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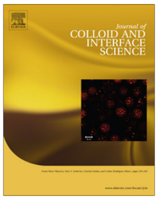

Adsorption and stabilizing effects of highly-charged latex nanoparticles in dispersions of weakly-charged silica colloids

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ABSTRACT

An experimental study was undertaken to determine the effectiveness of using highly-charged nanoparticles as stabilizers for colloidal dispersions. The specific systems used here involved cationic (amidine) and anionic (sulfate) polystyrene latex nanoparticles with an approximate diameter of 20 nm and silica microparticles of diameter 1.0 μm, and experiments were conducted at the isoelectric point of the silica. It was found that while both types of nanoparticles adsorbed to the silica microparticles and increased the zeta potential to values where stability was expected, long term stability was not achieved, even at bulk nanoparticle concentrations as high as 0.5 vol.%. It is theorized that the incomplete coverage of the microparticles by the nanoparticles (i.e., surface coverage never exceeded 50%) allowed either direct contact between bare patches of the underlying microparticles or, alternatively, for nanoparticles adsorbed on one microparticle to bridge to bare spots on a neighboring microparticle.

1. Introduction and Background

Control of the stability of colloidal dispersions, such as through the addition of electrolytes or polymeric stabilizers, remains a topic of great practical importance. As such, developing novel types of stabilizers and flocculants that allow fine tuning stability, or even reversibly controlling stability, is still of interest in many fields [1–4].

Over the past 20 years or so, control of stability using highly-charged nanoparticles has received growing interest. For example, numerous researchers have shown that otherwise stable dispersions of micron-sized particles can be flocculated using the depletion interaction that arises upon the addition of highly-charged, negatively-adsorbing nanoparticles [5–9]. One attractive feature of this approach is that because the nanoparticles do not deposit onto the surface of the microparticles, and furthermore because this depletion flocculation primarily occurs in shallow, secondary energy wells, the flocculation is potentially reversible upon dilution.

More recently, various researchers have investigated a phenomenon termed nanoparticle haloing in which highly-charged nanoparticles weakly adsorb to microparticles that are near their isoelectric point (IEP) [10–13]. The additional repulsive force produced by this haloing effect has been predicted to be strong enough to stabilize dispersions of such microparticles [14–18]. Other researchers have shown that in some systems, the repulsive force actually arises from strong, irreversible deposition of the nanoparticles as opposed to the weak adsorption suggested in the nanoparticle haloing phenomenon [19,20].

In previous work, the authors of this paper investigated the ability of polystyrene latex nanoparticles that were either positively (amidine) or negatively (sulfate) charged to stabilize dispersions of weakly-charged silica microparticles [21]. The results indicated that both nanoparticle types adsorbed to the surface (the amidine in greater quantities than the sulfate latex), and significantly increased the effective zeta potential of the microparticles beyond the point where the silica alone would be electrostatically stable. In suspensions containing the amidine latex nanoparticles, the silica suspensions were quite stable. However, the experiments also showed that the sulfate latex nanoparticles could not reproducibly stabilize the same suspensions at any of the concentrations used (up to 0.5 vol.%). The authors concluded that though the sulfate latex provided a net increase in the zeta potential, the lower degree of adsorption led to a patchy surface that was ineffective in preventing flocculation of the Brownian particles.

While this prior work clearly demonstrated the possibility of stabilizing weakly-charged microparticles using highly-charged nanoparticles, there were nonetheless numerous issues that remained unresolved. For example, in the previous work, while

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adsorption of both the amidine and sulfate nanoparticles resulted in significant increases in the zeta potential of the silica microparticles, only with the amidine nanoparticles was stability achieved. Furthermore, the degree of adsorption of the amidine nanoparticles, as judged by adsorption onto flat silica slides, appeared to be substantially greater than that of the sulfate nanoparticles, even though the absolute magnitude of the zeta potentials of the two types of nanoparticles in the bulk were similar and the adsorption tests were performed at the IEP of the silica slides.

The goal of this present work was to address some of these unresolved issues in order to definitively answer the question of whether relatively low concentrations of highly-charged latex nanoparticles can serve as effective stabilizers of weakly-charged silica microparticles. In the present study, measurements of zeta potential, degree of adsorption, and dispersion stability were performed using amidine and sulfate nanoparticles that had been thoroughly cleaned using dialysis with an ion-exchange resin. The purpose of the cleaning step was to ensure that any observed stabilizing effects arose from the nanoparticles themselves and not any surfactants or other additives that could be present in the suspension.

In addition, adsorption measurements of the amidine and sulfate nanoparticles were performed using the silica particles themselves at the same solution conditions, specifically pH, as those used in the stability tests. This was done to avoid possible effects of differences in geometry or IEP resulting from the use of flat silica slides, as was used in the prior work.

2. Materials and methods

2.1. Overview of experiments

Three different types of experiments were performed in this study to better understand the impact of the amidine and sulfate nanoparticles on both the interparticle forces and the stability behavior of the silica microparticles. First, a set of stability tests were performed over a range of nanoparticle concentrations, ranging up to 0.5 vol.%. The experiments with suspensions containing both silica microparticles and polystyrene nanoparticles were carried out at the isoelectric point of the silica microparticles such that the microparticles were inherently unstable due to insufficient net surface charge. Second, zeta potential measurements were performed to understand how the adsorption of nanoparticles changes the surface charge of the silica microparticles as a function of nanoparticle concentration. Finally, adsorption experiments were performed to determine the degree of adsorption of the nanoparticles on the silica microparticles at the silica IEP.

2.2. Materials

All the experimental solutions were prepared using water that had a resistivity of 18.2 MΩ-cm. The water was filtered by a RiOs 8 reverse osmosis system (Millipore, catalog #ZR0S6008Y) and subsequently treated by a Barnstead EASYpure II UV Ultrapure water system (Thermo Scientific, catalog #D7401). Fused silica slides (Corning 7980 fused quartz silica, item #3 × 1 × 1 mm) were obtained from TGP (Technical Glass Products, Inc., Painesville, OH). The silica microparticles used were supplied at a concentration of 10% w/v in water with a specified average diameter of 1.0 μm (Polysciences, Inc., Warrington, PA, catalog #24326-15). IDC brand polystyrene latex nanoparticles (Life Technologies, Carlsbad, CA) were used. The particles had a specified diameter of 0.02 μm, and experiments were done with both sulfate and amidine latex (catalog #S37200 and catalog #A37309, respectively). The titrants used were hydrochloric acid (Optima grade, Fisher Scientific, catalog #A466-250) and sodium hydroxide (1.0 N Mallinckrodt Standard grade, catalog #4693-60), each diluted to 0.1 M using pure water.

2.3. Nanoparticle solution preparation

The nanoparticle suspensions used in these experiments were dialyzed to remove any excess ions from the solution. The suspensions were made by diluting the stock solution with the purified, deionized water to a concentration of 0.5 vol.%. The solutions were prepared in 20 ml scintillation vials (Wheaton Science Products Inc., catalog #986540), which had been rinsed with ethanol and deionized water. Dialysis of the suspensions was performed by adding ion-exchange resin (Bio-Rad, catalog #143-7425) to each vial to the manufacturer specification of 5 g resin per 100 mL of solution. The vials were gently mixed for 4 h using a continuous sample rotator that was operating at 4 rpm to slowly invert the samples and redistribute the resin. At the end of the dialysis period, the nanoparticle solutions were decanted from the resin into clean vials.

2.4. Zeta potential measurements

Measurements of the zeta potential of silica microparticles and the two types of latex nanoparticles (separately) were obtained using a Zetasizer Nano ZS (Malvern Instruments Ltd., Worcestershire, UK), with measurements performed in disposable folded capillary cells (catalog #DTS1060C). Prior to the measurements, the cells were rinsed first with pure ethanol, then DI water, before being dried with ultra-high purity nitrogen. The measurements on the latex nanoparticles were performed as single measurements at a given pH. For the silica microparticles, multiple measurements were taken across a large pH range in a single experiment in order to determine the IEP. In this experiment, the Malvern MPT-2 Autotitrator was used to automatically adjust the pH of the sample.

A Micro-Electrophoresis Apparatus Mk II (Rank Brothers Ltd., Cambridge, England) was used to measure the effective zeta potential of the silica microparticles in suspensions of nanoparticles. Nanoparticle concentrations used for these measurements were equal to those used in the stability measurements, while the microparticle concentration was more dilute (approximately 0.01 vol.%) in order to allow observing individual silica particles in the cell. The zeta potential was determined from the electrophoretic mobility, which was calculated from the visually-measured particle velocity.

2.5. Stability

The stability of the silica microparticle dispersions was determined from visual observation. Suspensions of the desired concentrations of latex nanoparticles (0–0.1 vol.% of either amidine or sulfate) were prepared and titrated to the desired pH of 3.5 (the IEP of the SiO_2) using 0.1 M HCl before being transferred to the cuvettes. A quantity of silica microparticles was then added to the suspensions to reach 0.1 vol.% microparticles. The cuvettes were capped, inverted to evenly distribute the particles, and briefly sonicated before beginning the experiment. Photographs of the set of samples (placed against a black background for maximum contrast) were taken at regular intervals over a total observation period of six hours.

2.6. Nanoparticle adsorption

In order to better understand the adsorption behavior of the latex nanoparticles on silica microparticles, experiments were performed to directly visualize the adsorbed particles using scanning electron microscopy (SEM). An approximately 0.01 vol.%