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Droplet-based characterization of surfactant efficacy in colloidal stabilization of carbon black in nonpolar solvents

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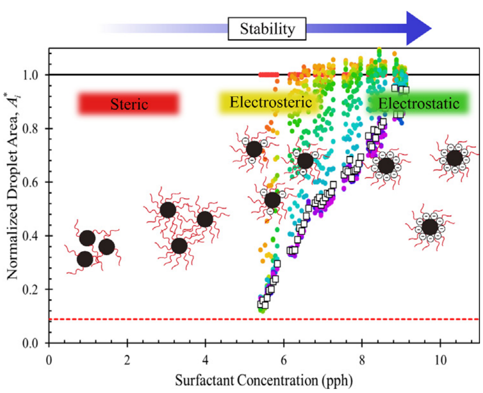
GRAPHICAL ABSTRACT



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ABSTRACT

Development of an electrostatic stabilization mechanism for colloidal suspensions in nonpolar fluids requires an improved understanding of the interactions between the inverse micelles and particles as well as the roles that steric and electrostatic effects play. A droplet-based millifluidic device is designed and used to investigate the stabilization effects of surfactants on colloidal suspensions. A system containing carbon black and the surfactant OLOA 11000 suspended in dodecane is chosen as a well-characterized system to study sedimentation quantitatively. This device takes advantage of sub-millimeter optical path lengths to characterize sedimentation at concentrations at which sedimentation is not observable in the bulk and to achieve higher resolution in composition. A simple image analysis algorithm has been developed and applied to quantify sedimentation. Conductivity measurements using electrochemical impedance spectroscopy (EIS) are coupled with the sedimentation experiments to identify the concentration ranges in which steric and electrostatic effects are dominant. A more gradual transition is observed than previously reported.

1. Introduction

The ability to predict and characterize the stability of colloidal particles in a solvent is one of the fundamental needs of colloidal

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science and is relevant to a wide range of industrial applications [1,2]. The stability of aqueous colloidal suspensions has been extensively studied and mechanisms for charge stabilization and steric stabilization, or electrosterics, have been elucidated [3–11]. However, less focus has been placed on understanding the mechanisms behind stabilization of systems in nonpolar media. The low dielectric constant ($\varepsilon \approx 2$) of nonpolar systems leads to high energy barriers of charge separation and as a result, electrostatics are thought to be an unlikely mechanism for stability in nonpolar media. However, with the addition of surfactant or 'dopant', charging and electrostatic stabilization have been observed in nonpolar solvents [1,2,12–16]. These systems are used extensively in industrial applications, but a fundamental understanding of the stabilization mechanism is still missing, partly due to a lack of detailed characterization.

It has been shown that the introduction of inverse micelles in nonpolar fluids leads to a measureable conductivity increase that is proportional to the inverse micelle concentration [1,17–21]. The mechanism of the charge production has not yet been elucidated, but it is generally thought that charged species are stabilized within the inverse micelle core and that the inverse micelles behave as charge carriers [22–26]. When particles are added to the system, some of the charge is imparted to the particle surface leading to electrostatic stabilization [2,14–16]. Particle charging has been observed in nonpolar fluids with PMMA [12,14,27], PS [14,28], carbon black [29–31], silica [23,32–34], and alumina [34] particles using various surfactants or dopants. Systematic studies are underway to understand the effects of each component and determine the underlying mechanism of particle charging [23,34]. Smith and Eastoe provide a detailed introduction into the three proposed mechanisms for charge transfer and particle charging in nonpolar fluids [2]. The acid-base mechanism originally proposed by Pugh et al. is a likely candidate to describe particle charging, especially for nonionic surfactants [29]. The suggested idea is that initially uncharged micelles (or single surfactant molecules) adsorb to the particle surface. Charge is then imparted into the micelle or surfactant molecule via an acid-base reaction with the sign of the particle being determined by the acidity and basicity of the particle and surfactant. Finally the charged micelle or surfactant desorbs from the surface leaving behind a charged particle surface. The degree by which the particles are stabilized has been investigated by various theoretical methods including a direct extension of DLVO theory [35] as well as a sum of Hamaker and Coulomb forces (ignoring the electrical double layer effects) [36,37] while some argue that at high concentrations the repulsive forces are not strong enough to stabilize the system [38,39]. An in depth comparison of electrostatic contributions is available in a review article [1].

One of the first reports that identified particle charging and electrostatic stabilization in nonpolar solvents used a system of carbon black particles dispersed in dodecane with the surfactant OLOA 1200 [29,30]. Carbon black is a powder of primary particles composed of graphene layers and is produced through the incomplete combustion of heavy petroleum [40]. The surfactant, OLOA 1200, is a nonionic commercial product with a structure described as a polyisobutylene tail with a succinimide linker to an amine head group dispersed in a cosolvent [41].

A simple method to characterize suspension stability is to place the formulated suspension in a vial and visually observe sedimentation in the sample with time [29,42]. While simple, this approach is complicated in opaque suspensions or strong optical absorbers like carbon black. Pugh et al. uses this methodology to characterize the stability of carbon black mixed with OLOA 1200 by visualizing samples with a fixed carbon black concentration and varying amounts of surfactant [29]. A gradual increase in suspension stability with increasing surfactant concentration is observed until a critical surfactant concentration is reached. Beyond this critical value, the suspensions are observed to be indefinitely stable. A shift in mechanism from steric stabilization at low OLOA 1200 concentration (weakly stable) to electrostatic stabilization above the critical OLOA 1200 concentration (highly stable) is proposed The proposed stabilization mechanism is consistent with viscosity and conductivity measurements [29].

In this work, we demonstrate the potential to provide more detailed characterization of the stability of a colloidal system using droplet-based millifluidics. This approach offers the advantages of smaller sample volumes, a higher resolution in composition space, a shorter optical path length, and it removes issues associated with particle adsorption to solid walls of sample jars. A test case of carbon black and OLOA 11000 in dodecane is used, similar to that studied by Pugh et al. [29]. The goal of this work is to probe the transition regime from steric to electrosteric stabilization with greater compositional resolution than previous studies. With this alternative measurement technique, it is possible to use sedimentation experiments to expand the understanding of the underlying stabilization mechanisms. A compact device is designed that allows for production and storage of droplets containing nonpolar colloidal suspensions. Each droplet in the device contains a different suspension composition which leads to significant increases in resolution and efficiency of the process. The droplets are observed for time periods up to many months and the sedimentation levels of suspension within the droplets are characterized as a function of time. The level of sedimentation provides insight into the degree of stabilization and information about the stabilization mechanism when paired with conductivity measurements.

2. Experimental

2.1. Materials

The carbon black used in these experiments is Monarch® 280 powdered carbon black donated by Cabot Corporation (Boston, MA, USA). The carbon black is reported to have a primary particle diameter of 30 nm and a BET adsorption surface area of 42 m^2/g [43]. Light scattering using a Zetasizer Nano ZS90 is performed on dilute samples of the carbon black and determined a primary particle aggregate diameter of 200 nm. The dodecane is purchased from Fisher Scientific (Pittsburgh, PA, USA) and is used as supplied.

The OLOA 11000 is reported to have a molecular weight of 950 g/mol and is donated by Chevron Oronite (San Ramon, CA, USA). The structure is reported to be a polyisobutylene chain with a succinimide linker to a triamine head group and is diluted in mineral oil [41]. The product is used as received. The fluorinated FC-70 oil is purchased from Hampton Research (Aliso Viejo, CA, USA) and is used as supplied.

2.2. Sample preparation

Samples of Monarch 280 Carbon Black and OLOA 11000 suspended in dodecane are produced in 50 mL vials at various concentrations of OLOA 11000. The OLOA 11000 is assumed to contain 75 wt% active surfactant and 25 wt% mineral oil [44]. Only the mass of the active surfactant is considered while producing suspensions and the amount of mineral oil is considered to have negligible impact on the particle stability and conductivity.

Dodecane and appropriate concentrations of OLOA 11000 are mixed and allowed to sit overnight before introducing carbon black to the system. Carbon black is heated in a vacuum oven at 200 °C for 4 h and then allowed to cool under vacuum to room temperature over 3 h to remove any absorbed water. Once dry, the carbon black powder is immediately introduced into the OLOA 11000 and