



## Regular Article

# Microstructure and rheology of particle stabilized emulsions: Effects of particle shape and inter-particle interactions



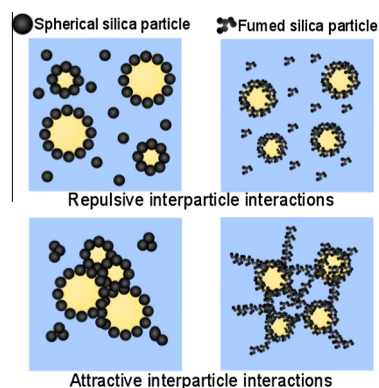
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## GRAPHICAL ABSTRACT



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## ABSTRACT

Using fumed and spherical silica particles of similar hydrodynamic size, we investigated the effects of particle shape and inter-particle interactions on the formation, stability and rheology of bromohexadecane-in-water Pickering emulsions. The interparticle interactions were varied from repulsive to attractive by modifying the salt concentration in the aqueous phase. Optical microscope images revealed smaller droplet sizes for the fumed silica stabilized emulsions. All the emulsions remained stable for several weeks. Cryo-SEM images of the emulsion droplets showed a hexagonally packed single layer of particles at oil-water interfaces in emulsions stabilized with silica spheres, irrespective of the nature of the inter-particle interactions. Thus, entropic, excluded volume interactions dominate the fate of spherical particles at oil-water interfaces. On the other hand, closely packed layers of particles were observed at oil-water interfaces for the fumed silica stabilized emulsions for both attractive and repulsive interparticle interactions. At the high salt concentrations, attractive inter-particles interactions led to aggregation of fumed silica particles, and multiple layers of these particles were then observed on the droplet surfaces. A network of fumed silica particles was also observed between the emulsion droplets, suggesting that enthalpic interactions are responsible for the determining particle configurations at oil-water interfaces as well as in the aqueous phase. Steady shear viscosity measurements over a range of shear stresses, as well as oscillatory shear measurements at 1 Hz confirm the presence of a network in fumed silica suspensions and emulsions, and the lack of such a network when spherical particles are used. The fractal structure of fumed silica leads to several contact points and particle interlocking in

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the water as well as on the bromohexadecane-water interfaces, with corresponding effects on the structure and rheology of the emulsions. The attenuation of droplet motion due to the formation of a particle network can be exploited for stabilizing emulsions and for modulating their rheology.

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## 1. Introduction

The ability of colloidal particles to adsorb strongly at immiscible liquid interfaces makes them potential alternatives to surfactants for stabilizing emulsions [1,2]. Even though it is thermodynamically favorable for partially wettable colloidal particles to locate at an oil-water interface rather than in one of the bulk phases, these particles reach their final positions at oil-water at logarithmically slow rates [3,4]. This transfer process can be accelerated by providing energy to the system. Once a partially wettable particle of diameter greater than 100 nm positions itself at its equilibrium location at an oil-water interface, thermal fluctuations will typically be insufficient to displace it from that location [5]. The adsorbed particles can create electrostatic, steric or interfacial viscosity related barriers against droplet coalescence, resulting in emulsions that remain stable for years [6,7].

Particle shape and inter-particle interactions can play significant roles in determining the microstructure and stability of particle-stabilized emulsions [8]. Madivala et al. [9] showed that ellipsoidal polystyrene particles above a critical aspect ratio are capable of forming stable emulsions, even when spherical particles with the same wetting properties do not form emulsions. The additional stability is partly a result of increased interfacial viscosity due to closer packing of ellipsoidal particles at the oil-water interfaces. San-Miguel and Behrens [10] showed that roughness on a colloidal particle surface enhances the stability of an emulsion, but the extent depended on whether the wettability of the rough particles were in the Wenzel or Cassie-Baxter regimes [9,11,12]. In both these cases the particles deform oil-water interfaces [8]. The resulting capillary interaction between the particles results in a more rigid network of these particles at the droplet interfaces compared to smooth spherical particles of the same effective size, contributing to the stability of these emulsions [13].

Particle shape and inter-particle interactions can influence the microstructure within the continuous phase and thus the rheology of the particle suspensions, or emulsions if excess particles are available in the continuous phase [14]. When the interactions between the particles are attractive, anisotropic particles such as fumed silica and clay (laponite or bentonite) can form volume filling networks at concentrations much lower than the spherical silica particles of the same hydrodynamic size [14–17]. The formation of such a network in the continuous phase of an emulsion can strongly influence emulsion stability, as it can affect droplet deformation and modulate droplet motion [18,19].

Here we report results from experiments geared towards understanding the roles of particle morphology and interparticle interactions on the microstructural characteristics and rheology of particle-stabilized emulsions. We used spherical silica and fumed silica particles of similar size. We tuned interparticle interactions by varying the amount of salt in the aqueous phase, from repulsive at low salt concentrations to attractive at high salt concentrations. For a given particle weight loading, the effective volume occupied by the fractal fumed silica particles in the suspension will be higher than that occupied by spherical silica particles. Depending upon the nature and extent of inter-particle interactions, this difference in effective volumes will have consequences on the rheology of the particle suspensions and emulsions.

We characterized the emulsions using optical microscopy, cryogenic scanning electron microscopy (cryo-SEM), and rheology.

## 2. Materials and methods

Spherical silica particles of diameter  $210 \pm 10$  nm were purchased from Fiber Optic Center. Hexylamine was adsorbed from a 0.06 mM aqueous solution on the surface of these spherical particles through electrostatic interactions between the silanol and amine groups, modifying particle hydrophilicity [20]. Fumed silica particles (Aerosil 816), with a hydrodynamic diameter of  $204 \pm 20$  nm, were provided by Evonik Corporation. These particles are surface functionalized with hexadecyltrimethoxysilane, making them partially hydrophobic [21]. The functionalization of the particles allows them to stabilize emulsions. Fig. 1(a) and (b) are TEM images of the spherical and fumed silica particles respectively. The specific surface area of spherical and fumed silica particles, reported by manufacturers, are  $10 \text{ m}^2/\text{g}$  and  $190 \text{ m}^2/\text{g}$  respectively [21].

Bromohexadecane (97%, Fisher Scientific) was used as the oil phase. The density of bromohexadecane is  $999 \text{ kg}/\text{m}^3$ , essentially matched with that of water. This choice of oil eliminated density-driven creaming in the emulsion, and allowed us to robustly probe the rheology of the emulsions. 0.1 mM and 50 mM NaCl solutions were used as the aqueous phases. The zeta potentials of the spherical and fumed silica particles in 0.1 mM NaCl were  $-48.2 \text{ mV}$  and  $-45.6 \text{ mV}$  respectively. For 50 mM NaCl, flocculation of spherical silica particles and network formation of fumed silica particles in the suspension leads to inconsistent values of electrophoretic mobilities [22,23], so we could not reliably measure zeta potentials. Assuming no specific binding of Na ions at silica surface [24] and by applying a constant potential boundary condition, we report the normalized interaction energy  $W/k_B T$  between 210 nm diameter spherical silica particles at different separation distances as a function of salt concentration in Fig. 1(c). At 0.1 mM NaCl, the energy of interaction is repulsive, with an energy barrier of  $\sim 150 k_B T$ , because of the charge on the particle surface. The interaction energy is attractive at 50 mM NaCl because of charge screening. Because these calculations are not straightforward for fractal particles, we have assumed that the energy of interaction for fumed silica particles is also repulsive at 0.1 mM NaCl and attractive at 50 mM NaCl, paralleling that for spheres. While the surface chemistry of the fumed and spherical silica particles are different because of a difference in the hydrocarbon chain length of the functional molecules bound to their surface, their charge densities, reflected in the zeta potentials in a 0.1 mM NaCl solution are very similar. We believe the surface charge density, charge screening due to addition of salt and geometry of the particles are the key properties that affect their aggregation behavior and thus the characteristics of the particle-stabilized emulsions.

## 3. Emulsion preparation and characterization

1:1 v/v bromohexadecane: water emulsions were prepared by vortexing the oil and aqueous phase at 3000 rpm for 2 min. The aqueous phase contained 2 wt% of silica ( $\sim 0.01$  fraction by volume). All of the bromohexadecane was emulsified. All samples

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