Nanoparticle Stabilization of Colloidal Microspheres

V. Tohver,[1] J. A. Lewis,[1] G. Long,[2] P. R. Jemian[1]
[1] *University of Illinois at Urbana-Champaign, Urbana, IL, U.S.A.*
[2] *National Institute of Standards and Technology, Gaithersburg, MD, U.S.A.*

Introduction

Colloidal interactions govern the phase behavior, structure, and properties of particulate suspensions. Traditionally, colloidal stability[1,2] is imparted using electrostatic or steric mechanisms. We have discovered a new colloidal stabilization route that arises from the preferential segregation of highly charged nanoparticles to regions near the surface of negligibly charged colloidal microspheres. We refer to this nanoparticle configuration as nanoparticle haloing.[3] Ultra-small-angle x-ray scattering (USAXS) measurements have been carried out to assess this the influence of nanoparticle stabilization on suspension structure.

Methods and Materials

Liquid cells specifically designed for USAXS with 1 mm x-ray path length and polyimide windows were used to hold the suspensions. Scattering measurements were taken over a *q* range of 10^{-4} to 10^{-1} ($Å^{-1}$) from suspensions of 0.01, 0.10, and 0.20 volume fraction ($\phi_{\mu sphere}$) of silica microspheres ($D = 0.570$ μm) stabilized with nonadsorbing zirconia ($D = 6$ nm; $\phi_{nano} = 10^{-3}$) nanoparticles under conditions close to the isoelectric point of silica. (Note: Under these pH conditions in the absence of zirconia nanoparticles, such suspensions are unstable and consequently flocculate.) As a benchmark, scattering measurements of $\phi_{\mu sphere} = 0.01$, 0.10, and 0.20 charged-stabilized silica microspheres in deionized water (pH ~5) were also taken in the absence of nanoparticles.

Results

Scattering curves showed regular, periodic oscillations in the measured intensity up to 10^{-2} $Å^{-1}$ for both nanoparticle and charge-stabilized systems. Suspensions containing nanoparticles also showed nonperiodic scattering peaks from 10^{-2} to 10^{-1} $Å^{-1}$. Analysis of scattering in this *q* range revealed a 6 nm diameter for the nanoparticles.

Discussion

Silica microspheres suspended in deionized water at pH ~5 have sufficient surface charge density to be stabilized electrostatically. In contrast, bare silica colloids suspended at pH 1.5 flocculate rapidly due to their low surface charge density. Earlier sedimentation and rheological studies indicate that silica microsphere stability at pH 1.5 improves with increasing nanoparticle additions. Reflectometry, supernatant, and zeta potential studies at pH 1.5 indicated that this stabilization arises as the highly charged nanoparticles segregate *near* the microsphere surface, thereby increasing the effective microsphere charge. In both the nanoparticle-stabilized and charge-stabilized cases, periodic oscillations up to 10^{-2} $Å^{-1}$ were observed, indicating microspheres are dispersed by either mechanism.

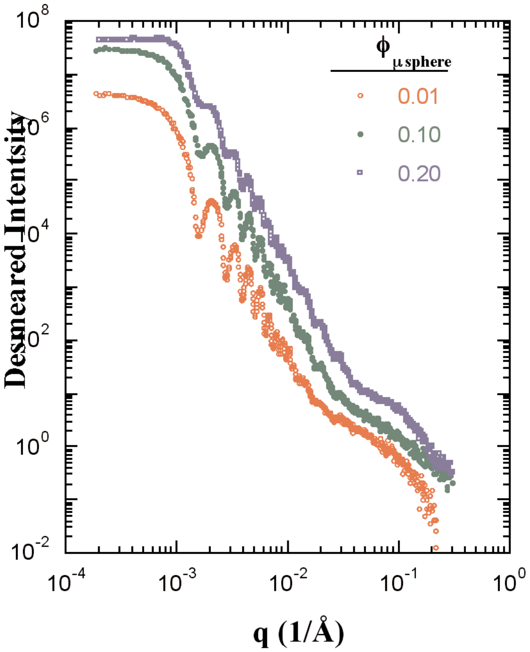

FIG. 1. USAXS from samples containing colloidal microspheres of varying volume fractions and nanoparticles of fixed volume fraction (ϕ_{nano} = 1.85 x 10^{-3}). Data shown were desmeared using a Lake program.

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