Temperature Effect on the Aggregation Kinetics of CeO₂ Nanoparticles in Monovalent and Divalent Electrolytes

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Abstract

Aggregation of engineered nanoparticles (NPs) plays a crucial role in their environmental transport, fate, bioavailability and biological effects. This study investigated the temperature effect on the aggregation kinetics of CeO₂ NPs in KCl and CaCl₂ solutions using time-resolved dynamic light scattering. The results show that in KCl and CaCl₂, the aggregation rate became faster as the temperature increased. The critical coagulation concentration (CCC) of CeO₂ NPs went down from approximately 100 to 10 mM in KCl and from approximately 10 to 2 mM in CaCl₂ solutions when the temperature increased from 4 to 37°C. The observations were analyzed in the framework of extended Derjaguin-Landau-Verwey-Overbeek (EDLVO) theory in order to find out the mechanisms underlying the temperature effect. Moreover, a theoretical model developed on the basis of EDLVO theory and von Smoluchowski’s population balance equation was used to predict the aggregation kinetics of CeO₂ NPs under different temperature. The model predictions agreed well with experimental data, suggesting that the model could be employed to predict the size change of NPs in solution. Overall, this work provides insights into NP aggregation using experimental and modeling approaches, and allows people to better understand and theoretically predict the environmental behavior and risk of NPs.

Keywords: Nanoparticle; Aggregation; Temperature; EDLVO

Introduction

Recently, engineered nanoparticles (NPs) have received enormous attention owing to their potential commercial and industrial applications in many sectors, such as cosmetics, textiles, pharmaceutical, catalysts and electronics [1,2]. But meanwhile, the release of NPs into the environment will very likely happen along with their large-scale manufacture and wide use, which will subsequently impose risks for ecosystems and human health [3]. It is thus important to evaluate the environmental and health risks of NPs before their mass production. Since the toxicological testing’s of NPs are expensive and time-consuming, researchers are developing theoretical models to evaluate and predict the behavior and risks of NPs in environmental systems [4-6].

Previous studies have shown that the aggregation of NPs plays an important role in their environmental risks by influencing their transport, fate, bioavailability and biological effects [7-11]. Understanding the fundamental principles underlying the aggregation process of NPs and quantitatively describing this process are essential prerequisites for characterizing the environmental behavior of NPs and further quantifying the risk. The aggregation of NPs is fundamentally governed by the interfacial force between interacting particles, which includes several either attractive or repulsive forces. When the attractive force is greater than the repulsive force, NPs approach each other and aggregate; otherwise, NPs stay stable. The famous Derjaguin-Landau-Verwey-Overbeek (DLVO) theory has been widely used to characterize the interfacial force between particles [12,13]. According to it, the vander Waals (vdW) force and electrostatic (EL) force compose the interfacial force. The DLVO theory achieved great success in explaining the stability of colloids in salt solutions. But for NP aggregation, many studies have found that a discrepancy exists between DLVO predictions and experimental observations [14]. This problem might be overcome by taking non-DLVO forces into account, such as the polar Lewis acid/base (AB) force [15] and steric force [16]. Here the AB force is the sum of the hydrophobic interaction force, hydrogen-bonding force and hydration force [15-17]. The precise theoretical analysis of NP interaction and quantitative description of NP aggregation can be obtained by incorporating those non-DLVO forces into the DLVO theory, which is known as the extended DLVO (EDLVO or XDLVO) theory [15].

On the basis of EDLVO theory, our previous studies have addressed the effects of ionic strength and natural organic matter on NP aggregation with modeling approaches [5,18]. It is well known that temperature also greatly influences the aggregation of NPs. Understanding the temperature effect is important for environmental and health risk assessments of NPs, as both natural water and human body fluids can be at temperatures that are remarkably different from the typically used room temperature. For example, river waters in some cold areas may be only 4°C, whereas the temperature of blood in the human body is as high as 37°C. NPs in these solutions would undergo different aggregation processes. The temperature effect, however, has not gained much attention in NP aggregation studies. In this study, we investigated the temperature effect on the aggregation of NPs in KCl and CaCl₂ solutions using time-resolved dynamic light scattering (TR-DLS). We selected CeO₂ NP as a model NP owing to its extensive commercial applications [19-21]. It has been listed as a priority nanomaterial for immediate testing by the Organization for Economic Co-operation and Development (OECD) [22]. We used the EDLVO theory to interpret the fundamentals of the temperature effect on NP aggregation. Furthermore, a kinetic model developed on the basis of EDLVO theory and von Smoluchowski’s population balance equation was used to predict the aggregation kinetics of CeO₂.
Characterizations of CeO$_i$ NPs

The morphology and primary particle size of CeO$_i$ NPs were determined using TEM. 5 µL of CeO$_i$ NP suspensions were deposited on a copper grid (400 mesh size) coated with carbon film (Ted Pella, Redding, CA, USA). A Philips EM420 TEM was employed to acquire images. Particle size distribution (PSD) was obtained with DLS on a Zetasizer Nano ZS instrument (Malvern Instruments). Briefly, 1.5 mL of 10 mg/L CeO$_i$ NP suspension was injected into a clean cuvette; the DLS instrument was then operated with a scattering angle of 173° from the incident laser beam, and the autocorrelation function automatically accumulated at least 10 runs for each sample. The electrophoretic mobilities' (EMPs) of 10 mg/L CeO$_i$ NPs were measured for a range of K$^+$ and Ca$^{2+}$ concentrations under different temperatures using the Zetasizer Nano ZS instrument. At least four parallel measurements were made for each condition. The measurement began immediately after the desired conditions were achieved to minimize the interference of aggregation.

Aggregation kinetics

The aggregation kinetics experiments were carried out at pH 5.7, at which the CeO$_i$ NPs are stable for at least 24 h. The pH values of the CeO$_i$ NP, KCl and CaCl$_2$ solutions were pre-adjusted to 5.7 to ensure that each measurement could start immediately after addition of K$^+$ and Ca$^{2+}$. For the aggregation experiment, the sample holder of the Zeta Nano instrument was preheated or precooled to the desired temperature. A premeasured amount of KCl or CaCl$_2$ was added to 1 mL of CeO$_i$ NP suspension in a cuvette. The NP suspension was then shaken slightly and placed in the sample holder.

Modeling the aggregation kinetics

According to the EDLVO theory, the total interfacial force between two metal oxide NPs is comprised of the vdW force, EL force and AB force [15]. The total interfacial energy (V$_i$) between NPs is computed by assuming that each force acts individually and is thus additive: $V_i = V_{vdw} + V_{EL} + V_{AB}$.

The vdW attractive energy (V$_{vdw}$) between two identical spherical particles, which considers the retardation effect, can be computed using Equation (1) [23]:

$$V_{vdw} (h) = \frac{A_H r}{12h(1+11.12h/\lambda^2)}$$ (1)

where $A_H$ is the Hamaker constant, which is 5.57×10$^{-20}$ J for CeO$_i$ in water [24]. $r$ is the particle radius. $h$ is the separation distance between the interacting surfaces. $\lambda$ is the “characteristic wavelength” of the interaction, which is often assumed to be 100 nm [25].

The EL repulsive energy (V$_{EL}$) between two identical spheres of radii r in 1-1 electrolyte solutions (e.g., KCl) is given by Equation (2a-c). In 2-1 electrolyte solutions (e.g., CaCl$_2$), Equation (2a) and (2b) are replaced by Equation (2d) and (2e), respectively [26-28]:

$$V_{EL} (h) = \frac{128\pi k_B T \eta^2 \gamma_i^2}{\kappa^2} \frac{r^2}{2r + h} \exp (-\kappa h)$$ (2a)

$$\gamma_i = \tanh \left( \frac{z_i e \psi}{k T} \right)$$ (2b)

$$\kappa^{-1} = \frac{z_i e \eta h^3}{2 \sqrt{2 \pi A c \varepsilon_{el}}}$$ (2c)

$$V_{EL} (h) = \frac{384\pi k_B T \eta^2 \gamma_i^2}{\kappa^2} \frac{r^2}{2r + h} \exp (-\kappa h)$$ (2d)

$$\gamma_i = \left[ \left( \frac{2 \exp \left( \frac{e \psi}{k T} \right)}{3 + 1/3} \right)^{-1/2} \right]$$ (2c)

where n is the concentration of electrolytes; $k_a$ is the Boltzmann constant; T is absolute temperature; z is the valency of the i$^+$ ion; e is unit charge; $\psi_i$ is the surface potential of the interacting particles in an aqueous medium, which can be calculated from the EPMs of NPs (U$_i$) (Figure 1), the solution viscosity (µ) and permittivity ($\varepsilon_{el}$) of water by the Smoluchowski Equation: $\psi_i = (U_i - \mu)(\varepsilon_{el})$ [27]; $\varepsilon_{el}$ is the vacuum permittivity; $\varepsilon$ is the relative permittivity of water; $\kappa^{-1}$ is the Debye length; $N_i$ is Avogadro’s number; and I is the ionic strength (M), I=0.5-Σ$c_i z_i^2$, where $c_i$ is the mol concentration of the i$^+$ ion.

Finally, the AB energy (V$_{AB}$) between two identical spheres is expressed by Equation (3):

$$V_{AB}(h) = \frac{\pi r^2 \lambda \Delta G_{m}^{AB}}{h} \exp \left( -\frac{h}{\lambda} \right)$$ (3)

where $\lambda$ is the correlation length or decay length of the molecules of the liquid medium, which is estimated to be 1 nm for pure water [29], and $\Delta G_{m}^{AB}$ is the AB free interaction energy between particles at the distance $h_{m}$ [30], which is the minimum equilibrium distance due to Born repulsion, 0.157 nm [29].

Figure 1: Characterizations of CeO$_i$ NPs. (a) TEM image of CeO$_i$ NPs. The inset is the particle size distribution of 10 mg/L CeO$_i$ NPs. The narrow particle size distribution and small PDI value imply that the NPs are relatively monodispersed. (b) Zeta potentials of CeO$_i$ NPs under different temperatures in KCl and CaCl$_2$ solutions.
Upon computing the total interaction energy ($V_I$), the aggregation kinetics of CeO$_2$ NPs can be obtained by Equation (4), which was developed on the basis of the EDLVO theory and von Smoluchowski's population balance equation [31]:

$$r_t = a \left( 1 + \frac{4 k_B T \eta_0}{3 \mu d_f} \right)^{1/3}$$

(4)

Where $r_t$ is the particle radius at time $t$, $a$ is the primary particle radius, $\eta_0$ is the initial number concentration of primary particles, $\mu$ is the solution viscosity, and $d_f$ is the fractal dimension of aggregates. $W$ is the stability ratio, which can be expressed by Equation (5) [32, 33]:

$$W = \left[ \int_0^{\infty} \frac{\lambda(u) \exp(V_A(u)/kT)}{(2 + u)^2} \, du \right] \left[ \int_0^{\infty} \frac{\lambda(u) \exp(V_A(u)/kT)}{(2 + u)^2} \, du \right]^{-1}$$

(5)

where $u$ is the normalized surface-to-surface separation distance ($h$) between two particles ($u = h/a$) and $V_A(u)$ is the attractive energy. Here, vdW energy is the only contributing term to $V_A(u)$ and thus $V_A = V_{vdW}$. $\lambda(u)$ is the correction factor for the diffusion coefficient, which is related to the separation distance by Equation (6) [34]:

$$\lambda(u) = \frac{6(u^2 + 13u) + 2}{6u^2 + 4u}$$

(6)

The number concentration of CeO$_2$ NPs is determined from the mass concentration. The lattice parameter $(a)$ of CeO$_2$ unit cell is 5.4087 Å [35], and each unit cell contains four Ce atoms and eight O atoms. The number of Ce atoms $(N)$ per CeO$_2$ NP with radius $r$ can be calculated by $N = 16\pi (r/a)^3/3$. The mass of a single CeO$_2$ NP is then obtained, and the number concentration of NPs can be computed.

**Results and Discussion**

**Characterization of CeO$_2$ NPs**

A TEM image of CeO$_2$ NPs is presented in figure 1. The NPs have a relatively uniform size distribution. The inset in figure 1 shows the PSD diagram of CeO$_2$ NPs, which was measured by DLS. Consistent with previous studies, the DLS-measured NP size is larger than that of primary particles, and the size distribution is quite small ($\sim 0.1$), indicating that the water layer surrounding the NP surface. The polydispersivity index (PDI) is quite small ($\sim 0.1$), indicating that aggregation and the water layer surrounding the NP surface. The PSD diagram of CeO$_2$ NPs, which was measured by DLS. Consistent with previous studies, the DLS-measured NP size is larger than that of primary particles, and the size distribution is quite small ($\sim 0.1$), indicating that the water layer surrounding the NP surface.

**Higher temperature promotes NP aggregation for two reasons. First, the solution viscosity $\mu$ was smaller at higher temperature; according to Equation (4), the particle aggregation was thus enhanced. Second, the interaction energy between NPs also changes as the temperature increases. The total interfacial energy $V_r$ can be calculated using Equation (1)-(3). Parameters involved in these equations could be either measured or computed. Surface potentials ($\psi_r$) of CeO$_2$ NPs under different temperatures were calculated from the EPMs with the Smoluchowski equation [27]. The other major parameters are listed in table S1.**

**The interaction energies for CeO$_2$ NPs under different temperatures were computed and are presented in figure 2, which shows that the interaction energy between NPs is lower at a higher temperature in both KCl and CaCl$_2$ solutions. The energy barrier reflects the aggregation tendency. The energy barrier diminished as the temperature increased. When the temperature increased from 4 to 37°C, the magnitude of the energy barrier decreased from 11 to 4 kBT and from 7 to 1 kBT in 0.01 M of KCl and 0.002 M CaCl$_2$, respectively. This suggests that NPs more easily overcome the energy barrier and aggregate at high temperatures. Moreover, according to Equation (1)-(3), the EL force is the only force that is influenced by the change in temperature (Figure S4). Parameters in Equation (3), such as the surface potential of NPs,**

**Figure 2: Interaction energy profiles of CeO$_2$ NPs in 0.01 M KCl. (a) and 0.002 M CaCl$_2$. (b) The solid, dotted and dashed lines correspond to 4, 25 and 37 °C, respectively.**

**Figure 3: Representative profiles of each energy term in 0.01 M KCl. (a) and 0.002 M CaCl$_2$. (b) at 4 °C.**

**Effect of temperature on the aggregation of CeO$_2$ NPs in KCl and CaCl$_2$**

The representative aggregation kinetics profile of CeO$_2$ NPs in KCl and CaCl$_2$ solutions under different temperatures were presented in figure 2. As the temperature increased, the NP aggregation became faster. The attachment efficiency $(a)$, or inverse stability ratio $(1/W)$, was calculated by normalizing the initial slopes of aggregation kinetics curves with the slopes obtained in the diffusion-limited aggregation regime (Figure 3). The critical coagulation concentration (CCC) for CeO$_2$ NPs in KCl was ca. 100, 40 and 10 mM at 4, 25 and 37°C, respectively. In CaCl$_2$, CCcs were ca. 10, 10 and 2 mM at 4, 25 and 37°C, respectively. The substantially lower CCcs for CeO$_2$ NPs in Ca$^{2+}$-solutions than those in K$^+$-solutions is because divalent ions more effectively screen the surface charge of NPs and subsequently enhance the aggregation. Higher temperature leads to a smaller CCC and thus promotes NP aggregation.

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Comparison of the simulated and experimental time evolution of the hydrodynamic radii of CeO$_2$ NPs in 0.01 M KCl (a) and 0.002 M CaCl$_2$ (b) solutions. The solid, dotted and dashed lines are model simulations corresponding to the conditions of 4, 25 and 37°C, respectively.

Figure 4: Comparison of the simulated and experimental time evolution of the hydrodynamic radii of CeO$_2$ NPs in 0.01 M KCl (a) and 0.002 M CaCl$_2$ (b) solutions. The solid, dotted and dashed lines are model simulations corresponding to the conditions of 4, 25 and 37°C, respectively.

solution permittivity and Debye length, are affected by temperature. The temperature has no impact on vdW and AB forces.

For a better understanding of the contribution of each energy term to the total interaction, the representative energy profiles are presented in figure 3 and figure S5 in the supporting information. Apparently, the AB repulsion energy contributes more relative to EL repulsion energy. This indicates that, compared with EDLVO theory, the conventional DLVO theory, which considers only EL and vdW energy, provides a less accurate description of the interfacial energy between CeO$_2$ NPs.

Modeling the aggregation kinetics of CeO$_2$ NPs

Equation (4) was used to model the aggregation kinetics of CeO$_2$ NPs. The initial number concentration of CeO$_2$ NPs is approximately $2.35\times10^9$ particles/m$^3$ in all aggregation experiments. The fractal dimension $d_f$ was reported to be ca. 1.8 [40-43]. The total interaction energy $V_T$ was computed according to Equation (1)-(3). The attractive energy, $V_{el}$, equals the vdW energy ($V_{vdw}$). The AB free interaction energy between particles at the distance $h$, $\Delta G_{ab}^{\inf}$, was consistent with our previous studies. Other parameters are listed in table S1. The modeling results were further compared with experimental observations, and representative comparisons are presented in figure 4 and figure S6 in the supporting information. At all temperatures, model predictions agreed well with experimental data. Some minor discrepancies between model predictions and experimental observations may be attributed to deviations in the surface potential of NPs and the size distribution of particles.

Conclusion

In conclusion, this work investigated the temperature effect on the aggregation of CeO$_2$ NPs with both experimental and modeling approaches. As the temperature increased from 4°C to 37°C, the CCCs for CeO$_2$ NPs decreased from ca. 100 to 10 mM in KCl and from ca. 10 to 2 mM in CaCl$_2$. The promotive effect of temperature on NP aggregation is ascribed to the smaller solution viscosity and lower interfacial energy barrier at higher temperature. For instance, the energy barrier height decreased from 11 to 4 k$_B$T in 0.01 M KCl and from 7 to 1 k$_B$T in 0.002 M CaCl$_2$, which resulted from the smaller repulsive EL energy at a higher temperature. The aggregation model based on the EDLVO theory gave fairly good predictions of NP aggregation under different temperatures. To the best of our knowledge, this is the first study to research the temperature effect on NP aggregation with modeling approaches, which is expected to benefit the theoretical predictions of the environmental behavior and biological effects of NPs and to further contribute to the environmental and health risk assessment of NPs.

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