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Short communication

Can nanoparticles stabilize microparticle suspension?

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ABSTRACT

The main purpose of this article is to verify the new stabilization mechanism caused by the formation of nanoparticle halos [V. Tohver, J.E. Smay, A. Braem, P.V. Braun, J.A. Lewis, Nanoparticle halos: a new colloid stabilization mechanism, Proc. Natl. Acad. Sci. U.S.A. 98 (2001) 8950], by adding different volume fractions of slightly positive charged zirconia nanoparticles in the negative charged micro-latex suspensions of different sizes, and observe the effect on stabilizing the suspension via jar settling experiments. The experimental results confirm that the zirconia nanoparticles do stabilize the micro-colloidal suspension at an optimal volume fraction in a finite volume settling system. The osmotic pressure exerted by nanoparticles on micro-colloids is applied to explain our experimental results.

1. Introduction

How to stabilize a colloidal suspension effectively has attracted many scientists' attention for a long time, since colloidal stability in liquids is commonly encountered in various industries, for example, in the paints [1] and micro-nano electronics [2] industries. The stability of the colloidal suspension is usually determined by the interaction forces acting on colloids, such as the electric double layer, van der Waals, Born, hydration and polymer steric forces [3]. However, a distinct interaction, known as the “depletion attraction,” may also play a substantial role in determining the stability of a suspension consisting of micro- and nano- particles [4,5]. This new attractive interparticle force is determined by the entropic effect, i.e., by the free volume which is accessible to the nanoparticles in solution where micro-colloids and nanoparticles interact mainly through hard-body-like potentials, which has been investigated theoretically [6–9] and experimentally [10–12]. The important role of this depletion force on the stability of colloidal suspension was evidenced by the novel experiment conducted by Tohver et al. [13], who used an optical microscopy equipped with a 100× oil lens to observe the aggregation behavior of near-neutral silica microspheres (with an volume fraction of $\phi_{micro} = 0.05–0.45$) in aqueous suspension when very small concentrations of highly positive charged zirconia nanoparticles (with an volume fraction of $\phi_{micro} = 10^{-6}–10^{-2}$) were added in the suspension of neutral silica microspheres at pH ≈ 2.5. From the phase diagram they constructed, it can be found that a homogenous fluid composed of stabilized silica microspheres and nanoparticles can be achieved only at intermediate nanoparticle volume fractions, and a colloidal gel will be formed when ϕ_{micro} is either above or below these intermediate fractions. They proposed that this remarkable stabilizing transition at intermediate nanoparticle volume fractions arises from the nanoparticle halo formation around the silica microspheres, whereas their reflocculation stems from traditional entropic depletion interactions. Their experimental results were elucidated by Liu and Luijten theoretically later on [14], who employed a Monte Carlo simulation scheme to prove that small nanoparticle concentrations can induce an effective repulsion and higher nanoparticle concentrations will cause the depletion attraction between colloids.

Since there is no report on testing the depletion role played by the nanoparticles on the stability of a micro-colloidal suspension, the main purpose of the present paper is to investigate their effect on the flocculated settling behavior of micro-latex suspensions by adding different volume fractions of slightly positive charged zirconia nanoparticles at pH = 5.0. Our experimental results prove that the zirconia nanoparticles can stabilize the micro-colloidal suspension at an intermediate volume fraction. The osmotic pressure exerted by nanoparticles on the depletion zone between two micro-colloids will be applied to explain the present experimental results.

2. Experimental materials and methods

In the present paper, based on the turbidity measurements, we conducted a series of jar settling tests for artificial latexes of various sizes with an equal initial concentration (*number of latexes/mL*) when different volume fractions of charged zirconia nanoparticles were added. Since most pH values of settling aqueous suspension adopted in the practical field are near the neutral pH ranges, instead of using the highly positive zirconia nanoparticles at the acidic

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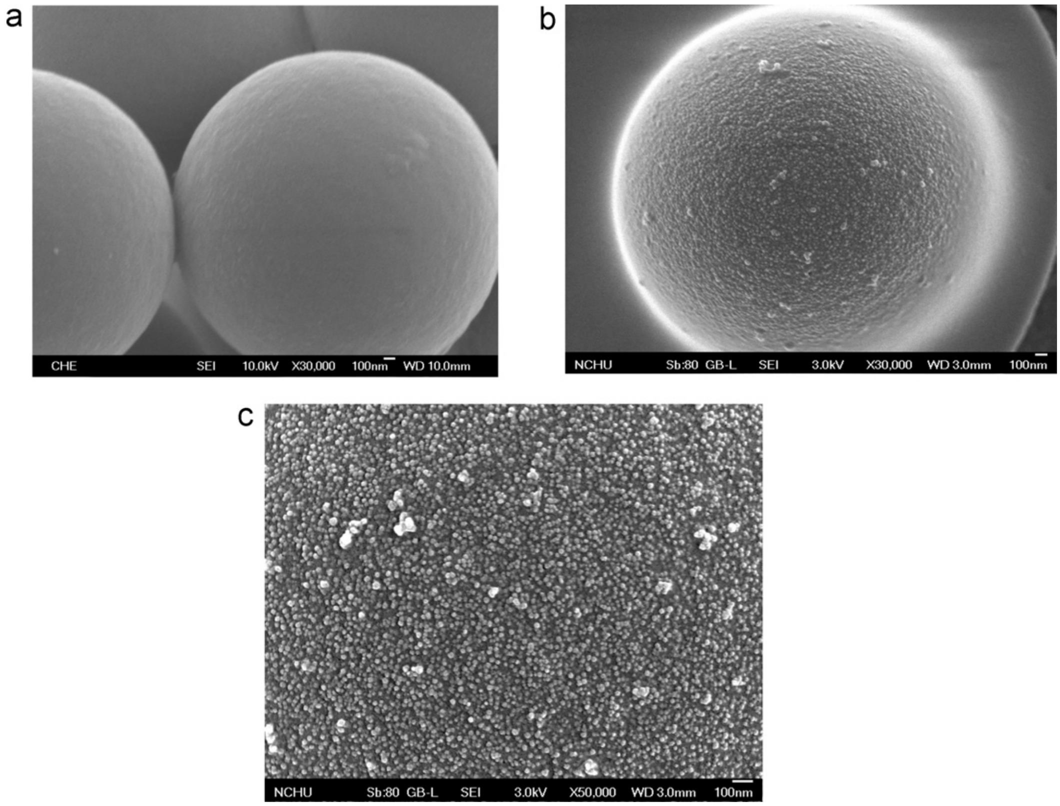

Fig. 1. The SEM images of 3.04 μm polystyrene latexes with/without the addition of 1.17 vol.% zirconia nanoparticles. (a) The bare latex image. (b) The image of polystyrene latex when 1.17 vol.% zirconia nanoparticles were added (30,000×). (c) The enlarge part of image (b) (50,000×).

experimental condition (pH = 2.5) adopted by Tohver et al. [13], the value of pH = 5.0 (which is close to the isoelectric point of zirconia nanoparticles pH = 5.2) is employed in the present settling experiments.

2.1. Artificial latexes and zirconia nanoparticles

The polystyrene latexes (averaged sizes of 1.16 μm and of 3.04 μm, density ρ = 1.06 g/cm^3), and the styrene divinylbenzene latex (averaged size of 6.2 μm and density of 1.089 g/cm^3), used in the suspension formats with pH = 6.5 were purchased from Sigma Chemical Inc., USA. The nanoparticle of zirconium oxide (averaged size of 7.5 nm and density of 6.506 g/cm^3) used in the suspension format with pH = 4.0 was obtained from Alfa Aesar Chemical Inc., USA. These colloidal latexes are proved to be spherical, smooth and monodisperse (see the SEM picture of the bare 3.04 μm polystyrene latexes in Fig. 1(a)). The stock solution of each latex sample were prepared by diluting the concentrated dispersion with de-ionized water to 0.5×10^{-6}, 1.0×10^{6} and 1.5×10^{6} *number of latexes/mL* (i.e., counted by Coulter counter, Multi-Sizer II with a 30 μm aperture tube), respectively, prior to each set of settling tests when different volume fractions of zirconia nanoparticles were added (range from 1.17×10^{-2} to 1.94 vol.%). The volume fractions correspond to those number concentrations of latexes/zirconia nanoparticles is summarized in Table 1. All chemicals used in the experiments were of analytic grade.

2.2. Zeta potential and SEM instruments

The electrophoretic measurements of zeta potentials of latexes/nanoparticles were conducted at 20 °C by using Zeta Sizer 3000HS, Malvern Instruments, UK. The SEM images were taken by Joel JSM-7401F FESEM, equipped with cold field emission source, offers a nominal resolution of 0.8 nm at 30 kV and 1.5 nm at 1 kV.

2.3. Turbidity measurement

The settling experiments of micro-colloidal suspensions were performed in the 15-mL standard bottles at ambient temperature, at which the temporal turbidities of suspensions were measured by using a nephelometer (Model 2100P, Hach Co., Loveland, CO). Due to the turbidity measurement limit of nephelometer, only the suspensions with diluted concentrations shown in Table 1 were employed in the present settling experiments. For each sample bottle, the turbidity was measured for each hour of settling time. From the initial slope of the temporal turbidity variation curve, the stabil-

Table 1
The zeta potentials of latexes/zirconia nanoparticles and the volume fractions correspond to those number concentrations of latexes/zirconia nanoparticles.

Micro-colloids	Zeta potentials at pH = 5.0	Particles/mL	0.5×10^{6}	1.0×10^{6}	1.5×10^{6}
6.2 μm latex	−25.8 mV	vol.%	6.24×10^{-3}	1.25×10^{-2}	1.87×10^{-2}
3.04 μm latex	−37.6 mV	vol.%	7.35×10^{-4}	1.47×10^{-3}	2.21×10^{-3}
1.1 μm latex	−50.0 mV	vol.%	3.48×10^{-5}	6.97×10^{-5}	1.04×10^{-4}
Nano-particles	Zeta potentials at pH = 5.0	Particles/mL	5.30×10^{14}	6.65×10^{16}	8.77×10^{16}
7.5 nm zirconium oxide	+8.2 mV	vol.%	1.17×10^{-2}	1.47	1.94