

Determination of critical coagulation concentration of silicon nanoparticles

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ABSTRACT

This paper investigated the determination of critical coagulation concentration using a time-resolved dynamic light scattering technique. Silicon nanoparticles were used as model nanoparticles. Zeta potential of silicon nanoparticles were quantified using a zetasizer. The key results of this study show that critical coagulation concentration of silicon nanoparticles in NaCl is 0.2 M while critical coagulation concentration decreased to 0.01 for CaCl₂ solution. This finding indicates that silicon nanoparticles are less stable in CaCl₂ because of the more effective surface charge screening process occurred. This study provides information on the stability of nanoparticles in electrolyte solutions and may be served as reference in the risk assessment of nanoparticle spills into the natural aquatic systems. Copyright © 2014 VBRI press.

Keywords: Critical coagulation concentration; time-resolved dynamic light scattering; silicon nanoparticles; zeta potential.



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Introduction

Nanotechnology industry has been growing rapidly in recent years. Nanomaterials have been introduced to our daily life and it is inevitable that some nanomaterials will be introduced into the environment [1-4]. Therefore, it has been recognized that it is of importance to evaluate the environmental health and safety impacts of the nanomaterials. Due to the intrinsic nature of the nanomaterials, some of them are insoluble and readily aggregate in the aquatic environment, which may limit their mobility and transport. However, other nanomaterials can still disperse in aquatic systems. Since the mobility of the nanoparticles in water is greatly dependent on their tendency to remain suspended, assessing the propensity of nanoparticles to aggregate allows for the prediction of their rate of sedimentation and hence their removal from the bulk water phase [4, 5]. Since the critical coagulation concentration represents the minimum amount of electrolyte needed to completely destabilize the nanosuspension, it provides a useful metric of colloidal

stability for nanoparticle and hence can be used in the prediction of the fate and transport of nanoparticles in natural and engineered systems [6-8]. The surface physical and chemical properties of nanoparticles have significant bearing on the aggregation behavior of nanoparticles. Due to the surface charge property of nanoparticles, it is of interest to know if the classic Derjaguin-Landau-Verwey-Overbeek theory can adequately describe the stability to aggregation and deposition of the nanoparticles [9-19].

Therefore, the objective of this study is to quantify the aggregation kinetics and colloidal stability of representative nanoparticle, silicone nanoparticles (silicone NPs). Silicone nanoparticles were chosen because they have wide potential application in many fields including microelectronics, biomedical imaging, and most recently energetics. In this study, time resolved dynamic light scattering (TR-DLS) were used to investigate the aggregation kinetics of silicone nanoparticles in the presence of calcium and sodium electrolytes. Critical coagulation concentration of these electrolytes was quantified by calculating the aggregation rates. To the author's knowledge, this paper is the first one to apply these state of the art experimental approaches to discriminate effect of electrolyte on the aggregation of silicone NPs in aqueous environment. Since stability of nanoparticles in aquatic conditions are related to their ecotoxicological effects, establishing the standard stability measuring procedure is critically important. This paper provided an effective approach to quantify stability of silicon nanoparticles using DLS method. The determination approach can serve as important reference for the risk

assessment of silicon nanoparticle spill in the natural aquatic systems.

Experimental

Silicon nanoparticle preparation

Silicon NP (American Elements, Los Angeles, CA) dispersions (10 mg/L) were ultrasonicated in an ultrasonic bath (Fisher Scientific) twice for a cycle of 30 min each to breakup aggregates. Between the two sonication periods, the dispersions were mixed with a magnetic stirrer for 15 min to homogenize the dispersion and to improve the efficiency of the subsequent ultrasonication. Silicon NPs were allowed to settle down and sub-samples were removed from the supernatant at various time intervals to assess the stability of the dispersion. Silicon concentration was measured using inductively coupled plasma-atomic emission spectroscopy analysis (ICP-AES, Vista-MPX, Varian, Palo Alto, CA). It was found that silicon concentration in the liquid phase decreased during the first 24 h and then kept stable. Therefore, stable supernatant was carefully separated after 96 h for use in the aggregation experiments. All experiments and measurements were conducted at pH 4.2, except where noted.

Preparation of solution

ACS-grade electrolyte (NaCl and CaCl₂) stock solutions were prepared and filtered using 0.1 μm alumina syringe filters (Anotop 25, Whatmann) before use.

Electrophoretic mobility measurement

A ZetaPALS analyzer (Brookhaven, NY) was used to measure the zeta potentials of Silicon NPs over a range of electrolyte concentrations at 25 °C. For each solution chemistry, 5-10 measurements were conducted for each of at least three samples.

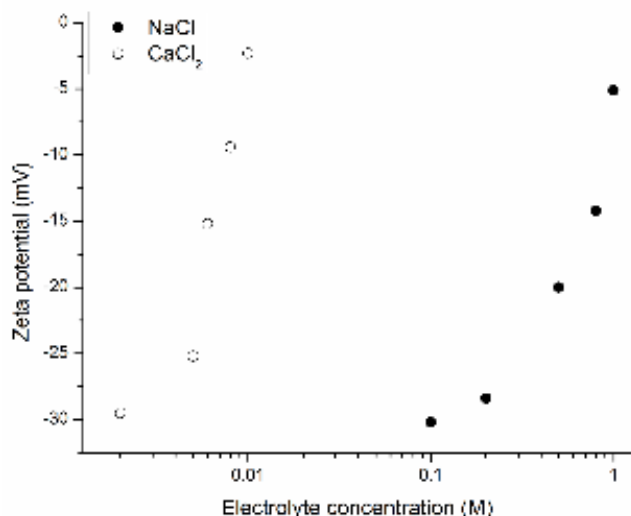


Fig. 1. Zeta potential of Silicon NPs in NaCl and CaCl₂ electrolyte solutions.

Aggregation kinetics measurement

Time-resolved dynamic light scattering (DLS) measurements were conducted to determine the aggregation

kinetics of the fullerene nanoparticles. A zetasizer by BrookHaven was used to carry out the DLS measurements. For the aggregation experiments, 1.9 mL of deionized water with a pH adjusted to 7.5 was introduced into the vial. Next, 0.1 mL of the Silicon NP stock suspension was added, resulting in a 20-fold dilution. Finally, a predetermined amount of electrolyte stock solution was introduced into the diluted suspension to induce aggregation. The vial was briefly hand-shaken to homogenize the suspension, before being introduced into the light scattering unit to start the DLS measurements. The CCC calculation was conducted following previous published procedure.

Results and discussion

Zeta potential of Silicon NPs in presence of monovalent and divalent cations

Zeta potential was measured at various cation concentrations as shown in Fig. 1. Zeta potential of the silicon NPs became more positive with the increase of cation concentration. The negative surface charge could be attributed to the silanol functional groups. Jarvis et al. reported similar zeta potential trend with pH for porous silicon microparticles and attributed the negative charge to surface SiOH species by aqueous oxidation. In addition, zeta potential of silicon NPs was more negative at high cation concentration, which might be due to the surface charge screening process caused by the cations present in aqueous solutions. From the figure it can also be observed that divalent cation can more efficiently increase the zeta potential. It might be due to the more positive charges divalent cation can carry in comparison with monovalent cations.

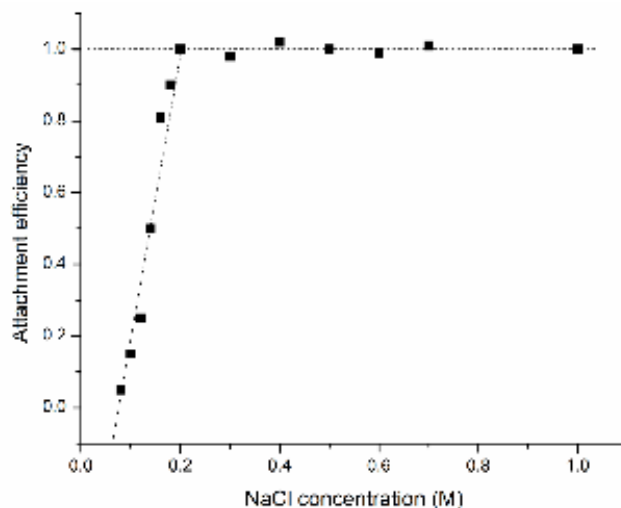


Fig. 2. Attachment efficiency of Silicon NPs in NaCl solution.

Aggregation kinetics in presence of monovalent and divalent cations

The aggregation kinetics of the Silicon NPs were first studied in presence of monovalent and divalent cations. Fig. 2 and Fig. 3 present the attachment efficiencies of the Silicon NPs in the absence of humic acid as a function of

NaCl concentration. The profile reveals two regimes typical of colloidal systems in which the aggregation kinetics can be explained by DLVO theory [9-20]. At lower NaCl concentrations, as the salt concentration is increased, the attachment efficiency increases due to the screening of the Silicon NPs surface charge, which in turn reduces the energy barrier to aggregation. This is known as the reaction-limited (slow) regime. Once the NaCl concentration reaches and surpasses the critical coagulation concentration (CCC), the nanoparticle surface charge is completely screened, thus eliminating the energy barrier to aggregation. This is known as the diffusion-limited regime, where the aggregation kinetics of the nanoparticles are controlled by diffusion [12-18].

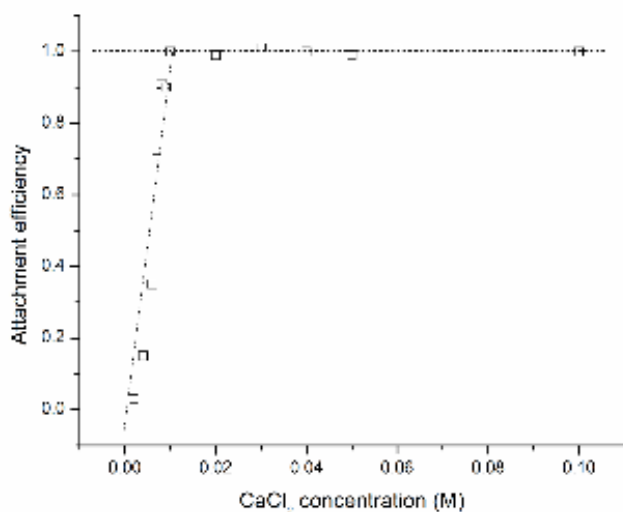


Fig. 3. Attachment efficiency of Silicon NPs in CaCl₂ solution.

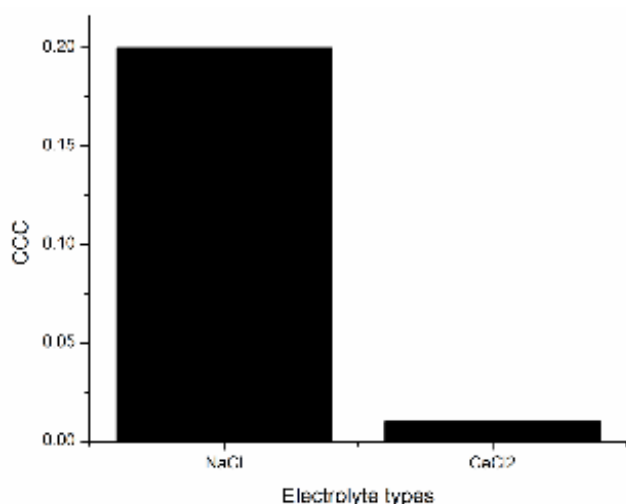


Fig. 4. CCC of Silicon NPs in NaCl and CaCl₂ solutions.

By extrapolating through the two regimes, the intersection of the two extrapolations yields the CCC of 0.2 M NaCl. The attachment efficiencies of the Silicon NPs are also presented as functions of CaCl₂ concentrations in Fig. 3. Just as in the case of NaCl, reaction-limited and diffusion-limited regimes are observed with both divalent

electrolytes, indicating DLVO-type aggregation behavior. Extrapolation between the two regimes yields CCC values of 0.01 M for CaCl₂ (Fig. 4). By comparing the calculated CCC values, it can be concluded that Silicon NPs are more stable in monovalent electrolyte solution than in divalent electrolyte solution. This is because divalent electrolyte that can be more efficient in removing negative charges of silicon NPs and thus promote the nanoparticles' self-aggregation. This observation is consistent with the Schulze-Hardy rule, which indicate that the stability of a nanosuspension is extremely sensitive the valence of the countions present in solution [8, 11, 15].

Conclusion

This study reported the CCC of silicon NPs in monovalent and divalent electrolyte solutions measured by the state-of-the-art technology of TR-DLS. Our finding indicated that silicon NPs are more stable in monovalent electrolyte solutions because divalent cations can more effectively neutralize the surface charge of nanoparticles, thus reduce the electrostatic repulsion between nanoparticles, resulting in tendency of self-aggregation. As CCC is an important concept in colloidal chemistry predicting the stability of colloids, the finding is especially of importance to predict the environmental transport and fate as well as the environmental risk assessment of silicon nanoparticles in the aquatic natural environment. Future study is recommended to determine the ecotoxicological effect of silicon NPs on microorganisms and higher organisms in water environment.

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