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Aggregation of polydisperse soil colloidal particles: Dependence of Hamaker constant on particle size



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ABSTRACT

The dispersion and coagulation of soil colloidal particles concern highly with their mobility and activity, as well as the role played in biogeochemical cycle of elements. Particle size is an important factor that affects both the van der Waals potential energy and electrostatic potential energy. However, the size effect of soil particles on surface charge properties and suspension stability has rarely been investigated. Results showed that the zeta potentials (in absolute values) of soil colloidal particles (CP, particle diameter less than 1000 nm) were higher than soil nanoparticles (NP, particle diameter less than 100 nm) for the same solution pH, while the specific surface area of soil NP was 1.6 times of soil CP; taken together, the surface charge density of soil NP was smaller than that of soil CP and the surface charge number of soil NP was slightly higher than soil CP. The stability of soil NP and CP was also different. The critical coagulation concentration (CCC) of soil NP was 1.4 times of soil CP, indicating higher mobility of smaller soil particle in natural conditions. Based on DLVO theory, the Hamaker constants of soil NP and CP were simulated to be 2.06×10^{-20} J and 1.86×10^{-20} J. It could be concluded that the size effect of soil particle influences suspension stability and particle mobility through its effect on Hamaker and the surface could deepen our understanding for aggregation mechanisms of soil colloid-sized particles and further help in predicting their environmental behaviors.

1. Introduction

Soil is a vast and natural reservoir for heterogenous particles in successive sizes from nanometer to millimeter (Wilson et al., 2008; Bakshi et al., 2015). Soil colloidal particles (CP) are featured with abundant negative charges and high adsorption ability, because of which soil CP release and further CP-facilitated transport of nutrients and contaminants through preferential flow are of significant importance to soil development and environmental quality (de Jonge et al., 2004; Makris et al., 2006; VandeVoort et al., 2013). Therefore, soil CPs play an active role in facilitating biogeochemical cycle of matter and elements.

The state of CPs—dispersion or flocculation is highly concerned with their mobility, thus study on aggregation of soil CPs enjoy a rich history. Valuable insights have been gained in homo- and hetero-aggregation of model soil clay minerals (montmorillonite, kaolinite, illite or hematite) and engineering NPs during the last two decades (Lagaly and Ziesmer, 2003; Heidmann et al., 2005; Wang et al., 2015; Xu et al., 2017). However, the properties of model soil clay minerals are quite different from those of natural soil particles (Wang and Keller, 2009). Soil materials are characterized by high heterogeneity and imperfect mineral cleavage due to complex composition (Vaz et al., 2002). It is about time to move forward and investigate the aggregation of complex soil systems.

Soil clay particles are normally nano-dimensional in at least one spatial dimension (Theng and Yuan, 2008), and nanoparticles (NP), also referred to nano-colloids, are believed to be more active concerning its smaller particle size and higher surface area (Dinesh et al., 2012). As an abundant naturally occurring nanoparticles, soil NP accounts for a large portion of natural NP besides natural aquatic NP and atmospheric particulate matter in nanoscale (Bakshi et al., 2015). Since soil NP may possess distinctively special properties, it is of great significance to

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distinguish the differences between NP and CP of heterogenous soil system and further focus on how particle size influences suspension stability and particle mobility.

Particle size is an indispensable variable in calculating the van der Waals potential energy. Moreover, the van der Waals force is highly dependent on Hamaker constant, which is size- and morphology-related; this is also why there is size effect for NPs (Pinchuk, 2012). The Hamaker constant defines the strength of the interactions, and is typically on the order of 10^{-21} – 10^{-19} J. Effect of particle size on aggregation has been discussed for synthesized NPs. However, whether the conclusions can be applied to natural NP are unknown, and the complex constitution of soil would possibly make it more puzzled. Pinchuk (2012) investigated the dependence of Hamaker constant on particle size of Ag NP and calculated that the Hamaker constant increased with decreasing size based on Lifshitz theory; it's the size dependence of permittivity that leads to size-dependence of the Hamaker constant for metal nanoparticles (Pinchuk, 2012; Jiang and Pinchuk, 2016). Later, they further tested and confirmed there was similar variation tendency of Hamaker constant for composite materials made by Ag NP and other metals (Pinchuk and Pinchuk, 2016). Nevertheless, the influence of soil particle size on its Hamaker constant and the size effect of soil particles have not been discussed so far.

Furthermore, particle size also influences the electrostatic potential energy through affecting zeta potential of charged particles. Zeta potential is a function of both the particle properties and the properties of the suspending medium, which is usually calculated from electrophoretic mobility by suitable equations (Lowry et al., 2016). However, there is no consistent conclusion for how zeta potential of particles changes with particle size. For instance, Madden et al. (2006) reported that the zeta potential of hematite particles in two sizes, namely 7 nm and 25 nm, decreased slightly with increasing particle size. In another study with hematite, He et al. (2008) showed that the absolute values of zeta potential of larger hematite (65 nm) were larger than those of smaller hematite (12 nm) at similar pH values. Therefore, the effect of particle size on surface charge properties is also not clear.

Based on the above analyses, particle size is an essential factor that would influence aggregation behaviors of soil particles, i.e. critical coagulation concentration (CCC), through affecting both the van der Waals potential energy and electrostatic potential energy (two components of DLVO interaction). The relationship of particle size and suspension stability/particle mobility of polydisperse soil CPs are thus worth to be elucidated. In the present study, the size effect of polydisperse soil CPs were demonstrated. The objectives are 1) to extract and characterize the electrostatic surface properties soil NP and CP; and 2) to quantify the differences in suspension stability of soil NP and CP by stating the size dependence of Hamaker constant. The results could help us further understand the aggregation mechanisms of soil colloidsized particles and their environmental behaviors.

2. Materials and methods

2.1. Soil sample

A typical agricultural soil was selected, namely Lou soil, of which the parent materials was loess and classified as Calcic Cambisol according to the FAO soil classification. Lou soil was collected from Yangling district ($34^{\circ}18'14''$ N, $108^{\circ}02'30''$ E) of Shaanxi province, China. A soil profile in the depth of about 2 m was dug in the field, and the soil layers were classified according to genetic horizons, and soil from the surface layer were used for the present study. After the soil samples were taken back into the laboratory, they were air-dried, gently crushed, and sieved with a 1 mm sieve. All the samples were stored in plastic bags until use.

The soil physical and chemical properties were analyzed with standard methods and shown in Table 1. The bulk density was measured with the cutting ring method. Soil pH was measured with a soil:

Table 1		1.7	5									
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Soil	Sampling depth (cm)	Bulk density (g/cm ³)	pH value	Organic carbon content (g/kg)	CEC (cmol/ kg)	CaCO ₃ content (g/kg)	Clay (%) < 0.002 mm	Silt (%) 0.02–0.002 mm	Sand (%) 2–0.02 mm	Illite (< 2 μm) (%)	Kaolinite (<2 µm) (%)	Chlorite (< 2 µm) (%)
Lou soil	0–28	1.35	8.34	7.28	25.93	51.67	25.40	40.55	34.05	44	19	21

water (mass: volume) ratio of 1: 2.5. The organic carbon content was determined with the potassium dichromate oxidation with external heating method. The cation exchange capacity of the soil was analyzed by first being saturated with NaOAc, then being replaced with NH₄OAc, and the amount of Na⁺ was measured. The CaCO₃ content was indicated by the volume of CO₂ released after being dissolved with HCl. The particle size distribution was measured with a Mastersizer 2000 analyzer (Marlvern Instruments, UK), before which the soil sample was firstly treated with 6% H₂O₂ and 3.65% HCl solution and then dispersed with sodium hexametaphosphate; the refractive indexes for suspending medium (water) and soil particles were set as 1.33 and 1.55 (Özer et al., 2010; Yang et al., 2015), respectively. The mineralogy of clay fraction (< 2 µm) was given by X-ray diffraction analysis.

2.2. Extraction of soil NP and CP

Soil NP (particle diameter less than 100 nm) and CP (particle diameter less than 1000 nm) were extracted by the high-speed centrifugation method combined with sonication (Tang et al., 2009; Li et al., 2012). Fifty grams of soil were weighted into a beaker containing 500 mL distilled water. The suspension was then sonicated with a probe-type ultrasonic cell disrupter (XO-900D, Nanjing Xianou Instruments Corporation, China) for an hour at a power of 50%, during which the suspension temperature was maintained below 30 °C. After sonication, the suspension was transferred into a 5 L beaker and distilled water was added to its full scale. An electronic blade stirrer (JB-200, Shanghai Nanhuihuiming Apparatus, China) was used to further disperse the soil suspension for another hour. Then all the suspension was poured to get through a 300-mush sieve slowly (the depth of water film on the sieve should be less than 2 mm), which could filter the particles larger than 50 µm and guarantee a soil: water (mass: volume) ratio of less than 1% to achieve favorable condition for centrifugation. The centrifugation time needed to get particles in diameters of less than 100 nm and 1000 nm could be calculated based on the Stokes' law (Tang et al., 2009) as shown in the following equation.

$$t = \frac{\eta \log(R_2/R_1)}{3.81C^2 r^2 \Delta d}$$
(1)

In which, R_1 is the distance from the surface of the liquid in the centrifuge tube to the center of the axis of the centrifuge, here is 5.7 cm; R_2 is distance from the particles in the centrifuge tube to the center of the axis of the centrifuge, here is 10.5 cm; *C* (rev/s) is the centrifuge speed; *r* (cm) is the radius of the particles left in the upper suspension in the centrifuge tube; Δd is the difference in density between the particles and water, and soil density is 2.65 g/cm³ while Δd is 1.65 g/cm³; η is the water viscosity coefficient (0.00839 g/(cm s) at 25 °C).

Working conditions in the present study were: for particles less than 100 nm, C = 158.33 rev/s, t = 565 s; for particles less than 1000 nm, C = 21.67 rev/s, t = 302 s. After the centrifugation, the upper suspension containing target soil NP or CP in the centrifuge tube was collected. It is worth to point out that single soil NP in suspension was invisible for human eyes, but soil NP suspension showed a color of light yellow compared with distilled water; and this suspension is normally discarded in normal chemical extraction procedures where the centrifugation speed was usually below 5000 rev/min. Therefore, to some extent study on soil NP is filling up a blind area in soil science.

To further obtain more stable samples, the suspension was dialyzed again water until its conductivity was close to that of distilled water for removing the excess electrolytes in solution. The desalted suspension was then divided into two portions: one portion was stored as suspension and the other portion was freeze-dried for further characterization.

2.3. Characterization of soil NP and CP

The morphology of soil NP and CP was recorded by atomic force microscopy (AFM, Dimension Icon with ScanAsyst, Bruker, USA).

Briefly speaking, the soil NP and CP suspensions (20 mg/L) were dripped on freshly-cleaved mica wafer substrate. The PeakForce Tapping mode was adopted to observe the samples and all images were examined using the NanoScope Analysis software. The size distribution curves of soil NP and CP were further obtained by a dynamic light scattering (DLS) apparatus (Nanobrook Omni, Brookhaven Instruments Corporation, USA). The specific surface areas of soil NP and CP were determined by BET method (NAVO 4200e, Quantachrome Instruments, USA).

The zeta potential values of soil NP and CP at different solution pHs (background electrolyte was NaCl of 10^{-3} mol/L) were measured by ZetaPALS equipped with a BI-ZTU Autotitrator (Brookhaven Instruments Corporation, USA). Here the Smoluchowski equation was used to convert electrophoretic mobility into zeta potential. According to Gouy-Chapmann theory (Li and Xu, 2008), the surface charge density could be calculated with the zeta potential of charged particles through the following equation:

$$\sigma = \sqrt{8\varepsilon\varepsilon_0 c_0 RT} \sinh\left(\frac{ZF\varsigma}{2RT}\right)$$
(2)

In which, σ (C/m²) is surface charge density; ε is the relative dielectric constant, for water, it is 78.54; ε_0 is the dielectric constant in vacuum, being $8.85 \times 10^{-12} \text{ C}^2/(\text{J m})$; $c_0 \text{ (mol/m}^3)$ is the electrolyte concentration; *R* is the gas constant, here equals 8.314 J/(mol K), *T* is the absolute temperature, here it is 298 K; *Z* is the valence; F is the Faraday constant, here is 96,485 C/mol; ζ (V) is zeta potential.

And the surface charge number is the product of surface charge density and specific surface area.

$$Q = 10^5 \frac{S\sigma}{F}$$
(3)

where Q (cmol/Kg) is the surface charge number; S (m²/g) is the specific surface area.

2.4. Determination of CCC

a

The aggregation curves of soil NP and CP in different electrolytes were monitored by time-resolved DLS measurements. The wavelength was 635 nm and the angle was 90°. The particle concentration of stock suspension was set as 200 mg/L. The suspension pH was adjusted to 8.0, which was close to the pH value of natural soil with addition of HCl or NaOH before measurement. All the electrolyte solutions, namely NaCl, CaCl₂ and LaCl₃, were filtered through a 0.22 µm filter prior to use. The adopted electrolyte concentrations for NaCl, CaCl2 and LaCl3 were 10-1000, 0.4-10 and 0.01-0.1 mmol/L, respectively, and the pH values of these electrolyte solutions ranged from 6.5 to 7.0. For each measurement, 1.8 mL of soil suspension and 1.8 mL of different concentrations of electrolyte solutions were mixed in a cuvette, which resulted in final particle concentration of 100 mg/L and pH range of 7.0-7.5. Then the cuvette was capped and carefully turned up and down for 2 times before being put into the analyzer. The measurement started immediately and each measurement lasted for 2 min considering the polydispersity of soil system; and the effective diameters $(a_{\rm h}(t))$ were recorded for 30 min. Based on the particle interaction theory (Schudel et al., 1997; Chen and Elimelech, 2006, 2009), the aggregation curves for each kind of electrolyte could be classified into reaction-limited aggregation (RLA) regime at low concentrations and diffusion-limited aggregation (DLA) regime at high concentrations based on the aggregation rate (k_{11}) (Lin et al., 1989). The k_{11} is concerned with the particle concentration N_0 and the gradient of $a_h(t)$ changing with time (*t*) at each concentration. Thus, we have:

$$\left(\frac{\mathrm{d}a_h(t)}{\mathrm{d}t}\right)_{t\to 0} \propto k_{11}N_0 \tag{4}$$

here N_0 is set as a fixed value. At high concentrations, k_{11} stays almost the same and designated as $(k_{11})_{fast}$. Therefore, the ratio of



Fig. 1. AFM images of soil nanoparticles (NP) and colloidal particles (CP), a. soil NP; b. soil CP; c is a typical height image of soil particles; d is phase image of c; e is the line profile of the red dashed line drawn in d and the red rectangle indicates phase shift. (For interpretation of the references to color in this figure legend, the reader is referred to the web version of this article.)

aggregation rates in RLA and DLA regimes, $k_{11}/(k_{11})_{fast}$ is defined as attachment efficiency (*a*) with the following equation.

$$\alpha = \frac{1}{W} = \frac{k_{11}}{(k_{11})_{fast}} = \frac{\frac{1}{N_0} \left(\frac{da_h(t)}{dt}\right)_{t \to 0}}{\frac{1}{(N_0)_{fast}} \left(\frac{da_h(t)}{dt}\right)_{t \to 0,fast}}$$
(5)

By calculating the attachment efficiency α , also known as the inverse stability ratio 1/W, through Eq. (5) for each electrolyte concentration (Chen and Elimelech, 2006; Xu et al., 2015), the curve of α changing with electrolyte concentration could be drawn and the CCC was indicated by the turning point of electrolyte concentration from RLA and DLA. In this way, the CCCs values of soil NP or CP suspensions in NaCl, CaCl₂ or LaCl₃ were determined, respectively.

2.5. Calculation of Hamaker constant

According to DLVO theory, the total potential energy $V_{\rm T}$ for a given system is the sum of van der Waals potential energy $V_{\rm A}$ and the electrostatic potential energy $V_{\rm R}$. Supposing the radius of particle is *a*, there are (He et al., 2008):

$$V_{\rm A}(h) = -\frac{\rm A}{6} \left[\frac{2}{s^2 - 4} + \frac{2}{s^2} + \ln\left(\frac{s^2 - 4}{s^2}\right) \right]$$
(6)

$$V_{\rm R}(h) = 2\pi\varepsilon\varepsilon_0 a\varphi_0^2 \ln(1 + e^{-kh}) \tag{7}$$

$$V_{\rm T} = V_{\rm R} + V_{\rm A} \tag{8}$$

In which, A (J) is the Hamaker constant of particles suspended in water; a (m) is the particle radius; h (m) is the distance between the

Table 2

Particle diameters and surface areas of soil nanoparticles (NP) and colloidal particles (CP).

Sample	Number-weighted diameter (nm)	Intensity-weighted diameter (nm)	Specific surface area (m^2/g)
soil NP	56.06	127.52	44.04
soil CP	205.64	361.80	28.36

surface of adjacent particles; and H (m) is the distance of two adjacent particles from center to center, and s = H/a; φ_0 (V) is the surface potential, here zeta potential (ζ) was used as replacement of surface potential (Chen and Elimelech, 2006, 2009); and zeta potential values of soil NP and CP in same concentrations of NaCl as adopted in the aggregation experiment were measured by ZetaPALS; $1/\kappa$ (m) is the thickness of the electric double layer and:

$$k = \sqrt{\frac{\mathbf{F}^2 \sum_{i=1}^n n_i Z_i^2}{\varepsilon \varepsilon_0 \mathbf{R} T}}$$
(9)

where $n_i \pmod{m^3}$ is the concentration for the *i*th species in the solution.

Based on the DLVO theory, the attachment efficiency α could be predicted by the following equation (Chen and Elimelech, 2006):

$$\alpha = \frac{\int_0^\infty \beta(h) \frac{\exp[V_A(h) / K_B T]}{(2a+h)^2} dh}{\int_0^\infty \beta(h) \frac{\exp[V_T(h) / K_B T]}{(2a+h)^2} dh}$$
(10)

In which, K_B is the Boltzmann constant being 1.38×10^{-23} J/K; $\beta(h)$ is a dimensionless factor correcting for the hydrodynamic resistance (interaction) between the two approaching particles:

$$\beta(h) = \frac{6h^2 + 13ha + 2a^2}{6h^2 + 4ha} \tag{11}$$

In this way, both the experimental α (Eq. (5)) and theoretical α (Eq. (10)) could be obtained if the Hamaker constant was known. Therefore, the MATLAB R2014b software was used to simulate the system taking Hamaker constant as the only fitting parameter (Xu et al., 2015), and the Hamaker constants of soil NP and CP could be calculated.

2.6. Visual MINTEQ simulations

NaCl, CaCl₂ and LaCl₃ were common electrolytes to evaluate the suspension stability of negatively-charged colloidal particles. Due to the facts that Lou soil contained CaCO₃ and the final suspension pH values were 7.0–7.5. Therefore, the species of La³⁺ and possible complex between La³⁺ and CO₃²⁻ were analyzed by Visual MINTEQ 3.1. The effects of ion species distribution on CCC values were further discussed.

3. Results and discussion

3.1. Size and morphology of soil NP and CP

The morphology of soil NP and CP for Lou soil was captured by AFM and shown in Fig. 1. It could be observed from Fig. 1a and b that welldefined single clay particles and larger aggregates coexisted in soil NP and CP. Fig. 1c and d shows that the soil particles extracted in this study had irregular edge contour, and the surface of the particle was also rather rough indicated by the small peaks in Fig. 1e. Fig. 1e also shows that the lengths of the particles were several times larger than their heights.

From the Particle analysis in the NanoScope Analysis software, the ranges of diameter and height for CP of Lou soil (19 particles detected) were 44.08–487.73 nm and 4.33–54.69 nm with corresponding average values being 92.24 and 20.49 nm. The average diameter and height for NP of Lou soil (144 particles detected) were 32.27 and 3.20 nm. Clearly, surface topography indicated that the diameters of CPs were larger than those of NPs, as well as the thicknesses of CPs.

AFM is one of the powerful techniques in studying morphology, measuring size and thickness of particles *in situ*, especially for minerals with surface heterogeneity and heterogeneous systems (Liu et al., 2003). Here, it seems that the AFM somehow captured smaller soil NP and CP, since the average diameters of CPs were lower than 100 nm, which might be due to the high polydiversity and complexity of soil sample, and the difficulty of AFM in characterizing the lateral dimension (Balnois et al., 1999). However, the heights of soil NP and CP were clearly-demonstrated. Furthermore, the phase image shown in Fig. 1d and f indicates that there was obvious phase shift (the red rectangle in Fig. 1f) across the soil particle, which suggested clay particles coated with organic matter (Plaschke et al., 2002; Liu et al., 2003). In conclusion, AFM images indicated flake-like (the diameters were several times higher than the heights) organo-mineral complex with irregular shape and rough surface; typical soil colloids were extracted.

The equivalent diameters (treated as spherical particles) of soil NP and CP were further determined by DLS and shown in Table 2. The number-weighted diameters of soil NP and CP were 56.06 and 205.64 nm. The diameter of soil CP was 3.7 times of that of NP in average. Since the light intensity scattered by each particle is proportional to the six power of its diameter, the intensity-weighted diameter is highly influenced by the large particles in suspension. Therefore, the number-weighted diameter is believed to be closer to its true physical diameter than the intensity-weighted diameter.

The multimode size distribution (MSD) curves of soil NP and CP are shown in Fig. 2. For soil NP, the size distribution curve followed positively skewed distribution with mode at 67.58 nm, and the percentages of particles in diameter of less than 100 nm were 97.80%. There were three peaks for the distribution of soil CP, and the relative percentages peaked at 180.02, 434.81 and 709.68 nm. The cumulative percentages



Fig. 2. Multimodal size distribution (MSD) of soil nanoparticles (NP) and colloidal particles (CP), a. NP; b. CP.



Fig. 3. Surface properties of soil nanoparticles (NP) and colloidal particles (CP) changing with solution pH in NaCl of 10^{-3} mol/L, a. zeta potential; b. surface charge density and charge number.

for particles in diameter of less than 1000 nm were 100.00%. For polydisperse system, the MSD curves usually present a more objective interpretation of the heterogenous sample.

3.2. Surface charge properties of soil NP and CP

The surface charge properties of soil colloidal particles include surface charge number, specific surface area, surface charge density and surface potential. The surface areas of Lou soil NP and CP were determined to be 44.04 and $28.36 \text{ m}^2/\text{g}$ (Table 2).

Since the surface potential cannot be determined directly through instrumental analysis, zeta potential is usually taken as surrogate. The zeta potential values of soil NP and CP at different solution pHs in NaCl of 10^{-3} mol/L were shown in Fig. 3a. In general, the absolute zeta potential values of soil CP were larger than those of soil NP. The absolute zeta potential values of all samples increased slowly with increasing solution pH. For soil NP, it was from -29.83 mV at pH 3.55 to -37.45 mV at pH 9.27 with a variation rate of 1.33 mV for each pH unit; for CP of Lou soil, it was from -42.31 mV at pH 3.80 to -45.61 mV at pH 9.34 with variation rate being 0.60 mV for each pH unit.

Based on Eqs. (2) and (3), the surface charge density and charge number could be calculated and shown in Fig. 3b. From Fig. 3b, it could be observed that the surface charge number of soil NP (in absolute values) is slightly larger than soil CP at any given solution pH. When soil particle size decreases, the number of exposed surface atoms increases, showing a tendency of increasing variable charges on surface (Qafoku, 2010). However, the main clay mineral of Lou soil is illite (Table 1), which is a permanently-charged mineral. That's the reason why the charge number of soil NP and CP were close and did not vary much with pH. However, the specific surface area of soil NP was 1.6 times of that of soil CP. And the zeta potential is positively proportional to surface charge density (Li and Xu, 2008), so the charge density and zeta potential (both in absolute values) of soil NP were smaller those of soil CP.

Here it is also obvious to note that the surface charge numbers of soil NP and CP were in the range of -0.15 to -0.05 cmol/Kg, and they were quite small. Although the zeta potential on shear plane of charged particles is widely taken as the replacement of surface potential, it is known that the absolute values of zeta potential is smaller than surface potential. It is believed that the surface potential could be 3–6 times of zeta potential (Li et al., 2003; Ding et al., 2015), which explains the smaller values of surface charge density of soil colloidal particles in the present study.

Zeta potential values of soil NP and CP in different concentrations of NaCl solutions were shown in Fig. 4. It could be seen from Fig. 4 that the differences were rather small; these measurements were used in calculating the Hamaker constants of soil NP and CP.



Fig. 4. Zeta potential values of soil nanoparticles (NP) and colloidal particles (CP) in different concentrations of NaCl solutions.

3.3. Dependence of Hamaker constant on particle size

The aggregation dynamics of soil NP and CP at different NaCl concentrations were presented in Fig. 5. The highest effective diameter of soil CP was around 2000 nm while that of NP system was around 2500 nm. Although the diameter of CP was higher than NP, the final effective diameter of NP was higher. Fig. 5 shows that as the electrolyte concentrations increased, the aggregation rate firstly increased, then stayed almost the same for the aggregation curves overlapped at large concentrations.

Based on Eq. (5), the attachment efficiency at each concentration could be calculated, in which the turning point could be obtained by the intersection point of two linear fitting line in RLA regime and DLA regime. From Fig. 6, the CCCs for soil NP and CP were 62.47 and 45.69 mmol/L. The CCC of soil NP was larger than that of soil CP. To be specific, the CCC value of NP was 1.4 times of CP. This indicates that when the size of the colloid-sized particle is smaller, its mobility is higher.

There are disagreements on how particle size affects the stability of NP suspensions. Sheng et al. (2016) reported that the CCC increased with decreasing hematite particle size while the reversed trend was reported by He et al. (2008). And Hsu and Liu (1998) proved in theory that the CCC decreased with increasing size; essentially, smaller particles possess thicker electric double layer and need higher electrolyte concentration to suppress the stronger electrostatic force. Our study confirmed the validity of the calculation in polydisperse soil colloidal system (Fig. 6). Researches have pointed out that particle concentration and experimental conditions could be the reasons why there were inverse trend for the same NP (Sheng et al., 2016).



Fig. 5. Typical aggregation curves of soil nanoparticles (NP) and colloidal particles (CP) in different concentrations of NaCl solutions.

Zeta potential of charged particles is believed to be another possible cause for this inconsistency. It is observed that how zeta potential changes with particle size and electrolyte concentration was irregular (He et al., 2008; Kedra-Królik et al., 2017; Madden et al., 2006). The unevenness of surface charge distribution and irregular shape of charged particles, especially NPs, make the accurate determination of zeta potential become difficult. Since zeta potential is an indispensable parameter in calculating the total DLVO interaction potential, the disagreements in the previous publications are inevitable. It is suggested that carefully-prepared stable suspension is a prerequisite for accurate determination of zeta potential.

According to the simulation results of experimental attachment efficiency and theoretical attachment efficiency (Eqs. (6)-(11)), the Hamaker constants of soil NP and CP were calculated to be 2.06×10^{-20} J and 1.86×10^{-20} J. It is worth to mention that the applicability of DLVO theory to non-spherical particles with particle anisotropy in predicting Hamaker constant and CCC values has already been validated previously (Sano et al., 2001; García-García et al., 2007; Zhu et al., 2014; Xu et al., 2015). Within a few previous publications, the Hamaker constants of clay minerals (including montmorillonite, kaolinite, illite and mica) and soils were reported to be in the range of $(2-6) \times 10^{-20}$ J and $(0.31-2.78) \times 10^{-20}$ J for clav-water and soilwater system, respectively (Berka and Rice, 2004; García-García et al., 2007; Zhu et al., 2014). Therefore, the Hamaker constants for Lou soil particles fall in reasonable range of previous reports. Furthermore, the Hamaker constant of soil NP was larger than that of soil CP; when the soil particle size is smaller (NP), the Hamaker constant is relatively larger. This variation tendency in heterogenous soil system is in accord with the trend found in Ag NP system and Ag-mental binary system (Pinchuk, 2012; Jiang and Pinchuk, 2016). Thus, the size effect of soil colloidal particles was demonstrated, and it may also come from the difference in permittivity.



Fig. 7. The critical coagulation concentrations (CCC) of soil nanoparticles (NP) and colloidal particles (CP) in Na $^+$ /Ca $^{2+}$ /La $^{3+}$ solutions.

3.4. Effect of electrolyte type on CCC

The CCC values of soil NP and CP in CaCl₂ and LaCl₃ solutions were also calculated, as indicated in Fig. 7. In the present study, the maximum suspension pH was 7.5 and LaCl₃ concentration was 1 mmol/L. Since La³⁺ is trivalent, possible hydrolysis and complexation with carbonate might occur. Therefore, Visual MINTEQ 3.1 was used to give detailed analysis. According to the calculations of Visual MINTEQ 3.1, LaCl₃ was in the state of undersaturation and the concentrations of La³⁺, LaCl²⁺ and LaOH²⁺ were 0.9627 mmol/L (96.27%), 5.9769 × 10⁻³ (0.60%) and 0.03131 (3.13%); hydrolyzed species did form, but the amount was very limited.

Lou soil contained CaCO₃ of 51.67 g/Kg with molecular weight of 100.1 g/mol. The soil suspension prepared was 200 mL with particle



Fig. 6. The critical coagulation concentrations (CCC) of soil nanoparticles (NP) and colloidal particles (CP).

concentration of 200 mg/L, which was equal to 0.1032 mmol/L CaCO₃ in soil suspension used in the aggregation and zeta potential determination experiments. Therefore, these input data calculated that La^{3+} accounted for 52.921% of the total La input, while other species like $LaCO_3^+$, $LaOH^{2+}$ and $LaHCO_3^{2+}$ were present in decreasing order. Moreover, the saturation index of $La_2(CO_3)_3$ was 7.575; however, due to short aggregation time allowed (30 min), the amount of precipitated solids might be very limited. As a matter of fact, the ability of La^{3+} in screening the negative charges of soil NP or CP was compromised due to complexation. On the other hand, the dissolution of CaCO₃ supplied about 0.1 mmol/L Ca^{2+} to the aggregation process, which had little influence on the aggregation kinetics in $LaCl_3$ system since the CCC in $LaCl_3$ was rather small. Therefore, there were deviations in the determined CCCs of soil NP and CP in $LaCl_3$ system.

Fig. 7 demonstrates the ability of different cations in inducing coagulation of soil suspensions. The DLVO theory generates the Schulze-Hardy rule that CCC is proportional to z^{-6} (z is the cation valence here) when the surface (zeta) potential is high (Sano et al., 2001); when the zeta potential is low, the CCC is proportional to z^{-2} (Elimelech et al., 1995; Hsu and Kuo, 1995; Petosa et al., 2010). As in practice, the CCC dependence on z should be between to z^{-6} to z^{-2} (Zhu et al., 2014; Lin et al., 2016). The ratios of CCCs in $Na^+/Ca^{2+}/$ La^{3+} were 1: $2^{-5.6}$: $3^{-7.0}$ and 1: $2^{-4.9}$: $3^{-6.8}$ for soil NP and CP, which were within reasonable ranges for Ca²⁺ system; while for La³⁺ system, the CCCs might be underestimated due to additional concentration of Ca²⁺ from dissolution of CaCO₃ as analyzed above. The zeta potentials of soil NP and CP in different concentrations of NaCl solutions were determined and shown in Fig. 4, the zeta potentials were low in the present study, which is also the case for common colloidal systems (Petosa et al., 2010).

Unlike the CCC values in Na⁺ system, the CCCs in Ca²⁺ or La³⁺ systems were closer to each other for these two particles. Similarly, Zhu et al. (2014) demonstrated that the CCCs of Liaoning soil (Inceptisol) NP in NaCl, CaCl₂ and LaCl₃ solutions were 140, 1.79 and 0.055 mmol/L, while the corresponding values of Hainan soil (Oxisol) nanoparticles were 103, 1.89 and 0.082 mmol/L; the tendencies were in agreement with the present study, suggesting certain soil NPs could be more stable in solution with monovalent cation, and less stable in solutions with bivalent and trivalent cations. More importantly, this implies that the heterogenous components of soil could also affect the stability of soil colloidal particles, such as the complexation of organic matter and clay minerals through polyvalent cations in soil system. Therefore, the size effect of soil particles is more obvious with monovalent cation. This also demonstrates the complexity of related work in soil system and calls for more effort dedicated to this area.

4. Conclusions

The size effect of polydisperse soil colloidal particles were demonstrated. Soil NP (1–100 nm) and CP (1–1000 nm) were extracted and characterized, and further their surface potentials and aggregation kinetics at different electrolyte solutions were determined, based on which their Hamaker constants were simulated by DLVO theory to be 2.06×10^{-20} J and 1.86×10^{-20} J, respectively. The differences in Hamaker constant for soil colloidal particles were in accord with the tendencies obtained from engineered NP (Ag, Ag-mental component, and hematite), which all results from the size dependence of permittivity. The Hamaker constant and mobility of soil NP were higher than that of soil CP due to this size effect. Size-dependent properties of soil particles have implications for their unique reactivity and extensive participation in environment, such as formation of soil mineral-organic complex and particle-nutrients/contaminants interaction.

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