



Experimental investigation of the effects of ionic micelles on colloidal stability



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ABSTRACT

The effects of ionic micelles (tetradecyltrimethylammonium bromide (C_{14} TAB) and sodium dodecylsulfate (SDS)) on the stability of a dispersion of highly charged silica particles was investigated both visually and using UV–vis absorption. As the surfactant concentration increased from 0 to 30 cmc, a clear critical flocculation concentration was observed with both surfactants. For SDS, restabilization was observed at 20 cmc. These stability results were compared to energy profiles that were calculated using measured force profiles between a single silica sphere and plate obtained with colloid-probe atomic force microscopy. It was found that flocculation would occur once the energy well formed by depletion attraction exceeded $3 k_B T$, while restabilization occurred once the long range structural energy barrier exceeded $8 k_B T$. These values are consistent with the energy levels needed for flocculation and restabilization predicted by other researchers.

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1. Introduction

The stability properties of colloidal suspensions can be affected by depletion interactions through what is known as depletion flocculation. In the 1950s, Asakura and Oosawa presented the first complete description of the depletion interaction [1,2]. This interaction, along with the related structural interaction, has been studied both theoretically and computationally [3–11], as well as experimentally [3,5,12–27] in a variety of systems.

Depletion flocculation was first reported in the early 20th century when Traube observed the creaming of natural rubbers [28]. Since that time, the ability of negatively adsorbing materials to induce flocculation of larger particles has been well studied [29–34]. In particular, Sharma et al. [35], Cowell et al. [36], and Sperry et al. [37] investigated the critical flocculation and restabilization concentrations of varying colloidal dispersions. Restabilization, sometimes referred to as depletion stabilization, occurs when a colloidal dispersion remains stable at high concentrations of depletant due to repulsive structural forces between the particles arising from ordering of the depletant in the gap region.

Micelles offer a unique type of negatively adsorbing material which can be used to induce depletion flocculation. Because micelles are only present above the surfactant critical micelle concentration (cmc), it is possible to effectively remove the depletant material (i.e. micelles) from the system by simple dilution.

Several authors have previously shown that micelles can act as flocculants in colloidal systems as a result of depletion interactions. Cockbain showed that oil particles could be aggregated in emulsions using soaps above their cmc [38]. Aronson also showed that emulsions of paraffin oil could be destabilized by anionic and nonionic micelles [39]. Ma presented findings on the stability behavior of polystyrene particles in varying concentrations of Triton X-100, a nonionic surfactant [40]. Flocculation of the polystyrene particles was observed at higher surfactant concentrations.

More recently, Furusawa et al. studied the flocculation behavior of dispersions of latex particles in both anionic and cationic surfactants using rheology [41]. These authors observed a maximum in the viscosity of the dispersion with increasing surfactant concentration, indicating the development of depletion flocculation at intermediate surfactant concentrations, and then restabilization at higher concentrations. They found the flocculation to be fully reversible through simple dilution.

Iracki et al. studied the 2D colloidal configurations of silica particles in solutions of sodium dodecylsulfate [42]. Agreement was found between video microscopy measurements and Monte-Carlo simulations for the ordering of the particles. Lüderitz et al. studied the interaction between a silica sphere and silicon wafer and a silica sphere and silica plate in a solution of hexadecyltrimethylammonium bromide (C_{16} TAB) micelles [43]. The authors observed that the interaction varied between the different surfaces and concluded that silica and silicon surfaces have differing aggregate morphologies.

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Much of the previous work on micelle induced depletion flocculation has simply focused on its occurrence (i.e., does flocculation occur and at what conditions). In the present work, comparisons will be drawn between observed phase behavior and the stability predicted using force profiles measured between a single particle and a plate obtained with the technique of colloid-probe atomic force microscopy. The system consists of silica (SiO_2) particles and micelles of the common surfactants tetradecyltrimethylammonium bromide (C_{14}TAB) and sodium dodecylsulfate (SDS). The stability of suspensions of micron-size SiO_2 particles was measured using both UV-vis absorption measurements and simple visual observation.

2. Theory

2.1. Flocculation and restabilization theory

Consider two charged colloidal particles interacting in a solution containing a negatively adsorbed species, such as ionic micelles. As the particles approach, a number of interactions can arise. At the simplest level, repulsive electrostatic and attractive van der Waals forces comprise the well-known DLVO forces. However, the presence of the micelles makes the picture more complicated. At short distances, the micelles will be excluded from the gap region and an attractive depletion force can arise [1–2]. At sufficiently high micelle concentrations, ordering of the micelles in the gap region will lead to longer-range, oscillatory structural forces [12–13,24].

It should be noted here that some adsorption of surfactant onto the larger microparticles may occur. This is especially true in the case of C_{14}TAB onto silica due to the driving force of opposite surface charges. However, based on previous results from the authors [44], even with such adsorption, a repulsive force will still exist between the microparticles and the micelles, making the assumption of negatively adsorbing species still valid.

To predict the stability of a dispersion of such particles, the pair interaction energy profile, $E(h)$, is evaluated, which is related to the force profile, $F(h)$, as

$$F(h) = -\frac{dE(h)}{dh}. \quad (1)$$

If the charge on the particles is sufficiently large, such that flocculation in the near-contact primary energy well created by strong van der Waals forces is unlikely, then the stability of the dispersion will be controlled by the relative strengths of the depletion and structural interactions. The essential components of the energy profile can then be represented as shown in Fig. 1. Here the energy

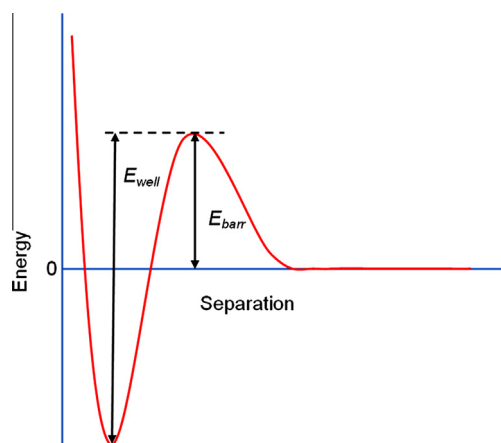


Fig. 1. Schematic representation of the interaction of two particles in a dispersion containing a depletant species.

well is created by the interplay between the repulsive electrostatic interaction and the attractive depletion interaction, while the longer-range barrier represents the short range component of the structural interaction.

The two primary determinants of stability in this system will be the depth of the secondary energy well, E_{well} , and the height of the long range energy barrier, E_{barr} . Previous work has shown that the stability of the system can be predicted using these two variables [35,45].

For low concentrations of depletants, both E_{well} and E_{barr} are small and the electrostatic force between the dispersed particles will be sufficient to maintain stability. As the concentration of depletants increases, E_{well} initially increases faster than E_{barr} because the latter parameter is a 2nd order concentration effect. Specifically, the depth of E_{well} depends primarily upon the nature of the interaction between the depletant and the larger species, while E_{barr} depends strongly upon depletant–depletant interactions. At low concentrations, depletant–depletant interactions will be insignificant, and therefore, E_{barr} will be small. With increasing concentration, however, depletant–depletant interactions increase such that E_{barr} increases faster than E_{well} .

Once E_{well} becomes sufficiently larger, flocculation occurs (termed the critical flocculation concentration). At even higher depletant concentrations, E_{barr} increases to the point that the particles will not have sufficient energy to overcome it and stability is re-established. The point is termed the critical restabilization concentration.

2.2. UV-vis absorption theory

UV-vis spectroscopy can be used as a means to quantify the flocculation behavior of a colloid dispersion. The total absorbance from a colloidal dispersion can be related to the wavelength of incident light through the simple power law expression

$$A = k\lambda^n \quad (2)$$

where A is the absorbance, k is a constant dependent upon particle size, density, and refractive index, λ is the wavelength of light, and n is the turbidity exponent which is a function of particle size [46].

Eq. (2) arises from the theory of Rayleigh scattering which describes the relationship between the intensity of scattered light and wavelength for systems where particle size is much smaller than the wavelength of incident light. For Rayleigh scattering, intensity scales as λ^{-4} . In experiments, where the particle size is on the order of the wavelength of light used, the turbidity exponent will increase with increasing particle size. Therefore, flocculation behavior can be quantified as an increase in the turbidity exponent over time, which can be determined from the slope of a log–log plot of total absorbance versus wavelength. That is

$$\log A = \log k + n \log \lambda. \quad (3)$$

3. Materials and methods

3.1. Materials

Water was purified using a Barnstead EASYpure II water purification system (Thermo Fisher Scientific Inc., Asheville, NC, USA) equipped with a 0.22 μm final filter. Powdered myristyltrimethylammonium bromide (C_{14}TAB) ($\geq 99\%$) (Sigma–Aldrich Co., St. Louis, MO, USA) and sodium dodecylsulfate ($\geq 99\%$) (Sigma–Aldrich Co., St. Louis, MO, USA) were used to make micelle solutions. Note the choice to use C_{14}TAB instead of the more common C_{16}TAB was due to its similar characteristics but lower Krafft temperature. Specifically, the Krafft temperature of C_{14}TAB is below 10 $^\circ\text{C}$

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