1438-1444.
- (126) Loosli, F.; Le Coustumer, P.; Stoll, S. Effect of Electrolyte Valency, Alginate Concentration and PH on Engineered TiO₂ Nanoparticle Stability in Aqueous Solution. *Science of The Total Environment* **2015**, *535* (28-34.

- (127) Shih, Y. h.; Zhuang, C. m.; Peng, Y. H.; Lin, C. h.; Tseng, Y. m. The Effect of Inorganic Ions on the Aggregation Kinetics of Lab-Made TiO₂ Nanoparticles in Water. *Sci. Tot. Environ.* **2012**, 435 (446-452).
- (128) Matijevic, E.; Stryker, L. J. Coagulation and Reversal of Charge of Lyophobic Colloids by Hydrolyzed Metal Ions. *J. Colloid Interf. Sci.* **1966**, 22 (1), 68-77.
- (129) Stryker, L. J.; Matijevic, E. Counterion Complexing and Sol Stability. II. Coagulation Effects of Aluminum Sulfate in Acidic Solutions. *J. Phys. Chem.* **1969**, 73 (5), 1484-1487.
- (130) Sani-Kast, N.; Scheringer, M.; Slomberg, D.; Labille, J.; Praetorius, A.; Ollivier, P.; Hungerbühler, K. Addressing the Complexity of Water Chemistry in Environmental Fate Modeling for Engineered Nanoparticles. *Sci. Tot. Environ.* **2015**.
- (131) Pinchuk, P.; Jiang, K. Size-dependent Hamaker constants for silver and gold nanoparticles. 95491J. 2015. *Int.Soc.Opt.Photon*.
- (132) Pinchuk, A. O. Size-Dependent Hamaker Constant for Silver Nanoparticles. *J. Phys. Chem. C.* **2012**, 116 (37), 20099-20102.
- (133) Wijenayaka, L. A.; Ivanov, M. R.; Cheatum, C. M.; Haes, A. J. Improved Parametrization for Extended Derjaguin, Landau, Verwey, and Overbeek Predictions of Functionalized Gold Nanosphere Stability. *J. Phys. Chem. C.* **2015**, 119 (18), 10064-10075.
- (134) Kim, T.; Lee, C. H.; Joo, S. W.; Lee, K. Kinetics of Gold Nanoparticle Aggregation: Experiments and Modeling. *J. Colloid Interf. Sci.* **2008**, 318 (2), 238-243.
- (135) Kim, T.; Lee, K.; Gong, M. s.; Joo, S. W. Control of Gold Nanoparticle Aggregates by Manipulation of Interparticle Interaction. *Langmuir* **2005**, 21 (21), 9524-9528.
- (136) Zhang, Y.; Chen, Y.; Westerhoff, P.; Crittenden, J. Impact of Natural Organic Matter and Divalent Cations on the Stability of Aqueous Nanoparticles. *Wat. Res.* **2009**, 43 (17), 4249-4257.
- (137) Zhang, Y.; Chen, Y.; Westerhoff, P.; Hristovski, K.; Crittenden, J. C. Stability of Commercial Metal Oxide Nanoparticles in Water. *Wat. Res.* **2008**, 42 (8-9), 2204-2212.
- (138) Karimian, H.; Babaluo, A. A. Halos Mechanism in Stabilizing of Colloidal Suspensions: Nanoparticle Weight Fraction and PH Effects. *J. Europ. Cer. Soc.* **2007**, 27 (1), 19-25.
- (139) Faure, B.; Salazar-Alvarez, G.; Bergström, L. Hamaker Constants of Iron Oxide Nanoparticles. *Langmuir* **2011**, 27 (14), 8659-8664.
- (140) Liu, X.; Wazne, M.; Christodoulatos, C.; Jasinkiewicz, K. L. Aggregation and Deposition Behavior of Boron Nanoparticles in Porous Media. *J. Colloid Interf. Sci.* **2009**, 330 (1), 90-96.
- (141) Kosmulski, M. The Significance of the Difference in the Point of Zero Charge Between Rutile and Anatase. *Advances in Colloid and Interface Science* **2002**, 99 (3), 255-264.

- (142) Buettner, K. M.; Rinciog, C. I.; Mylon, S. E. Aggregation Kinetics of Cerium Oxide Nanoparticles in Monovalent and Divalent Electrolytes. *Colloid Surfaces A: Physicochem. Engin. Asp.* **2010**, *366* (1-3), 74-79.
- (143) Gaboriaud, F.; Ehrhardt, J. J. Effects of Different Crystal Faces on the Surface Charge of Colloidal Goethite ([Alpha]-FeOOH) Particles: an Experimental and Modeling Study. *Geochim. Cosmochim. Acta.* **2003**, *67* (5), 967-983.
- (144) French, R. H.; Cannon, R. M.; DeNoyer, L. K.; Chiang, Y. M. Full Spectral Calculation of Non-Retarded Hamaker Constants for Ceramic Systems From Interband Transition Strengths. *Solid State Ionics* **1995**, *75* (13-33).
- (145) Vold, M. J. Van Der Waals' Attraction Between Anisometric Particles. *J. Colloid Sci.* **1954**, *9* (5), 451-459.
- (146) Bullard, J. W.; Cima, M. J. Orientation Dependence of the Isoelectric Point of TiO₂ (Rutile) Surfaces. *Langmuir* **2006**, *22* (24), 10264-10271.
- (147) Assemi, S.; Nalaskowski, J.; Miller, J. D.; Johnson, W. P. Isoelectric Point of Fluorite by Direct Force Measurements Using Atomic Force Microscopy. *Langmuir* **2006**, *22* (4), 1403-1405.
- (148) Fa, K.; Jiang, T.; Nalaskowski, J.; Miller, J. D. Interaction Forces Between a Calcium Dioleate Sphere and Calcite/Fluorite Surfaces and Their Significance in Flotation. *Langmuir* **2003**, *19* (25), 10523-10530.
- (149) Oberndorfer, J.; Dobiáš, B. A Collection of Papers Presented at the 10th European Conference on Chemistry of Interfaces Adsorption Mechanism of Anionic Surfactants on Sparingly Soluble Minerals. *Colloid Surf.* **1989**, *41* (69-76).
- (150) Hiemstra, T.; van Riemsdijk, W. H. Effect of Different Crystal Faces on Experimental Interaction Force and Aggregation of Hematite. *Langmuir* **1999**, *15* (23), 8045-8051.
- (151) Fa, K.; Paruchuri, V. K.; Brown, S. C.; Moudgil, B. M.; Miller, J. D. The Significance of Electrokinetic Characterization for Interpreting Interfacial Phenomena at Planar, Macroscopic Interfaces. *Phys. Chem. Chem. Phys.* **2005**, *7* (4), 678-684.
- (152) Kershner, R. J.; Bullard, J. W.; Cima, M. J. Zeta Potential Orientation Dependence of Sapphire Substrates. *Langmuir* **2004**, *20* (10), 4101-4108.
- (153) Frens, G. Particle Size and Sol Stability in Metal Colloids. *Kolloid-Zeitschrift und Zeitschrift für Polymere* **1972**, *250* (7), 736-741.
- (154) Watillon, A.; Joseph-Petit, A. M. Interactions Between Spherical Particles of Monodisperse Polystyrene Latices. *Discuss. Faraday Soc.* **1966**, *42* (143-153).
- (155) Iler, R. K. Coagulation of Colloidal Silica by Calcium Ions, Mechanism, and Effect of Particle Size. *J. Colloid Interf. Sci.* **1975**, *53* (3), 476-488.

- (156) Kotera, A.; Furusawa, K.; Kudo, M. K. Colloid Chemical Studies of Polystyrene Latices Polymerized Without Any Surface-Active Agents. *Kolloid-Zeitschrift und Zeitschrift für Polymere* **1970**, 240 (1-2), 837-842.
- (157) Elimelech, M.; O'Melia, C. R. Effect of Particle Size on Collision Efficiency in the Deposition of Brownian Particles With Electrostatic Energy Barriers. *Langmuir* **1990**, 6 (6), 1153-1163.
- (158) Baalousha, M.; Ju-Nam, Y.; Cole, P. A.; Gaiser, B.; Fernandes, T. F.; Hriljac, J. A.; Jepson, M. A.; Stone, V.; Tyler, C. R.; Lead, J. R. Characterization of Cerium Oxide Nanoparticles—Part 1: Size Measurements. *Environ. Toxicol. Chem.* **2012**, 31 (5), 983-993.
- (159) Baalousha, M.; Le Coustumer, P.; Jones, I.; Lead, J. R. Characterization of Structural and Surface Speciation of Representative Commercially Available Cerium Oxide Nanoparticles. *Environ. Chem.* **2010**, 7 (4), 377-385.
- (160) Huang, R.; Carney, R. P.; Stellacci, F.; Lau, B. L. T. Colloidal Stability of Self-Assembled Monolayer-Coated Gold Nanoparticles: The Effects of Surface Compositional and Structural Heterogeneity. *Langmuir* **2013**, 29 (37), 11560-11566.
- (161) Shulepov, S. Y.; Frens, G. Surface Roughness and the Particle Size Effect on the Rate of Slow, Perikinetic Coagulation. *J. Colloid Interf. Sci.* **1995**, 170 (1), 44-49.
- (162) Baalousha, M.; Sikder, M.; Prasad, A.; Lead, J.; Merrifield, R.; Chandler, G. T. The Concentration-Dependent Behavior of Nanoparticles. *Env. Chem.* **2016**, 13 (1), 1-3.
- (163) Zhang, H.; Smith, J. A.; Oyanedel-Craver, V. The Effect of Natural Water Conditions on the Anti-Bacterial Performance and Stability of Silver Nanoparticles Capped With Different Polymers. *Wat. Res.* **2012**, 46 (3), 691-699.
- (164) El Badawy, A. M.; Scheckel, K. G.; Suidan, M.; Tolaymat, T. The Impact of Stabilization Mechanism on the Aggregation Kinetics of Silver Nanoparticles. *Sci. Tot. Environ.* **2012**, 429 (1), 325-331.
- (165) Lodeiro, P.; Achterberg, E. P.; Pampin, J.; Affatati, A.; El-Shahawi, M. S. Silver Nanoparticles Coated With Natural Polysaccharides As Models to Study AgNP Aggregation Kinetics Using UV-Visible Spectrophotometry Upon Discharge in Complex Environments. *Sci. Tot. Environ.* **2016**, 539 (7-16).
- (166) Lin, S.; Cheng, Y.; Liu, J.; Wiesner, M. R. Polymeric Coatings on Silver Nanoparticles Hinder Autoaggregation but Enhance Attachment to Uncoated Surfaces. *Langmuir* **2012**, 28 (9), 4178-4186.
- (167) Tiraferri, A.; Chen, K. L.; Sethi, R.; Elimelech, M. Reduced Aggregation and Sedimentation of Zero-Valent Iron Nanoparticles in the Presence of Guar Gum. *J. Colloid Interf. Sci.* **2008**, 324 (1-2), 71-79.

TOC