ABSTRACT

Yang, Yung-Jih Ph.D., Purdue University, December 2016. Experimental and Modeling Studies of Colloidal Suspension Stability of High-Density Particles in Aqueous Solutions. Major Professors: Elias I. Franses and David S. Corti

Agglomeration and sedimentation of suspended colloidal particles occur in many natural phenomena, in consumer products, and in engineering applications. Stabilized colloidal pigment dispersions were used in ancient Egypt and in ancient France thousands of years ago. Present day applications include the manufacturing of paints and coatings, enhanced oil recovery, waste-water treatment, pharmaceutical dispersions, biotechnology, and inkjet printing. The most common problem in colloidal science is how to stabilize suspended colloidal particles against agglomeration by controlling their interparticle forces. If the particles agglomerate, the sizes of the resulting agglomerated particles increase, increasing the sedimentation (or creaming) rate, and the suspensions can become unstable. In certain coating processes, preventing the agglomeration of dispersed particles is less important, since the particles may agglomerate after the coating is applied and dried. By contrast, strategies for preventing sedimentation, whether or not agglomeration occurs, are particularly important for suspensions containing high-density particles. For such suspensions, few fundamental studies are available in the literature, even though their uses are widespread. This thesis focuses principally, for the first time in substantial detail, on the stability of aqueous (or other) suspensions against not only agglomeration but also sedimentation. Strategies for preventing the sedimentation of suspensions containing high-density particles, especially for inkjet printing applications, are another focus of the thesis.

Titania particles are a common pigment material for high-quality white inks. Their density ($4.2\ g/cm^3$) is quite high, compared to other pigments, causing them to be quite susceptible to settling. To stabilize these high-density particles, three surfactants were chosen as dispersants and stabilizers. One was an anionic single-chain surfactant, sodium dodecylsulfate (SDS); a second was a nonionic single-chain surfactant, Triton X-100 (TX100); a third was a cationic double-chain surfactant, didodecyldimethylammonium

bromide (DDAB). The targeted titania particles were quite polydisperse in size with diameters $d_{TiO_2} = 280 \pm 100$ nm.

In the aqueous SDS solutions with concentration above its cmc (ca. 8 mM in water), the particles were well dispersed and remained stable against coagulation, mainly due to the strong electrostatic interactions produced by the adsorbed surfactants on the particle surfaces. Nonetheless, the particles still settled by 0.5 cm in 45 h, and that is the best stability against sedimentation that can be achieved by using SDS as the stabilizer. Moreover, at higher SDS concentrations, above 60 mM, the particles flocculated in short times and settled in 1 to 2 h. The flocculation is attributed to the strong depletion interactions, induced by the SDS micelles (*Yang et al. JCIS 2015*). On the other hand, by using TX100 as the stabilizer ($\text{cmc} \cong 0.24$ mM in water), a slower sedimentation occurred with surfactant concentrations above 20 mM, mainly due to the viscosity effects of the suspension medium. Moreover, unlike the particles in aqueous SDS solutions, no apparent depletion-induced flocculation was observed in the TX100 solutions with the concentrations up to 250 mM. The micelle-induced depletion, however, was masked by the viscosity effects.

By contrast, when the double-chain surfactant DDAB was used as the stabilizer, the particles remained suspended for at least 18 months at the surfactant concentration of 2 wt% (43.3 mM). At this concentration, the vesicles formed a tightly close-packed structure with a volume fraction over 0.7, as evidenced by cryo-TEM (cryo-transmission electron microscopy) images. Thus, the particles were trapped in such close-packed structures. Several independent lines of evidence, including dynamic light scattering, zeta potential measurements, and viscosity measurement, support the inference. The highly shear-thinning DDAB dispersions have viscosities of 10^4 to 10^6 mPa $\cdot$ s at low shear stresses form 0.002 to 0.02 Pa, and viscosities of 10 mPa $\cdot$ s at high shear stresses form 5 to 10 Pa. In such suspension media, the titania particles respond to the low-shear-stress viscosities, which are responsible for the very small, if any, sedimentation rates. Nonetheless, the flowability of the bulk titania suspensions is still quite suitable for the ink-jet printing applications, because of their low high-shear-stress viscosities (*Yang et al. Langmuir, 2015*; *PCT international patent application, 2016*).

To elucidate the key factors of this vesicular stabilization mechanism, we have used Brownian dynamics simulations (BDS). BDS were done for binary mixtures of high-density particles and non-settling particles (light particles), which mimic the behaviors of "rigid" vesicles. The key factor in these mechanisms is confirmed to be the volume fraction of the light particles ϕ_2, as would be expected. As ϕ_2 exceeds a threshold of about 0.3 to 0.5, depending on the sizes of the light particles, the high-density particles can remain suspended indefinitely. The simulation results indicate, consistently with the experimental data, that a general method for long-term stabilization against sedimentation of the high-density particles can be provided by the dispersions of the light particles, which do not impede significantly the flow of the bulk suspensions.

As mentioned earlier, the particles will settle faster if they agglomerate when settling. To investigate the effects of agglomeration on the sedimentation times, we have developed novel models to predict the measured (or net) sedimentation time t_s, which is a characteristic time used in this thesis for quantifying the extent of the stability against sedimentation. In our models, to a first approximation, the processes of sedimentation and agglomeration are assumed to be decoupled and to occur sequentially, with agglomeration followed by sedimentation. The key idea of the models is to predict the agglomeration time, t_{an}, for forming a cluster with n primary particles (or monomers) and compare it to the intrinsic sedimentation time of that cluster, t_{sn}, obtained from the Stokes law. As the particles agglomerate or as n increases, t_{an}, increases and t_{sn} decreases. When t_{an}, and t_{sn} are about equal, which should occur for some cluster size $n = n^*$, both the agglomeration and the sedimentation rates are important, and the net sedimentation time is predicted to be roughly equal to t_{an^*} or t_{sn^*}.

The models are evaluated with the initially monodisperse silica suspensions (*Yang et al. Langmuir, 2016*). By adding an electrolyte, NaBr, into the stable suspensions, the agglomeration rate increases and depends on the NaBr concentration, c_{NaBr}. The model predictions are consistent, qualitatively and semi-quantitatively, with the data of the sedimentation half-times. The models can also be used in predicting the sizes and the densities of the clusters, and in predicting the Fuchs-Smoluchowski stability ratios by fitting the models to the experimental data.