ABSTRACT

In the practical applications of colloidal dispersions and suspensions, such as inks, paints, and food industry, the suspended particles must be stabilized, and remain well-dispersed for long times. Particles denser than the suspending media may inevitably sediment rapidly even with no agglomeration occurring. Therefore, an ideal dispersant is necessary for stabilization of particle suspensions against both agglomeration and sedimentation while the suspensions remain flowable. Moreover, because many suspension media may have salts, the ideal dispersant also needs to be an effective stabilizer against sedimentation under salinity conditions.

DDAB (didodecyldimethylammonium bromide) , a cationic double-chain surfactant, forms lamellar liquid crystal phases when dispersed in water. It also easily forms aqueous vesicle dispersions (unilamellar closed particles with an inside solvent compartment) and liposomes (multilamellar vesicles, MLVs, or lamellar liquid crystallites) at relatively low DDAB weight fractions, w_D. To better understand the phase/dispersion behavior of DDAB and the corresponding optical properties, the new analytical solutions of the spherical particles have been obtained for the light scattering theory in the Rayleigh (R) and the Rayleigh-Debye-Gans (RDG) regimes for single and independent scattering. Moreover, the specific Rayleigh ratio R_θ^{**} and the specific turbidity τ^{**} were derived analytically for both scattering regimes. Spectroturbidimetry (ST) data at 25 °C for DDAB were compared to the τ^{**} predictions. τ^{**} data for DDAB vesicles are consistent with the RDG predictions, which are also used to estimate the vesicles' sizes.

For a better understanding the effect of the preparation method and salinity on the formation of DDAB vesicles, the spectroturbidimetry was used to measure the average radius of the unilamellar DDAB vesicles prepared via the two different methods in water and in NaBr salt solutions, being ~24 nm after sonication (SS method) and ~74 nm after extrusion/ultrafiltration (SE method). The radii were larger when the vesicles were produced in 10 mM NaBr, ~65 nm for the SS method and ~280 nm for the SE method. The τ^{**} of these vesicular dispersions increased with decreasing w_D until a constant value was reached at w_D^*, which depends on the preparation method and the dispersion medium. The constant values of τ^{**} are indicative of single and independent scattering, and were used to estimate vesicle radii by solving the τ^{**} equations derived for the RDG regime. Estimates of the average distances between the vesicles and their

corresponding Debye lengths were obtained to evaluate the importance of inter-vesicle electrostatic interactions, which could lead to dependent scattering at higher weight fractions.

For the stabilization of particle suspensions against sedimentation, the DDAB SS dispersions could completely stabilize silica and titania particles against sedimentation in pure water. The sedimentation velocities, v_{sed}, of the particles sedimenting in the DDAB SS dispersions tracked with photography could be obtained, and were used in the determination of the effective viscosities of the DDAB dispersions, which range from 1.35 to 1.87 cP at $w_D = 0.009$ and from 4.34 to 5.57 cP at $w_D = 0.018$. At $w_D = 0.025$, the DDAB dispersion behaved as a highly shear-thinning fluid, could completely prevent particles from sedimentation while the suspensions retain flowable. Since the stabilization mechanism is the formation of the close-packed vesicle dispersions, one may speculate on other potential stabilizers with similar phase and dispersion properties. To further understand the feasibility of the vesicle stabilization mechanism at various NaBr concentrations, w_{NaBr}, the salinity effects on the stabilization of silica particles against sedimentation were also examined. It was found that at $w_{NaBr} < 0.0020$ and at $w_D > 0.060$, the DDAB dispersion could stabilize silica particles against sedimentation for at least two weeks. The relationship of the phase and dispersion behavior of DDAB/aqueous NaBr solutions to their stabilizing effectiveness will be further studied.

A first discovery of iridescent liquid-like aqueous vesicle dispersions formed from the DDAB is reported. Iridescence arises for some solid crystallites and thin films, but has not yet been observed in liquid-like systems. Photography and ST were used to study the visual appearances and the absorbances due to scattering of DDAB vesicle dispersions for w_D between 0.020 to 0.030. The DDAB vesicle dispersions exhibited iridescent colors for $w_D = 0.023$ to 0.027, due to the formation of "soft" crystallites formed by self-assembled vesicles. Effective vesicle radii from 30 to 60 nm were inferred from the ST measurements. The volume fractions of the vesicles ϕ_V and their effective volume fractions ϕ_V^*, which account for the electrostatic double layers around a vesicle, were also estimated. The high values of ϕ_V^* for the iridescent dispersions indicate that they contain neighboring vesicles with highly overlapping electrostatic double layers, even though their values of ϕ_V remain relatively low. Hence, strong electrostatic repulsive interactions arise between the vesicles, which probably drive the formation of "soft" crystallites, and thus the observed iridescence.