



## Phase and sedimentation behavior of oil (octane) dispersions in the presence of model mineral aggregates



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### ABSTRACT

Adsorption of suspended particles to the interface of surfactant-dispersed oil droplets can alter emulsion phase and sedimentation behavior. This work examines the effects of model mineral aggregates (silica nanoparticle aggregates or SNAs) on the behavior of oil (octane)–water emulsions prepared using sodium bis(2-ethylhexyl) sulfosuccinate (DOSS). Experiments were conducted at different SNA hydrophobicities in deionized and synthetic seawater (SSW), and at 0.5 mM and 2.5 mM DOSS. SNAs were characterized by thermogravimetric analysis (TGA) and dynamic light scattering (DLS), and the emulsions were examined by optical and cryogenic scanning electron microscopy. In deionized water, oil-in-water emulsions were formed with DOSS and the SNAs did not adhere to the droplets or alter emulsion behavior. In SSW, water-in-oil emulsions were formed with DOSS and SNA–DOSS binding through cation bridging led to phase inversion to oil-in-water emulsions. Droplet oil-mineral aggregates (OMAs) were observed for hydrophilic SNAs, while hydrophobic SNAs yielded quickly sedimenting agglomerated OMAs.

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### 1. Introduction

Oil enters marine environments naturally and through accidental release (spills), leading to environmental health and safety concerns offshore and nearshore. The application of oil dispersants is considered to be the most feasible and effective means of breaking surface oil slicks, and has been studied for decades (Lessard and Demarco, 2000; Gong et al., 2014; *Oil Spill Dispersants: Efficacy and Effects*, 2005). The surfactants disperse the slick into micrometer-scale oil droplets that are degraded by natural microbial processes (Das and Chandran, 2011). Smaller oil droplets with larger specific surface areas exhibit higher biodegradation due to increased bioavailability. This was the approach taken in the Gulf of Mexico in 2010 to treat the Deepwater Horizon (DWH) oil spill. In this case, Corexit® series 9500 and 9527 were sprayed at the ocean surface and injected deep sea, at the wellhead, to prevent the oil from forming a surface slick and migrating inland (Atlas and Hazen, 2011; Mathew et al., 2012). While successful in this endeavor, it has been estimated that as much as 30% of the oil released may be entrapped within the sediment on the ocean floor (Kini et al., 2012).

Oil entrapment within sediments highlights the importance of oil-solid (mineral) and oil-dispersant-solid interactions, and the effect of these interactions on oil fate and transport (Gong et al., 2014). Previous studies have shown that the formation of oil mineral aggregates (OMAs), also referred to as oil suspended particular material (SPM) aggregates (OSAs), is instrumental for dispersion and degradation of spilled oil (Wang et al., 2011; Weise et al., 1999). These aggregates are formed when oil, either as dispersed droplets, as adsorbed oil, or as a free phase liquid with suspended particles in an aqueous suspension collide and adhere. Intuitively, the addition of dispersants has been shown to enhance the formation of OMAs by increasing the oil/water surface area for particle adhesion. As in Pickering emulsions, which are emulsions formed using solid particles (Aveyard et al., 2003), the formation of OMAs depends on the properties of the mineral particles, including size and hydrophobicity, and salinity (Binks and Lumsdon, 1999; Omotoso et al., 2002; Stoffyn-Egli and Lee, 2002). Additionally, Bandara et al. (2011) have suggested that electrostatic interactions between the particles and the oil/water interface, mediated by cation bridging, lead to the formation of OMAs.

In a recent review article, Gong et al. (2014) have identified a knowledge gap relating to interactions between oil, dispersants, and suspended particles; and the effects of dispersants on particle sorption/desorption at oil/water interfaces. Using anionic particles and anionic or nonionic surfactants, Katepalli et al. (2013) have

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shown that in all cases the surfactants displaced the particles from an oil/water interface. Their study was conducted in deionized water and supports the concept that cation bridging may be important to particles adhering at dispersant-laden interfaces. A significant amount of additional work is needed using conditions and compositions that are relevant to ocean environments and to the process of oil spill dispersion (i.e. surfactants present in commercial dispersants) to better understand oil-dispersant-particle interactions, OMA formation and stability, and OMA transport or sedimentation.

The objective of this work was twofold; to create a model mineral aggregate that does not employ organic surface treatments and to examine oil/surfactant/water emulsion phase behavior in the absence or presence of the mineral aggregates. Silica nanoparticle aggregate (SNAs) were used as model mineral aggregates. Silica particles have been extensively used to stabilize oil/water Pickering emulsions and also as a model mineral to form OMAs (Binks and Lumsdon, 1999; Binks and Horozov, 2005). In this study, SNAs were formed from primary particles that were heat-treated to control surface silanol (Si–OH) density, which influenced the hydrophobicity and the hydrodynamic diameter of the SNAs. Dioctyl sodium bis(2-ethylhexyl) sulfosuccinate (DOSS), known also as Aerosol<sup>®</sup> OT or AOT, was used to form octane/DOSS/deionized water and octane/DOSS/synthetic seawater emulsions in the presence of SNAs. DOSS was selected because it is the anionic surfactant in Corexit<sup>®</sup> 9500A and 9527 (ca. 10–30 wt%). It has also been shown to adsorb to silica by divalent cation (Ca<sup>2+</sup>) bridging Wang et al., 2013.

## 2. Materials and methods

Silica nanoparticles (15–20 nm primary diameter) were obtained from SkySpring Nanomaterials Inc. DOSS (99%) was acquired from Sigma Aldrich and n-octane, (anhydrous, ≥99.0%), sulfuric acid, and hydrogen peroxide were acquired from Fisher Scientific. Artificial seawater was prepared according to the ASTM D1141-98 standard and consisted of 24.53 g/L (419.7 mM) NaCl; 5.20 g/L (54.6 mM) MgCl<sub>2</sub>; 4.09 g/L (28.8 mM) Na<sub>2</sub>SO<sub>4</sub>; 1.16 g/L (10.5 mM) CaCl<sub>2</sub>; 0.695 g/L (9.3 mM) KCl; 0.201 g/L (2.4 mM) NaHCO<sub>3</sub>; 0.101 g/L (0.8 mM) KBr; 0.027 g/L (0.4 mM) H<sub>3</sub>BO<sub>3</sub>; 0.005 g/L (<0.1 mM) SrCl<sub>2</sub>; and 0.003 g/L (<0.1 mM) NaF. From this composition the total monovalent cation concentration was 489.9 mM and the total divalent cation concentration was 65.1 mM.

### 2.1. Surface modification of silica nanoparticles

Silica nanoparticles were fully hydroxylated by treating for 4 h in piranha solution prepared by adding sulfuric acid to hydrogen peroxide at 75/25 (v/v). The slurry was rinsed with deionized water and centrifuged using an International Equipment Company (IEC) clinical centrifuge for 20 min at 200 g. This was repeated six times to remove the piranha solution. To tune the hydrophobicity on the particles, the particles were heated at 200 °C, 400 °C or 600 °C for 90 min in a Thermo Scientific Precision Compact oven. Heat treatment is a common method to control silanol density on silica nanoparticles and an alternative to chemical modification (e.g. silylation) Dugas and Chevalier, 2003; Potapov and Zhuravlev, 2005. Chemical modification was avoided to eliminate stabilizing ligands interacting with DOSS.

### 2.2. Thermogravimetric analysis (TGA)

Silanol density (OH/nm<sup>2</sup>) was quantified by a TA Instrument Q100 thermogravimetric analyzer. Treated silica particles were

first heated from 25 °C to 120 °C at 10 °C/min, and held for 10 min to remove physically adsorbed water. In the second heating step, the silica particles were heated from 120 °C to 800 °C at 20 °C/min and held at 800 °C for 10 min to measure the loss of silanol groups.

### 2.3. Dynamic light scattering (DLS)

Hydrodynamic diameter measurements were conducted on a Malvern Instruments Zetasizer Nano ZS (Worcestershire, UK). For size determination, 1 mL samples were placed in 10 × 10 × 45 mm quartz cuvettes and dynamic light scattering (DLS) was performed at 25 °C at 173° backscatter angle with 120 s equilibration time. The average hydrodynamic diameters reported are based on 11 scans and duplicate sample preparation.

### 2.4. Preparation of emulsions

SNA suspensions at 0.1 and 1 wt% concentration were prepared by adding the treated particles to deionized water or artificial seawater followed by probe sonication at 30% amplitude (2 W) for 30 s. Sterile ultrafiltered deionized water was obtained from a Millipore Direct-3Q ion-exchange system. DOSS was dissolved in octane at 1 mM or 5 mM. All emulsions were prepared in duplicate by adding equal volumes of octane + DOSS and water + SNAs in glass vials, and vortex mixing for 1 min. The total DOSS concentration in the system was 0.5 mM (0.2 g/L) and 2.5 mM (1.1 g/L), which was below and at the critical micelle concentration (CMC) of ca. 2.5 mM, respectively (Frank and Zograf, 1968). Samples were analyzed visually and by microscopy over the course of three weeks. Samples were prepared in triplicate and the results are shown immediately after emulsion formation (up to 2 h) and after three weeks.

### 2.5. Microscopy

The microstructure of the emulsions was determined using a Fisher Scientific Micromaster II microscope. This included the top and bottom liquid phases and the SNA sediments. Samples were prepared by adding ca. 15 μL of a solution on a microscope slide.

Cryogenic field emission scanning electron microscopy (cryo-SEM) and energy dispersive X-ray spectroscopy (EDS) were conducted using a Zeiss Sigma IV FE-SEM operating at 3 keV. Specimens were prepared by placing ca. 50 μL of a sample onto a sample holder and freezing in liquid nitrogen within a Gatan cryogenic transfer stage. The solidified sample was fractured within the stage using a flat-edge knife at –130 °C, and then warmed to –100 °C for 2 min to sublime some of the residual octane and water. The sample was cooled back to –130 °C and sputtered with a gold-palladium composite (10 mA, 60 s, 1 mbar argon). The sample was then transferred to the imaging stage and maintained at –150 °C during imaging. Sample preparation and imaging were performed under a high vacuum.

## 3. Results and discussion

### 3.1. SNA preparation and characterization

The preparation and characterization of SNAs is shown in Fig. 1. SNAs were formed from heat-treated particles dispersed by probe sonication in deionized water or synthetic seawater. According to DLS measurements, the average hydrodynamic diameter of the SNAs measured shortly after preparation increased with increasing heat treatment temperature from approximately 1 μm at 200 °C to 5.5 μm at 600 °C (Fig. 1B). There was not a significant difference in

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