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FORMATION AND STABILITY OF EMULSIONS: EFFECT OF SURFACTANT-PARTICLE INTERACTIONS AND PARTICLE SHAPE

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FORMATION AND STABILITY OF EMULSIONS:
EFFECT OF SURFACTANT-PARTICLE
INTERACTIONS AND PARTICLE SHAPE

BY

HARI KATEPALLI

A DISSERTATION SUBMITTED IN PARTIAL FULFILLMENT OF THE
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OF
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ABSTRACT

Formation and stability of emulsions is one of the important topics in the field of colloids and interfacial science. Surfactants and colloidal particles are often used to stabilize emulsions. Surfactants are amphiphilic molecules; they minimize the energy required for the emulsion formation by reducing oil-water interfacial tension. Colloidal particles are not amphiphilic, but partially wettable particles favors the adsorption at oil-water interface with a desorption energy well above thermal energy. With sufficient coverage at the interface, they act as barriers against droplet coalescence and enhance the emulsion stability. In this work, the response of particle-stabilized (Pickering) emulsions to the addition of different surfactant solutions and the stability of surfactant stabilized emulsions to the addition of particle suspensions were studied. There were different end points for emulsion droplets and different particle release modes for Pickering emulsions depending upon the interactions between surfactants and particles, surfactant-particle ratio, and mixing conditions. The effect of particle shape on the formation of Pickering emulsions is also studied. It is found that the inter-particle interactions and particle shape play major role in determining the microstructure and final stability of the emulsions. The combinations of optical, confocal, and Cryogenic scanning electron microscopy were used to determine the final stability and structure of the emulsions.

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PREFACE

This dissertation is written in manuscript format. The first chapter is an introduction about emulsions. The second chapter entitled “The Response of Carbon Black Stabilized Oil-in-Water Emulsions to the Addition of Surfactant Solutions” was published in *Langmuir* (*Langmuir*, **2013**, 29, 6790-6797) in June 2014. The third chapter entitled “The Response of Surfactant Stabilized Oil-in Water Emulsions to the Addition of Particles in an Aqueous Suspension” was in review in *Langmuir*. The fourth chapter entitled “Microstructure and Rheology of Particle Stabilized Emulsions: Effect of Particle Shape” is in preparation for *Colloids and surfaces A: Physicochemical and Engineering Aspects*

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CHAPTER 1

1.1 Introduction:

An emulsion is a dispersion of one immiscible liquid with in a second liquid. Depending on the component that gets dispersed in other, they are classified as Oil-in-Water (O/W) or Water-in-Oil (W/O) emulsions. They find applications in many different fields such as food, cosmetics, pharmaceuticals, and oil recovery etc... Formation of emulsion is an energy intensive process.¹ Figure 1.1 shows a system in which liquid 1 represented by a large drop of area A_1 is immersed in liquid 2, which is subdivided into a large number of smaller droplets with total area A_2 .

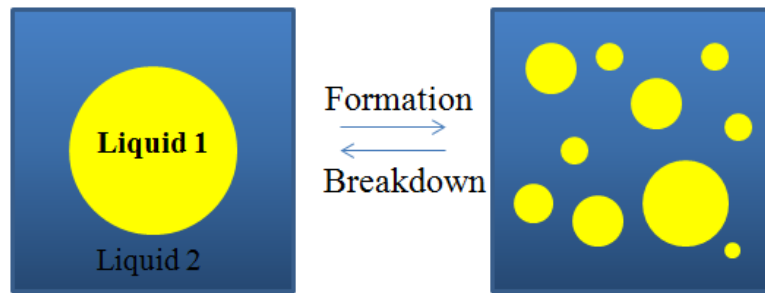


Figure 1.1: Schematic representation of emulsion formation and breakdown.

The free energy of emulsion formation is given by,

$$\Delta G_{form} = \Delta A\gamma_{12} - T\Delta S \quad (1)$$

Where, ΔA is the change in interfacial area, γ_{12} is interfacial tension, ΔS is change in entropy and T is the temperature of the system. In most cases, $\Delta A\gamma_{12} \gg T\Delta S$ i.e. ΔG_{form} is positive. So, in the absence of any stabilizing mechanism emulsions will become unstable. Surfactants and colloidal particles are often used to stabilize emulsions.

Figure 1.2 shows a schematic of surfactant molecule and a colloidal particle at oil-water interface. Surfactants are amphiphilic molecules and they have a natural

tendency to go to oil-water interface. They reduce the oil-water interfacial tension; thereby minimizes the energy required for emulsion formation. The adsorbed surfactant molecules at the interface act as electrostatic or steric barriers against droplet coalescence and increase the emulsion stability.² Hydrophilic to hydrophobic balance of the surfactant molecules dictate the nature of the emulsion (O/W or W/O) being formed.

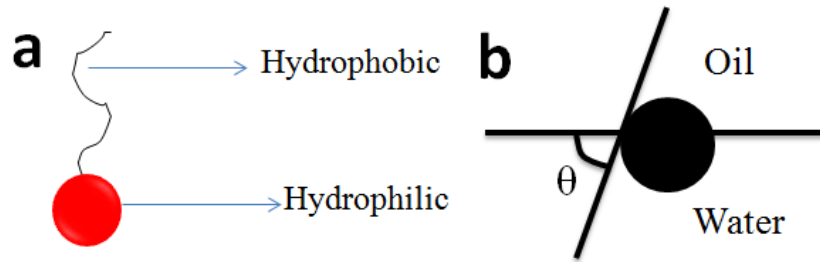


Figure 1.2: Schematic representation of (a) surfactant molecule (b) colloidal particle at oil-water interface.

Colloidal particles are not amphiphilic in nature but particles that are partially wettable in each of two immiscible phases will favor locating at the liquid-liquid interfaces.^{3, 4, 5} Unlike surfactants they do not reduce the oil-water interfacial tension, but strongly get adsorbed at the oil-water interface. However, adsorption of the particles on the oil-water interface is a slow process^{6, 7} and needs to be enhanced by mixing. The energy, ΔE required to remove a single spherical particle from an oil-water interface is given by

$$\Delta E = \pi r^2 \gamma_{O/W} (1 - |\cos \theta|)^2, \quad (2)$$

Where, r is the radius of the particle, $\gamma_{O/W}$ is the oil-water interfacial tension, and θ is the three-phase contact angle made by the particle at the oil-water interface. For a 10nm particle, and $\gamma_{O/W} = 50 \text{ mN/m}$, ΔE is $\sim 10^3 \text{ kT}$ for $35^\circ < \theta < 145^\circ$. Therefore, thermal

fluctuations will be insufficient to remove a particle from the interface if the contact angle is within this range. Once at the interfaces, these particles contribute to electrostatic, steric or rheological barriers against droplet coalescence and effectively stabilize emulsions.^{8, 9} Wettability of the particles dictates the nature of the emulsion (O/W or W/O) being formed.¹⁰

Recently there is lot of interest in using surfactants and colloidal particles together for emulsion formation. It is driven by a notion that surfactants decrease the oil-water interfacial tension hence lower the particle adoption energy at the interfaces^{11, 12} or they will modify the wettability¹⁰ of the particles and promote their adsorption at the interfaces. The synergy between particle and surfactant mixtures has been exploited to make particle-stabilized emulsions.^{13, 14, 15, 16} Surfactant-particle interactions can be tuned by varying the charge on the head group, the tail length and concentration of the amphiphile,^{12, 17, 18} with potentially useful consequences on emulsion behavior. The relative concentration of surfactant to particles and surfactant-particle interactions play major role in determining final composition of the oil-water interface^{19, 20} and the nature of the emulsion being formed. The Information on the stability of the individual emulsions in presence of other emulsifiers can give great insights in designing better emulsifiers.

Addition of surfactants to a particle-stabilized emulsion or addition of colloidal suspensions to a surfactant-stabilized emulsion are different class of experiments, as they allows the amphiphile to adsorb on the liquid-liquid interfaces as well as on the particles in a controlled way. Here, we studied the effect of addition of surfactant solutions to the stability of the particle-stabilized emulsions and the effect of addition

of fumed silica suspensions to the stability of the surfactant stabilized emulsions. We also looked the effect of particle shape on the formation and stability of Pickering emulsions. The interactions between the colloidal particles are carefully controlled and the subsequent effects on the emulsion formation and stability are studied. The combination of optical, confocal, and cryogenic scanning electron microscopy were used to determine the final stability and structure of the emulsions.

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CHAPTER 2

The Response of Carbon Black Stabilized Oil-in-Water Emulsions to the

Addition of Surfactant Solutions

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2.1 Abstract:

We use carboxyl-terminated, negatively charged, carbon black (CB) particles suspended in water to create CB-stabilized octane-in-water emulsions, and examine the consequences of adding aqueous anionic (SOS, SDS), cationic (OTAB, DTAB) and nonionic (Triton X-100) surfactant solutions to these emulsions. Depending upon the amphiphile's interaction with particles, interfacial activity and bulk concentration, some CB particles get displaced from the octane-water interfaces, and are replaced by surfactants. The emulsions remain stable through this exchange. Particles leave the octane-water interfaces by two distinct modes that depend on the nature of particle-surfactant interactions. Both happen over time scales of the order of seconds. For anionic and nonionic surfactants that bind to the CB through hydrophobic interactions, individual particles or small agglomerates stream away steadily from the interface. Cationic surfactants bind strongly to the carboxylate groups, reduce the magnitude of the surface potential, and cause the CB particles to agglomerate into easily visible chunks at the droplet interfaces. These chunks then leave the interfaces at discrete intervals, rather than in a steady stream. For the longer chain cationic surfactant, DTAB, the particle ejection mode reverts back to a steady stream as the concentration is increased beyond a threshold. This change from chunks of particles leaving intermittently to steady streaming is because of the formation of a surfactant bilayer on the particles that reverses the particle surface charge and makes them highly hydrophilic. The charge reversal also suppresses agglomeration. Zeta potentials of CB particles measured after exposure to surfactant solutions support this hypothesis. These results are the first systematic observations of different particle release modes

from oil-water interfaces produced by variations in interactions between surfactants and particles. They can be generalized to other particle-surfactant systems and exploited for materials synthesis.

2.2 Introduction:

The ability of surfactants to lower liquid-liquid interfacial tensions is a key property that makes them useful in the preparation of oil-in-water (O/W) or water-in-oil (W/O) emulsions. The hydrophilic-hydrophobic balance of the surfactant molecules dictates the nature (W/O or O/W) of the emulsions that are formed.^{2, 21} While observed first by Ramsden⁴ and Pickering³ over a century ago, particle-stabilized emulsions are another class of materials that are generating renewed interest. Unlike surfactants, particles do not have to be amphiphilic, or Janus-like, to locate at oil-water interfaces. Instead, a particle with partial wettability in both immiscible liquid phases can reside preferentially at oil-water interfaces. These interfacially active particles can stabilize emulsions. In addition, the potential to take advantage of the particle shape, size, surface characteristics, as well as other intrinsic properties allows particle-stabilized emulsions to have functionalities that are difficult to replicate using surfactants.²²

The energy required to displace a spherical particle from a liquid-liquid (designated as oil-water in our case) interface into one of the surrounding liquid phases is given by

$$\Delta E = \pi r^2 \gamma_{o/w} (1 - |\cos \theta|)^2, \quad (1)$$

where r is the radius of the particle, $\gamma_{o/w}$ is the oil-water interfacial tension and θ is the three phase contact angle measured through either the oil or water. For $r = 100\text{nm}$, $\gamma_{o/w} = 50\text{mN/m}$ and $\theta = 90^\circ$, Eq. (1) gives $\Delta E \sim 10^5 k_B T$. Therefore, once a partially wettable particle is at the interface, it cannot leave spontaneously. This is one of the

important distinguishing features of particle-stabilized emulsions, allowing, among other things, for them to remain stable even when the dispersed phase is at a very low volume fraction.

During the formation of a particle-stabilized emulsion, fresh oil-water interfaces must be covered with an adequate number of particles to stabilize the droplets within a time scale that is less than that for drop coalescence. Because breaching of particles into oil-water interfaces is slow⁷, this process needs to be enhanced by mixing. The particles can be charged, providing repulsive interactions between drops, they can provide steric barriers, and increased interfacial viscosity that suppresses thinning of the intervening liquid during approach of drops, thus resisting coalescence.^{5, 8, 9, 23}

In many practical situations it will be a combination of surfactants and particles that will provide the optimum characteristics for the emulsion, the surfactants often providing the low interfacial tension to facilitate drop formation, and the particles providing enhanced stability¹¹. The synergy between particle and surfactant mixtures has been exploited to make particle-stabilized emulsions.^{13, 14, 15, 16} Surfactant-particle interactions can be tuned by varying the charge on the head group, the tail length and concentration of the amphiphile,^{12, 17, 18} with potentially useful consequences on emulsion behavior.^{10, 24, 25, 26} The ability to tune particle surface characteristics using surfactants has been exploited for porous materials synthesis.^{27, 28} In all of these experiments, the particles were modified with surfactants prior to the formation of emulsions.

Addition of surfactants to a particle-stabilized emulsion is a different class of experiments, as it allows the amphiphile to adsorb on the liquid-liquid interfaces as

well as on the particles in a controlled way. Binkset *al.*¹³ studied the effect of the addition of non-ionic surfactant C12E7 on tricaprylin-in-water emulsions stabilized by surface modified silica particles, and observed a coalescence induced increase in emulsion droplet size after the addition of surfactant. Whitby²⁹ and coworkers¹⁹ studied the effect of addition of sodium dodecyl sulfate to dodecane-in-water emulsions stabilized by fumed silica particles. They observed the displacement of particles from the emulsion upon addition of surfactants, and attributed it to a drop in the oil-water interfacial tension upon addition of surfactant, as well as the applied shear during mixing.

The key distinguishing features of the work reported here are comprehensive sets of experiments that utilize optical microscopy to carefully monitor changes to a charged particle-stabilized emulsion upon addition of surfactants that interact with the particles either through hydrophobic or ion binding. We examine final states and transients, and support our observations using a simplified thermodynamic analysis, as well as zeta potential measurements and confocal microscopy. Our analysis and experiments suggest modes for particle displacement from these interfaces that have not been observed previously.

In order to establish the framework for our observations, we analyze two cases shown in Figure 2.1, and determine the free energy difference between a surfactant- and particle-stabilized emulsion drop, $\Delta E_{\text{surf}} - \Delta E_{\text{part}}$. If this quantity is positive, a surfactant stabilized emulsion would be more stable than a particle stabilized one. Therefore, from energetic considerations, addition of surfactants would cause particles to be displaced from interfaces as the system seeks a lower energy state.

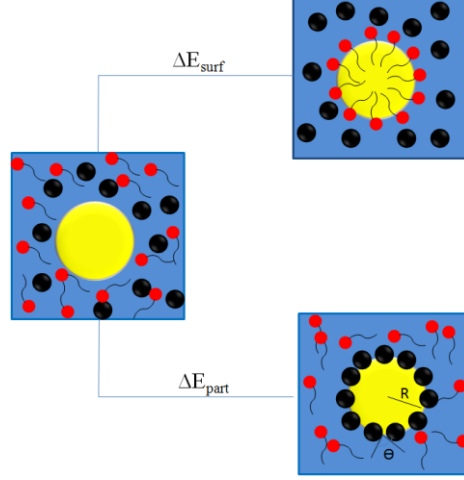


Figure 2.1: The basis for calculation of the free energy difference (we ignore entropic effects) between a surfactant- and a particle-stabilized emulsion. The ground state is an oil droplet with particles and surfactants in the aqueous phase. ΔE_{surf} is the energy difference between the ground state and a state where only surfactants are at the oil-water interface. ΔE_{part} is the energy difference between the ground state and a state where only particles are at the oil-water interface. The sign of $\Delta E_{\text{surf}} - \Delta E_{\text{part}}$ is the energy difference between a surfactant- and a particle-stabilized drop. R is the radius of the drop and θ is the contact angle measured through the aqueous phase.

For this simplified analysis, we assume no interactions between particles and surfactants, and ignore entropic contributions. Under these conditions,

$$\Delta E_{\text{surf}} = -4\pi R^2(\gamma_{o/w} - \gamma_{\text{surf}}), \quad (2)$$

$$\Delta E_{\text{part}} = -n \pi r^2 \gamma_{o/w} (1 - |\cos \theta|)^2. \quad (3)$$

Here R is the drop radius, r the particle radius (particles are assumed to be spheres in this analysis), $\gamma_{o/w}$ is the interfacial tension of the bare oil/water interface, γ_{surf} is the interfacial tension of the surfactant-laden oil water interface, and n is the number of particles at the interface. If the area fraction of the interface covered by particles is ϕ , and assuming $R \gg r$,

$$n \sim 4 \phi R^2 / (r \sin \theta)^2. \quad (4)$$

Substituting Eq.(4) into the expression for ΔE_{part} gives the condition

$$\frac{\gamma_{o/w} - \gamma_{surf}}{\gamma_{o/w}} \Rightarrow \phi \left[\frac{(1 - |\cos\theta|)}{\sin\theta} \right]^2 \quad (5)$$

for a surfactant-stabilized drop to have a lower free energy than a particle-stabilized one. For $\theta = 90^\circ$, this criterion simplifies to

$$(\gamma_{o/w} - \gamma_{surf}) / \gamma_{o/w} > \phi, \quad (6)$$

that is, the fractional change in oil-water interfacial tension upon addition of surfactant must be greater than the fractional surface coverage of the interface by particles.

Therefore, addition of a surfactant to a particle-stabilized emulsion can cause particles at an oil-water interface to get displaced if the inequality in Eq.(5) or Eq.(6) is satisfied.

Eqs. (1), (5) and (6) will need to be modified if the particles are not spherical, or the surfactant adsorbs on particles spontaneously in addition to occupying the oil-water interfaces. For fractal particles, as is the case in our experiments as well as those done with fumed silica, the cusps on the particles cause them to get pinned at the liquid-liquid interfaces.^{23, 30, 31} Thus, for an equivalent size, the energy barrier for a fractal particle to leave the interface will be greater than that for a spherical particle given by Eq. (1). If the surfactant interacts with the particles and adsorbs on them spontaneously, this exothermic process will cause the free energy change to be greater than ΔE_{surf} , and the displacement of particles will be energetically more favorable than the case with no particle-surfactant interactions. In addition, this adsorption could change the contact angle θ , with concomitant consequences that can be understood using Eq.(5).

When a surfactant solution is added to a particle-stabilized emulsion, the response will therefore depend upon the ability of surfactant molecules to lower the interfacial

tension, as well as the interactions between the particles and surfactants. Local variations in oil-water interfacial tension, and the Marangoni forces that result, can also aid the displacement of particles from the interfaces. We do not quantify this phenomenon. We also note that it is likely that after addition of surfactants to a particle-stabilized emulsion, the final sample has both particles as well as surfactants at the oil-water interfaces.

In this work, we report the behavior of carboxyl-terminated carbon black-stabilized octane-in-water emulsions after addition of anionic (sodium octyl sulfate, SOS, and sodium dodecyl sulfate, SDS), nonionic (Triton X-100) and cationic (octyltrimethyl ammonium bromide, OTAB, dodecyl trimethyl ammonium bromide, DTAB) surfactant solutions at different concentrations. The carbon black particles are negatively charged at neutral pH, and are hydrophilic. Lowering the pH of the aqueous dispersion protonates some of the surface carboxylate groups, reduces the magnitude of the surface charge (although it is still negative), and makes the particles partially hydrophobic. This hydrophilic/hydrophobic characteristic is required for the particles to stabilize an emulsion. The anionic and nonionic surfactants interact with the negatively charged particles through hydrophobic binding of the surfactant tails to carbon, while the cationic surfactants adsorb strongly through ionic interactions. We examine the base (no surfactant) emulsion, and the sample after each of the surfactant solutions has been in contact with the base emulsion for 24 h., and observe that the emulsion does not destabilize through particle-surfactant exchange. We carefully monitor the transients in the initial stages of evolution of the emulsion, and show qualitative differences in the modes by which the particles leave the interface that

depend on the extent of particle-surfactant interactions and the activity of the surfactant.

2.3 Materials:

SOS (97%) was purchased from Fisher Scientific. SDS (98%), OTAB (98%) and DTAB(98%) were purchased from Sigma Aldrich. These surfactants were chosen to have matching 8- and 12-carbon tail lengths, allowing us to compare charge and hydrocarbon tail length effects. Triton X-100 was obtained from Alfa Aesar. All surfactants were used as received. A 15wt% carbon black(CB) particle suspension, at pH-7.5, was provided by Cabot Corporation. The CB particles in this suspension are carboxyl terminated because of the covalent linkage of para amino benzoic acid (PABA) to carbon. The PABA treatment level has been reported to be between 0.1 – 4.0 $\mu\text{mole}/\text{m}^2$.³² The particles have a fractal morphology with a nominal size of ~120nm, and a BET (nitrogen adsorption) specific surface area of ~200m²/gm. The aqueous CB suspension contains no surfactants. Octane (99%) was purchased from Acros Organics. Hydrochloric acid(HCl, 37wt%) was obtained from Sigma Aldrich. The surfactant solutions were prepared with water obtained from a Millipore Milli Q system.

2.4 Sample preparation

A 0.015wt% CB dispersion was used to prepare the emulsions. The zeta potential of the carbon black particles was measured to be -61.3mV. The pH of the carbon black dispersion was adjusted to 3.2 with HCl to protonate some of the surface carboxylate groups, thus rendering the particles partially hydrophobic. The particle zeta potential at this pH is -10.2mV. The viscosity of the suspension increases significantly because

these partially hydrophobic particles form a network in the aqueous medium. To form the 'base' emulsion, 0.2ml of octane were added to 2ml of the CB particle dispersion and vortexed at 3000 rpm for 2 min.

The CB-stabilized emulsions were diluted with a volume of surfactant solution equal to the volume of the aqueous phase in the emulsion. The suspensions were then mixed very gently to avoid foaming or create any new oil-water interfaces. The concentrations of the surfactant solutions, also at pH-3.2, were varied between 0.1mM to just above the critical micelle concentrations (CMC) for the anionic (SDS, CMC=8.2mM²; SOS, CMC=130mM²¹) and cationic(DTAB, CMC=15.2mM²;OTAB, CMC=140mM²) surfactants. The nonionic surfactant concentration was varied between 0.01mM to 1mM (Triton X-100, CMC =~0.4mM³³). After addition of surfactant solutions, the emulsions were left at 25°C for 24h. before being observed using bright field optical microscopy on a Nikon Eclipse TE2000 inverted microscope. The images were analyzed using Image Tool 3.0® to obtain emulsion drop sizes. All samples were prepared in a 20ml vial.

The consequence of surfactant addition to the emulsion was monitored in real time using an inverted optical microscope. In these experiments, 20µl of the emulsion were confined between glass slides. 5µl of a surfactant solution, immobilized at the end of a pipette, were placed at the edge between the slides (Figure 2.2).

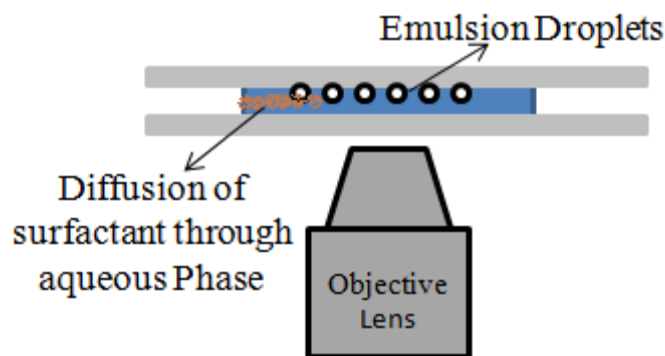


Figure 2.2: Schematic representing the experiment to observe the transients in the system after the addition of surfactant. A small sample of the CB stabilized emulsion is sandwiched between two glass slides placed on an inverted microscope. The surfactant solution is added to the edge of this sandwich. The surfactant diffuses to the emulsion drops, and the response is observed.

The surfactant diffused to the drops, and the response was observed. To provide more direct confirmation of the presence of particles at the drop interfaces, we did confocal fluorescence microscopy (Zeiss LSM 700) using Rhodamine B labeled CB particles. Pendant drop experiments were done using a KRÜSS Easy Drop FM 40 goniometer to obtain the octane-water interfacial tensions in the presence of different surfactants. Insight into adsorption of surfactants on the particles and the consequences of this on the behavior of the emulsions was obtained by monitoring the zeta potential of the carbon black particles in water at different concentrations of added surfactants. The zeta potentials were measured using a Malvern Zetasizer Nano-ZS instrument.

2.5 Results and discussion

Figure 2.3 shows an optical micrograph of an octane-in-water(9% v/v octane) emulsion prepared by vortexing octane and the carbon black dispersion. The preparation method results in polydispersed drops of size $101 \pm 46 \mu\text{m}$. The emulsion remained stable for at least 6 months with no measureable change in drop size distribution. This emulsion

sits on top of a clear transparent aqueous phase that contains little or no CB particles, as shown in the inset. At the concentrations used in our experiments there were enough particles to fully cover all octane-water interfaces in this base emulsion³⁴.

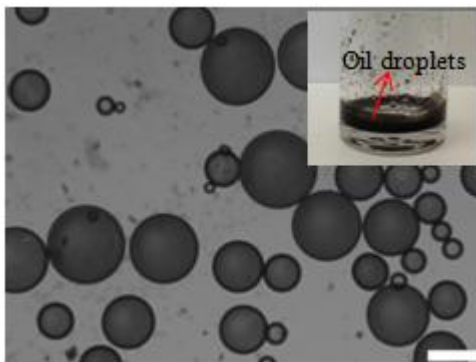


Figure 2.3: Optical micrograph of an octane-in-water CB stabilized emulsion imaged after 24 h. after formation. Oil droplets are in equilibrium with clear aqueous phase, shown in the inset. The average drop size is $101 \pm 46\mu\text{m}$. Scale bar = $100\mu\text{m}$.

To establish a potential end point for samples after addition of surfactants, we successfully prepared stable octane-in-water emulsions using SDS, Triton X-100 and DTAB at their respective CMC concentrations. We were unable to create stable emulsions with SOS and with OTAB because of the low surface activity of these short chain surfactants.

2.5.1 Effect of surfactants on CB-stabilized emulsions:

For SOS, a threshold concentration of $\sim 10\text{mM}$ had to be exceeded before we noticed any impact. At concentrations just above the threshold, addition of SOS shows no obvious changes (Figure 2.4(a)) to the emulsion images, but as shown in the inset, we observe a slight darkening of the aqueous phase indicating release of CB particles. As the concentration of SOS is increased further, the aqueous phase becomes distinctly darker and the droplet interfaces becomes lighter (Figure 2.4(b)), indicating additional displacement of particles from the oil-water interfaces. A sample vial under these

conditions is shown in the inset. The displaced particles remain stably suspended in the aqueous phase.

The octane-water interfacial tension is 16.8mN/m at the CMC for SOS, giving a maximum fractional change in interfacial tension of 0.67. We suggest that this reduction in interfacial tension is not sufficient to displace particles from the nearly fully particle-covered interface. The loss of particles is related to their increased hydrophilicity arising from surfactant adsorption through hydrophobic interaction of the surfactant tails with the CB. Binding of the surfactant to the CB particles through hydrophobic interactions increases the charge and the hydrophilicity of the particles, rendering them stable in the aqueous phase.

In contrast to SOS, addition of SDS even at low concentrations causes a much greater darkening of the aqueous phase, and the resulting drops appear lighter indicating greater loss of CB particles(Figures 2.4(c) and 2.4(d)) from the octane-water interfaces. For 0.5mM SDS, the detached particles accumulate at the bottom of the aqueous phase, but remain freely suspended in the aqueous phase when the concentration is increased to 5mM, as shown in the insets. At the lower SDS concentration only a small amount of surfactant is available for adsorption. Particle displacement is favored by a lowering of the interfacial tension, and the detached particles are hydrophobic enough to aggregate in the aqueous phase. The octane-water interfacial tension is 51.2 mN/m,³⁵ reducing to ~8mN/m at the CMC for SDS,³⁶ giving a maximum fractional change in interfacial tension of ~ 0.84. This drop in interfacial tension combined with the increase in hydrophilicity of particles due to surfactant

adsorption is responsible for CB displacement at the higher surfactant concentration.

At these concentrations,

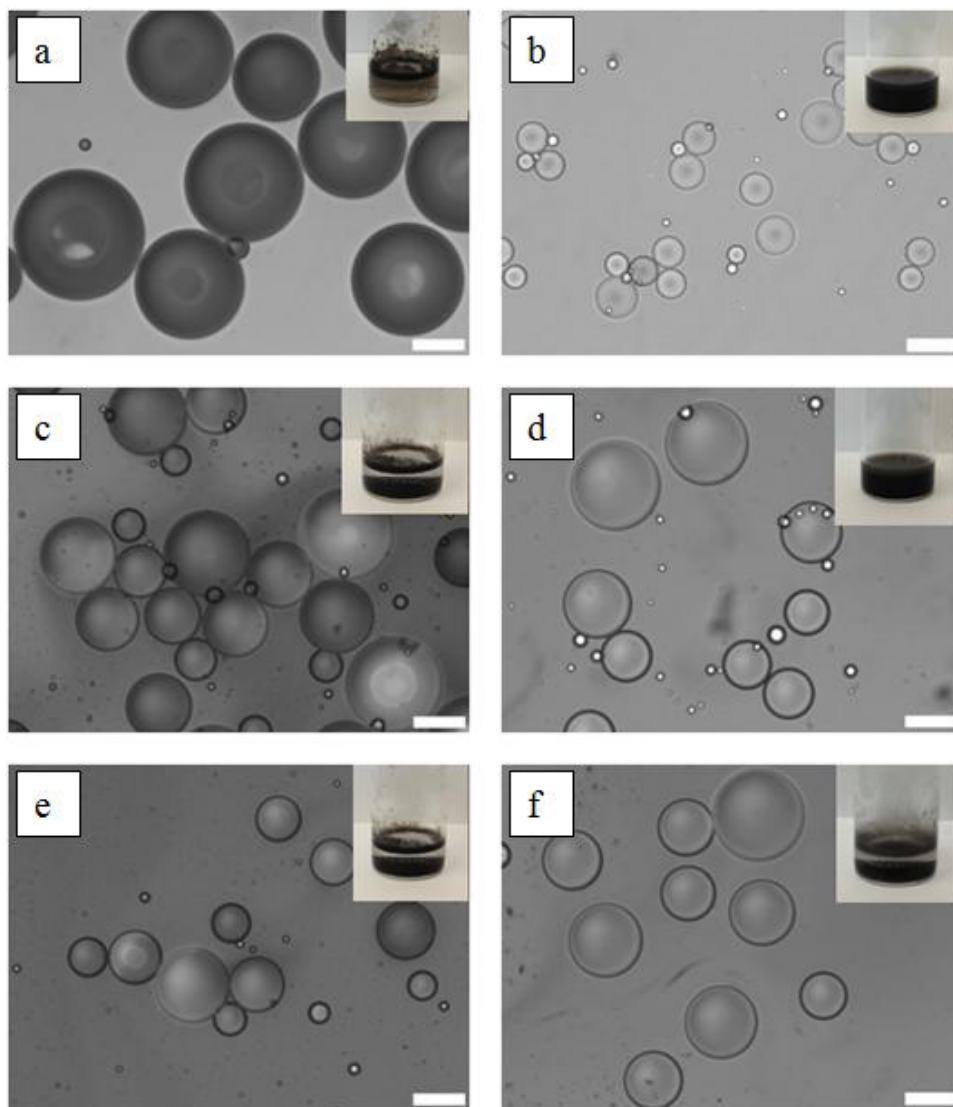


Figure 2.4: Optical micrographs of octane-in-water emulsions stabilized by carbon black particles diluted with anionic and non-ionic surfactants. Surfactant concentrations are (a) 10mM SOS; the inset shows the slightly darkened aqueous phase due to particle displacement from the drop surfaces (b) 100mM SOS; the inset shows the distinctly darkened aqueous phase – the displaced CB particles remain stably suspended in the aqueous phase.(c) 0.5mM SDS; the inset shows the aggregated CB particles at the bottom of the vial (d) 5mM SDS; the inset shows the distinctly darkened aqueous phase due to the suspended CB particles displaced from the droplet interfaces (e) 0.2mM Triton X-100; inset shows the aggregated CB particle at the bottom of the vial (f) 0.5mM Triton X-100;the inset shows the aggregated CB particle at the bottom of the vial. Scale bars= 100 μ m.

amphiphile adsorption on particles is greater, the displaced particles are more hydrophilic and they remain stably suspended in the aqueous phase. The inset in Figure 2.4(d) shows a vial at these conditions. The emulsion phase remains intact in the vial through this exchange, and there is no significant change in the average droplet size.

Figures 2.4(e) and 2.4(f) shows images of the emulsion droplets after the addition of two concentrations of Triton X-100. As is the case for the anionic surfactants, particles get displaced from the oil-water interfaces. However, for both concentrations, the CB particles aggregate and settle at the bottom of the aqueous phase in the vials, as shown in the insets. The octane-water interfacial tension decreases to about $\sim 3\text{mN/m}$ ³³ at the CMC for Triton X-100 giving a fractional change in interfacial tension 0.94. From our simple energy analysis, it appears as though this drop on interfacial tension is enough to displace particles from the octane-water interfaces. Non-ionic surfactants can adsorb on the CB particles through hydrophobic interactions². The settling of the displaced CB particles to the bottom of the aqueous phase in the vial suggests that the adsorbed surfactant layer does not provide sufficient steric stabilization to keep the CB particles from aggregating³⁷, and that charge interactions are important for keeping the particles stably suspended.

We examined the transient response of the emulsion to the addition of these surfactants and show results in Figure 2.5. For the anionic surfactants, particles are ejected in a steady stream from different regions of the droplet interfaces as soon as the surfactant is introduced into the system, shown in Figures 2.5(a) and 2.5(b). A

similar behavior is observed when Triton X-100 is introduced into the emulsion, as shown in Figure 2.5(c). The steady streaming of CB particles away from the octane-water interfaces is a result of hydrophobic binding of surfactants to the particles with little change in surface charge, as well as a lowering of the octane-water interfacial tension.

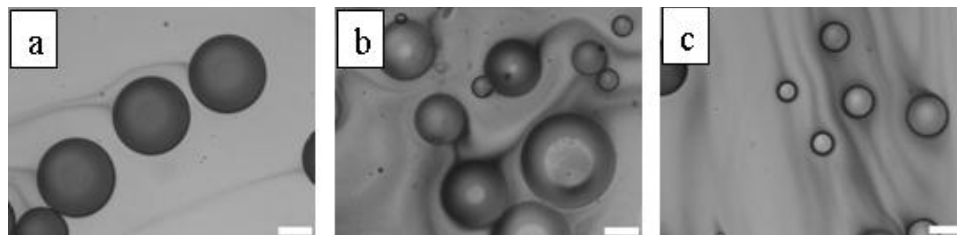


Figure 2.5: Images showing particle displacement from CB stabilized octane drops in water when exposed to anionic and non-ionic surfactants. In all cases, the particles leave the interface in steady streams of single particles or very small agglomerates. Surfactant concentrations are (a) 20mM SOS (b) 10mM SDS (c) 1mM Triton X-100. Scale bars =100 μ m.

Figure 2.6, shows images of the CB stabilized emulsions exposed to cationic surfactant solutions. For OTAB, no change is observed to the drops or in the aqueous phase up to a threshold concentration of 50mM (Figure 2.6(a) is taken at 20mM OTAB). As the concentration goes beyond this value, the aqueous phase darkens, indicating that some particles leave the interface. The sample at 150mM OTAB is shown in Figure 2.6(b). The detached particles accumulate at the bottom of the aqueous phase in the vials shown in the inset. For DTAB, we do not observe any change to the emulsion up to 2mM surfactant concentration (Figure 2.6(c)). With a further increase in the surfactant concentration, the aqueous phase becomes dark and clusters of particles are visible on the droplet interfaces, shown in Figure 2.6(d). Interestingly, we captured a drop-drop coalescence event in this system, as shown in

Figure 2.6(e). We also observed an increase in average drop size from $\sim 100\mu\text{m}$ to $\sim 141\mu\text{m}$ at these intermediate surfactant concentrations because of drop coalescence.

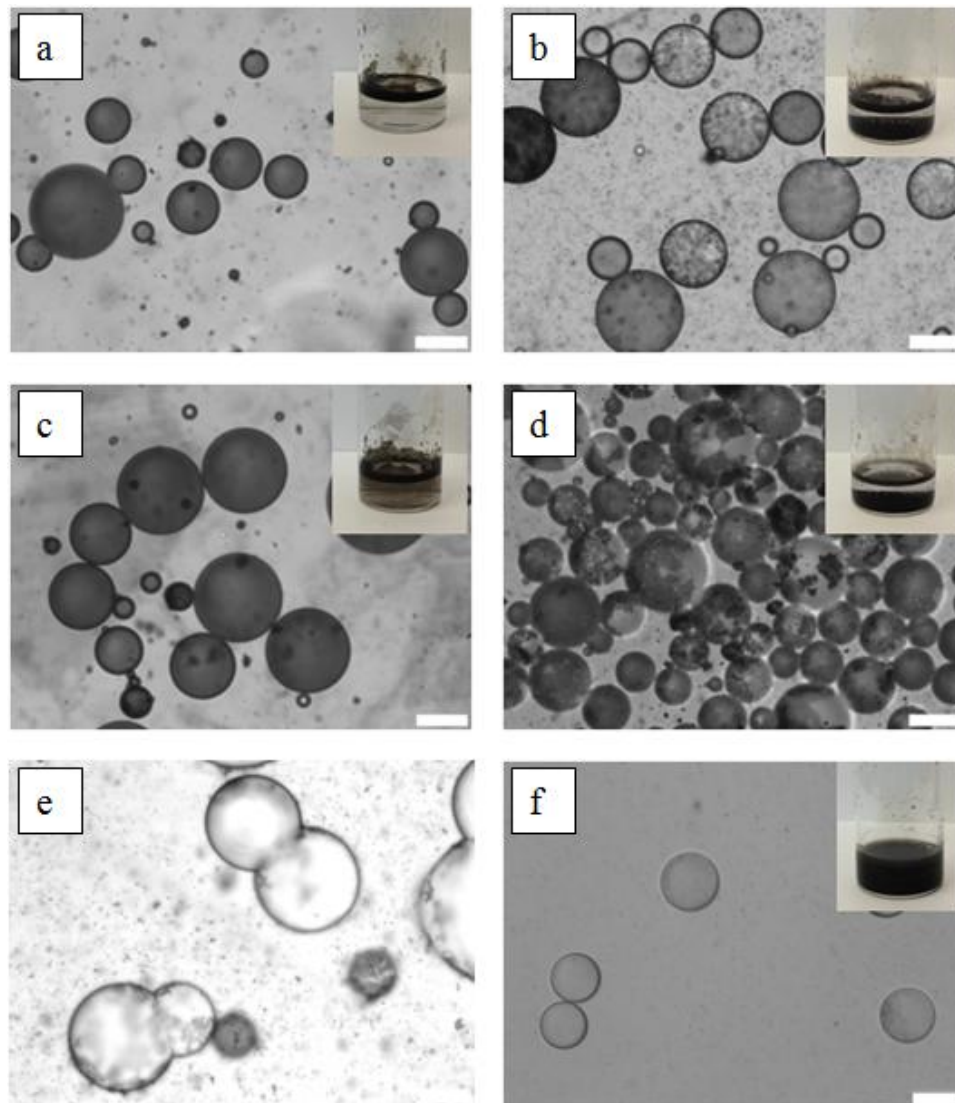


Figure 2.6: Images of octane-in-water emulsions stabilized by carbon black particles after addition of cationic surfactant solutions. Surfactant concentrations are (a) 20mM OTAB; the inset shows a clear aqueous phase after the addition of surfactants, indicating minimal displacement of particles from the droplets (b) 150mM OTAB; the inset shows aggregated particles at the bottom of the vial (c) 1mM DTAB; the inset shows a clear aqueous phase after the addition of surfactant (d) 5mM DTAB; the inset shows aggregated particles at the bottom of the vial (e) Drop-drop coalescence event observed after addition of 5mM DTAB (f) 10mM DTAB; inset showing the distinctly darkened aqueous phase due to the suspended CB particles displaced from the droplet interfaces. Scale bars = $100\mu\text{m}$.

The detached particles accumulate at the bottom of the aqueous phase in the vial, as shown in the inset. When the concentration of DTAB approaches the CMC, we do not see any particle clusters on the droplet interfaces, but the CB particles get displaced from the emulsion droplets and remain dispersed in the aqueous phase. An image of these emulsion drops is shown in Figure 2.6(f) with the inset showing a darkening of the aqueous phase caused by displacement of the particles from the drops to the continuous phase.

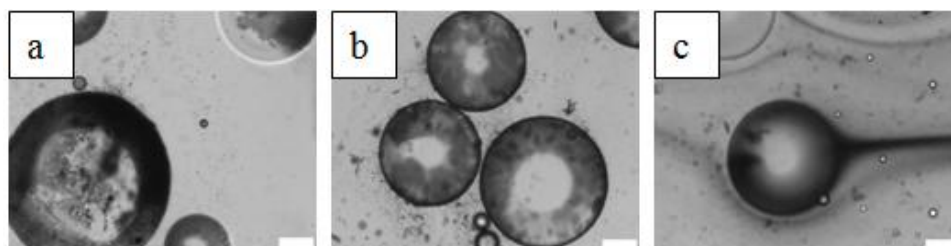


Figure 2.7: Images of particle-stabilized emulsions after addition of cationic surfactant solutions. (a) 150mM OTAB; clusters of CB particles form, and get displaced intermittently from drop interfaces (b) 5mM DTAB; clusters of CB particles get displaced from drop interfaces (c) 10mM DTAB; steady streams of CB particles get displaced from drop interfaces. Scale bars = 100 μ m.

The transient experiments reveal that particle ejection from the droplet interface is complex when these cationic surfactants are added to the CB-stabilized emulsion. For OTAB, clusters of CB particles get ejected out of the droplet interfaces, as shown in Figure 2.7(a). While not apparent from the figure, the particle aggregates are released intermittently from the oil drop surfaces. For DTAB, a similar intermittent removal of clusters is observed up to a threshold concentration (Figure 2.7(b)). As the concentration of surfactant is increased further and approaches the CMC, particle clusters are no longer formed, and particles are ejected as a steady stream from many locations on the drops, shown in Figure 2.7(c).

We invoke surfactant adsorption on to particles by ionic interactions. The octane-water interfacial tensions are 8.42mN/m and 21.36 at the CMC for DTAB and OTAB. The fractional change in interfacial tensions are 0.83 and 0.58. These changes appear small enough that the lowering of interfacial tension is an unlikely cause of particles leaving the interfaces. For OTAB, particles aggregate into clusters over the full concentration range studied, and leave the interface in that form. Bilayers are not favored because of the small hydrophobic chain length³⁵. Similarly, for DTAB, surfactant binding makes the particles hydrophobic at low surfactant concentration³⁶, and they are not released into the aqueous phase. The reduced particle surface potential also leads to particle aggregation on the oil droplet interface. With increasing surfactant concentration the CB particles start to become hydrophilic within complete bilayer formation, and the particles get ejected as small clusters from the droplet interfaces. The energy of detachment of a particle from the interface scales as the square of its size. The irregular morphology of these large agglomerates also causes them to be pinned strongly at the interfaces. The particle release kinetics is therefore much slower, and the clusters leave from the oil droplet at irregular intervals. The coalescence of emulsion droplets when a DTAB solution is added is a consequence of reduced electrostatic repulsion between drops because of particle charge neutralization and detachment. When the surfactant concentration is increased further, the CB particles becomes very hydrophilic because of complete bilayer formation at the particle surfaces.¹ The particles then assume a positive charge, and this repulsive interaction suppresses interparticle aggregation. The increased hydrophilicity promotes the displacement of particles into the aqueous phase. We note that our

results are similar to those obtained by Subramanian *et al.*,^{37,38} who observed polystyrene particles getting ejected as singlets and small agglomerates from air-water interfaces when particle stabilized foams were exposed to different surfactants.

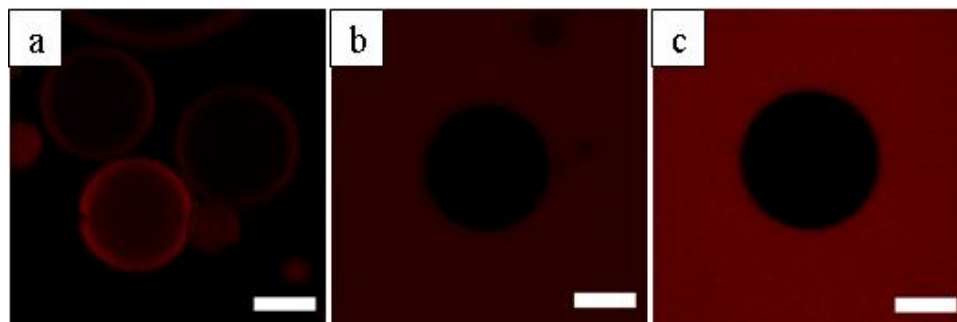


Figure 2.8. Confocal fluorescence microscope images of emulsion droplets (a) CB stabilized emulsion droplets labeled with 2 μ M Rhodamine-B (b) Emulsion droplet after the exposure to 10mM SDS (c) Emulsion droplet after exposure to 20mM DTAB. The loss of a fluorescence signal around the drops in (b) and (c) and the fluorescence increase of the aqueous phase confirm the transfer of particles from the interface to the bulk aqueous phase. Scale bars=50 μ m.

In order to confirm the presence of particles at the oil-water interfaces, we labeled the CB by exposing the aqueous suspension to 2 μ M of rhodamine B, and used confocal fluorescence microscopy to image the drops. Figure 2.8(a) shows the surfactant-free CB-stabilized emulsion. The bright ring around the drops and the lack of signal from the continuous phase indicate that the particles are at the interfaces. Figures 2.8(b) and 2.8(c) show the emulsion droplets after exposure to 10mM SDS and 20mM DTAB solutions respectively. The absence of the bright ring around the emulsion drop and the increased fluorescence in the aqueous phase is indicative of particles being displaced by surfactants.

2.5.2 Zeta potential measurements:

We support these observations and explanations by monitoring the zeta potentials of carbon black particles in presence of anionic and cationic surfactants at pH 3.2. The results are shown in Figure 2.9.

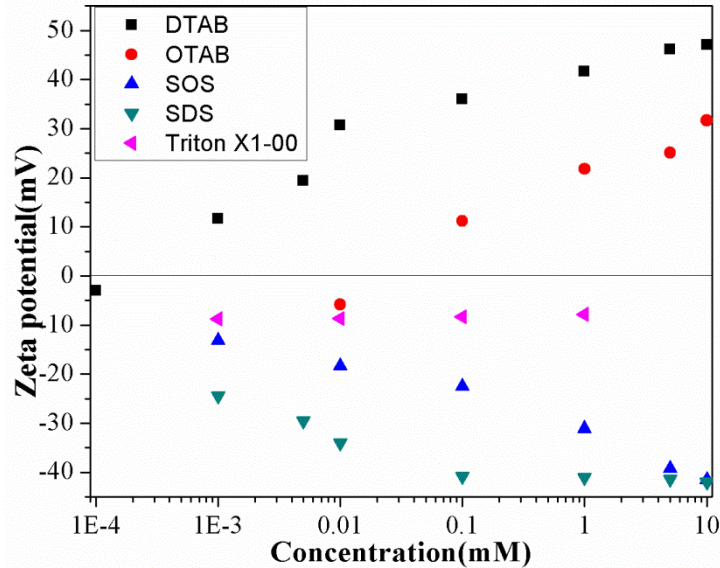


Figure 2.9: Zeta potentials of 0.0075 wt% CB particles after exposure to different surfactant solutions at pH3.2.

The zeta potential of the CB particles becomes more negative as the concentration of the anionic surfactants increases because of the hydrophobic binding of the surfactant to the CB particles. The decrease in zeta potential with increase in surfactant concentration suggests that counterion binding is not significant. For OTAB and DTAB the zeta potential of the CB particles becomes more positive as the concentrations of the surfactant increase. We note that the greater the magnitude of zeta potential the more hydrophilic the particles are, and the easier they will get displaced from the drop interfaces into the continuous aqueous phase. As expected, we do not observe any change in the zeta potential of CB particle with an increase in Triton X-100 concentration.

Figure 2.10 shows images of the particle dispersions in water in the presence of different surfactants. If there is no surfactant present in the solution, the CB particles tend to aggregate at the bottom of the vial leaving a clear aqueous phase at pH-3.2.

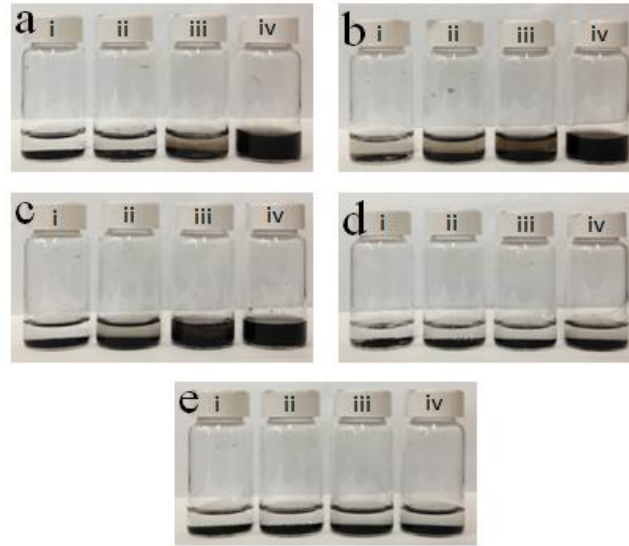


Figure 2.10: Stability of the 0.0075wt% aqueous CB particle dispersions in the presence of different surfactants at pH3.2 (a)SOS(i) 0.1mM,(ii) 1mM (iii) 10mM (iv)100mM; the aqueous becomes increasingly darker with an increase in surfactant concentration. (b)SDS(i) 0.01mM(ii) 0.1 mM (iii) 1mM (iv)5mM; the aqueous becomes increasingly darker with increase in surfactant concentration. (c) DTAB(i) 0.1mM(ii) 1 mM (iii) 10mM (iv)20mM; the aqueous becomes increasingly darker with increase in surfactant concentration.(d) OTAB(i) 0.1mM,(ii) 1 mM (iii) 10mM (iv)100mM; the CB particles agglomerate at the bottom of vial leaving a clear aqueous phase. (e) Triton X-100 (i) 0.01mM,(ii) 0.1 mM (iii) 0.5mM (iv) 1mM; the CB particles agglomerate at the bottom of vial leaving a clear aqueous phase.

When SOS, SDS and DTAB concentrations are increased the aqueous phase becomes increasingly darker, suggesting that the surfactant is adsorbing on the particles and keeping them stably suspended. For OTAB the CB particles go to the bottom of the vial at all surfactant concentrations, suggesting that the particles are not hydrophilic enough to stay suspended in the aqueous phase. Finally, for Triton X-100, the CB particles go to the bottom of the vial at all the surfactant concentrations, suggesting that the adsorbed surfactant molecules do not produce adequate steric stabilization to

keep the particles suspended. These experiments in conjunction with the zeta potential measurements provide evidence of different levels of particle-surfactant interactions and their consequence on particle ejection from octane-water interfaces.

2.6 Conclusions:

We studied the effect of addition different surfactant solutions on CB-stabilized oil-in-water emulsions. We show conditions for which the displacement of particle from the oil droplet interfaces is thermodynamically favorable. The details of particle ejection are complex, and are strongly influenced by particle-surfactant interactions, the surface activity as well as the concentration of the surfactant. For anionic and non-ionic surfactants, which interact with CB through hydrophobic binding, the particles are released in steady streams from the oil droplet interfaces. Cationic surfactants cause CB particle clustering. Clusters of particles then get released intermittently from the interfaces. When the cationic surfactant concentration is increased further, the mechanisms of particle release changes to a steady stream of particles because of bilayer formation on the particles. The interfacial properties of surfactant molecules and the change in wettability of particles in the presence of surfactants play a major role on particle desorption from the oil-water interfaces.

2.7 Acknowledgements:

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CHAPTER 3

The Response of Surfactant Stabilized Oil-in Water Emulsions to the Addition of Particles in an Aqueous Suspension

In review in *Langmuir*

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3.1 Abstract:

As a model for understanding how surfactant-stabilized emulsions respond to the addition of interacting and non-interacting particles, we investigated the response of dodecane-in-water emulsions stabilized by SDS(anionic), CTAB(cationic) and Triton X-100(non-ionic) surfactants to the addition of an aqueous suspension of negatively charged fumed silica particles. The stability of the emulsion droplets and the concentration of surfactants/particles at the oil-water interfaces are sensitive to surfactant-particle interactions, mixing conditions and the particle concentration in the bulk. Addition of the particle suspension to the SDS-stabilized emulsions showed no effect on emulsion stability. The emulsion droplets coalesce when fumed silica particles were added to emulsions stabilized by Triton X-100. Depending on the concentration of silica particles in the suspension, the addition of fumed silica particles to CTAB-stabilized emulsions resulted in droplet coalescence and phase separation of oil and water, or formation of particle-coated droplets. Vigorous (vortex) mixing allows the particles to breach the oil-water interfaces, and the particles help stabilize emulsions. While we have examined a specific particle suspension and a set of three surfactants, these observations can be generalized for other surfactant-particle mixtures.

3.2 Introduction:

Surfactants minimize the energy required for the emulsion formation by reducing the oil-water interfacial tension, and they hinder the coalescence of the dispersed phase by forming electrostatic or steric barriers around droplet surfaces. The hydrophilic to hydrophobic balance of the surfactant molecule dictates whether an oil-in-water(O/W)

or water-in-oil(W/O) emulsion is formed.¹ Colloidal particles that are partially wettable in each of two immiscible phases will favor locating at the liquid-liquid interfaces.^{2, 3, 4} The energy, ΔE required to remove a single spherical particle from an oil-water interface is given by

$$\Delta E = \pi r^2 \gamma_{o/w} (1 - |\cos \theta|)^2, \quad (1)$$

where r is the radius of the particle, $\gamma_{o/w}$ is the oil-water interfacial tension, and θ is the three-phase contact angle made by the particle at the oil-water interface. For a 10nm particle, and $\gamma_{o/w} = 50\text{mN/m}$, ΔE is $\sim 10^3 kT$ for $35^\circ < \theta < 145^\circ$. Therefore, thermal fluctuations will be insufficient to remove a particle from the interface if the contact angle is within this range. Once at the interfaces, these particles contribute to electrostatic, steric or rheological barriers against droplet coalescence and effectively stabilize emulsions.^{5, 6, 7}

Interactions between surfactants and particles have been exploited for the formation of stable emulsions.^{8, 9, 10} Surfactants decrease the oil-water interfacial tension allowing more interfaces to be created during mixing,^{11, 12} or they interact with particles, modify their wettability^{13, 14} and affect their adsorption energy at the interfaces (Eq. 1). In emulsions made with both surfactants and particles, the surfactant to particle ratio and surfactant-particle interactions play a major role in determining the final balance of particles and surfactants at the oil-water interfaces,^{15, 16} as well as the type of emulsion that is formed.^{17, 18}

The addition of surfactants to particle-stabilized emulsions can result in desorption of particles from oil-water interfaces.^{15, 19} The extent of desorption is influenced by the charge on the particles, and the ionic nature and concentration of

surfactant. For the converse case, addition of charged colloidal particles to surfactant-stabilized emulsions may result in desorption of surfactant from the oil-water interfaces or adsorption of particles on those interfaces. Each of these scenarios can affect the stability of the emulsion.

Surfactant-stabilized emulsions have been used previously as templates to form particle-coated droplets.^{20,21} Binks et al.²² observed coalescence of nonionic-surfactant stabilized emulsions after the addition of fumed silica particles. Surfactant adsorption on the particle surfaces reduced the concentration of amphiphiles at the oil-water interfaces, which resulted in coalescence of the emulsion droplets.

The presence of surfactant molecules on the interface can create barriers for particle adsorption on those interfaces. The magnitude of these barriers can be estimated using DLVO theory. For repulsive electrostatic interactions between the surfactant and the particles, the magnitude of these adsorption barriers vary between $\sim 10^{-11}$ - 10^{-9} N, depending on the size of the particles and the charges on the oil-water interface and on the particles.²³ The force exerted on a 100nm colloidal particles due to Brownian motion is of the order of $\sim 10^{-14}$ N,²⁴ insufficient to spontaneously overcome this repulsive barrier. During vigorous (e.g. vortex mixing) mixing, the force on the particles varies between 10^{-11} - 10^{-8} N,²³ thus allowing particles to breach the oil-water interfaces.

In this work, we investigate the consequence of controlled addition of an aqueous suspension of particles to surfactant-stabilized emulsions. The addition of the suspension is followed either by gentle shaking or by more vigorous (vortex) mixing. In accordance with our estimates of forces, we show that mixing conditions can make

a difference to the final state of the emulsions. We chose anionic, cationic, and non-ionic surfactants, and used negatively charged fumed silica in an aqueous suspension. The changes to the emulsion are monitored visually, and by a range of techniques including optical, confocal, and cryogenic scanning electron microscopy. We identified four different end states for emulsion droplets that depend on surfactant-particle interactions, particle concentrations and mixing conditions. These results are generic and can apply to other systems with similar particle-surfactant interactions.

3.3 Materials:

Sodium dodecyl sulphate (SDS, 99%, CMC = 8.2mM) and Cetyltrimethylammonium bromide (CTAB, 99%, CMC = 0.89mM) were purchased from Sigma-Aldrich. Triton X-100 (98%, CMC = 0.2-0.3mM) was purchased from Alfa Aesar. Dodecane (99%), Rhodamine B (97%) and NaCl (99.5%) were purchased from Fisher Scientific. Hydrophilic fumed silica particles (Aerosil 200- A200) were provided by Evonik Corporation. The particles are fractal in nature with a specific surface area of $\sim 200\text{m}^2/\text{g}$, and are negatively charged when suspended in water because of dissociation of surface silanol groups. The nominal size of the fumed silica particles varies from 120nm -180nm. Millipore Milli Q water is used for the preparation of the surfactant solutions and particle suspensions. All surfactants were used without any further purification.

3.4 Sample preparation and analysis:

Dodecane-in-water emulsions were made with surfactant concentrations at about two times the CMC for each surfactant. The fumed silica suspensions did not contain surfactants. To form the “base” emulsion, 0.2 mL of dodecane was added to 1 mL of

the surfactant solution and vortexed at 3000 rpm for 1 min. The emulsions were diluted with a volume of particle suspension equal to the volume of the aqueous phase in the emulsion. The final surfactant concentration is therefore at their corresponding CMC values. The final silica particle concentration was varied between 0.05 wt% to 1wt%. The emulsions and the particle suspensions were mixed in two different ways. The first was gentle shaking to avoid foaming or creation of any new oil–water interfaces. This gentle shaking also minimizes convective transport of the particles. For the second case, they were vortexed at 3000rpm for 1min. The samples were allowed to rest for 24h after mixing, after which they were analyzed using a range of techniques.

Brightfield optical microscopy images were processed with Image-J to obtain average droplet sizes and size distributions. Silica particles were labeled with 0.5 μ M of Rhodamine B for confocal fluorescence microscopy on a Zeiss LSM 700. At the concentration we used for labeling, we do not expect the Rhodamine B to affect emulsion properties.²⁵ Cryogenic Scanning Electron Microscopy (Gatan Alto 2500 cryopreparation system attached to a Zeiss Sigma VP field emission scanning electron microscope) was used to look at the fine structure around the emulsion droplets. Zeta potentials were measured (Malvern Zetasizer Nano-ZS) to get additional insights on surfactant-particle interactions.

3.5 Results and Discussion:

Figure 3.1 shows images and size distributions of the dodecane-in-water emulsions stabilized with SDS, CTAB and Triton X-100. The emulsions are polydispersed with

average droplet sizes 19 μm , 22 μm and 12 μm respectively and the distribution remains stable for months, well beyond the duration of our experiments.

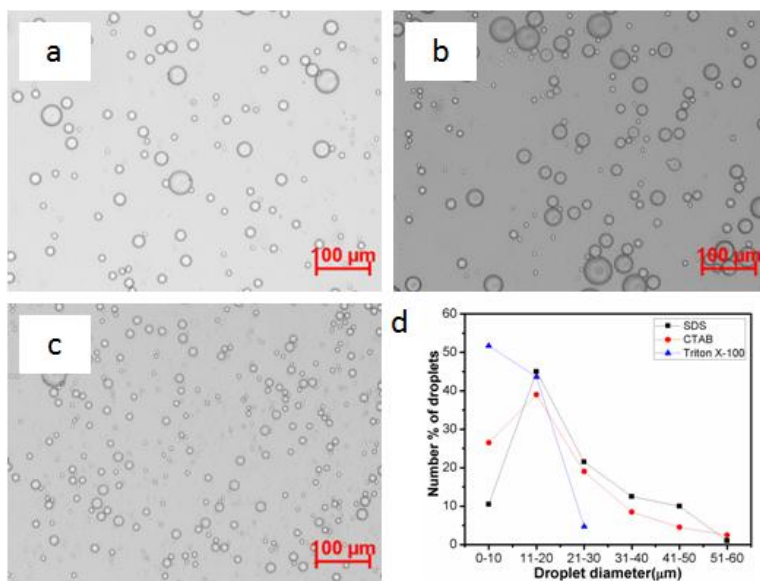


Figure 3.1: Bright field microscopic images of dodecane in water emulsions stabilized with (a) 16mM SDS (b) 2mM CTAB (c) 0.4mM Triton X-100 (d) size distributions of the emulsion droplets stabilized with different surfactants. Emulsions stabilized with Triton X-100 have smaller droplets compared to emulsions stabilized with SDS and CTAB.

Fig. 3.2(a) shows average droplet sizes after addition of different concentrations of fumed silica, followed by gentle mixing. We note little change in the mean droplet sizes for the SDS-stabilized emulsion, a rise in size for the Triton-X stabilized emulsion, and a rise followed by an insignificant change in the droplet sizes for the CTAB-stabilized emulsions. Further insights into this behavior are obtained by examining droplet size distributions for each of these cases. Fig. 3.2(b) shows little change to the droplet size distribution for the SDS-stabilized emulsions. There will be little or no adsorption of the SDS surfactant moieties on silica surface.²⁶ Repulsive interactions between the particles and the surfactant covered droplets will result in no particles at these interfaces, and therefore a minimal effect on the emulsions. For

emulsions stabilized with Triton X-100, we observe an increase in droplet size with an increase in silica concentration (Fig. 3.2(c)). Non-ionic surfactants with ethoxylated groups can form hydrogen bonds with hydroxyl groups on silica surfaces.^{9, 26} As the particle concentration increases, more surfactant get adsorbed on particle surfaces, depleting surfactant from the interfaces. The loss of the stabilizing amphiphile results in droplet coalescence.²²

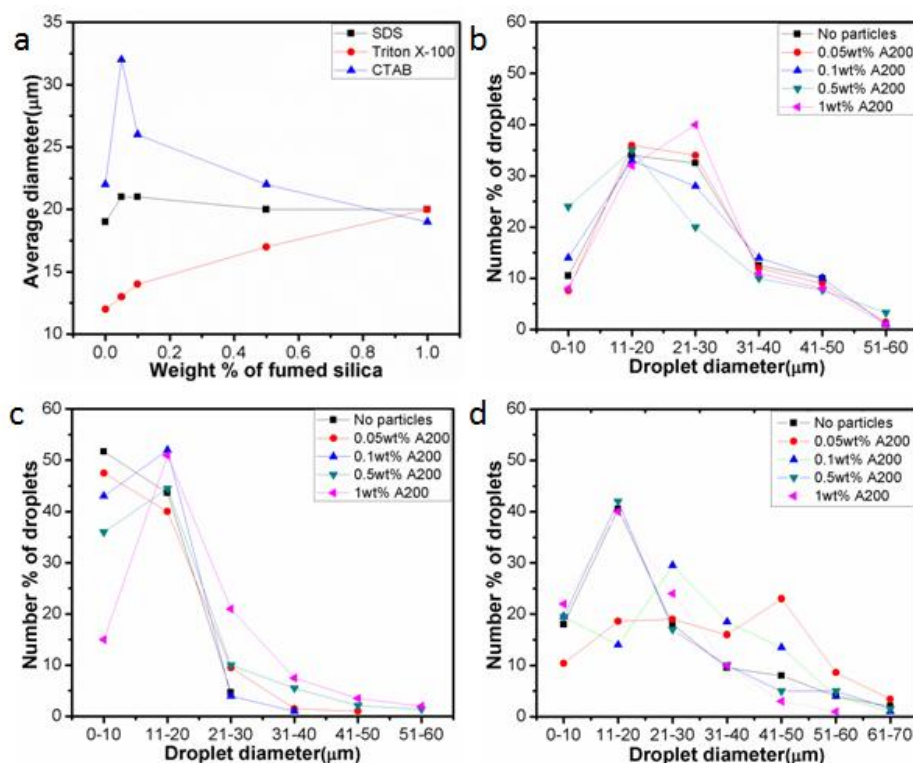


Figure 3.2: a) Average diameter and droplet size distributions of (a) surfactant stabilized emulsion droplets. Droplet size distributions for (b) SDS, (c) Triton X-100 and (d) CTAB emulsion droplets stabilized after gentle mixing with fumed silica (A200) suspensions.

Strong attractive electrostatic interactions dominate between silica particles and CTAB. We observed a partial phase separation of oil and water at 0.05 wt% of silica particles. At low particle concentrations, surfactant adsorption on particle surfaces depletes surfactant from the interfaces and results in droplet coalescence and an

increase in average droplet size (Fig. 3.2(d)). As the particle concentration increases, they bind to the surfactant- stabilized droplets and form particle coated emulsions that are stable.

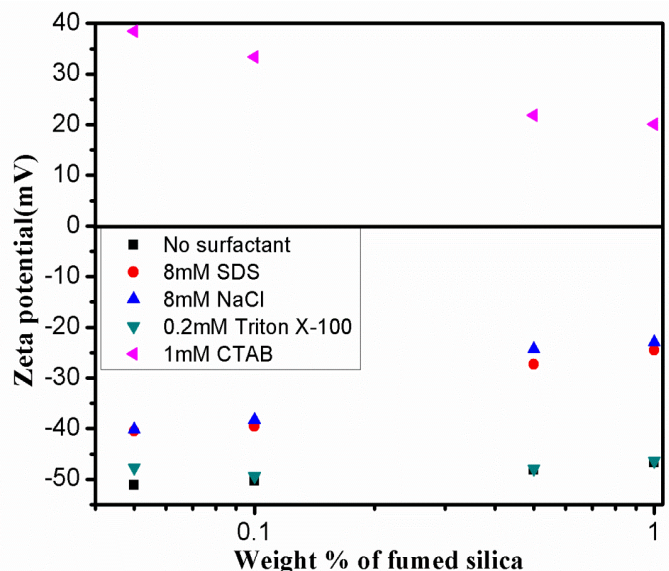


Figure 3.3: Zeta potential of fumed silica particles in the presence of different surfactants and at a NaCl concentration of 8mM. Error bars are about the size of the symbols.

We monitored surfactant particle interactions by measuring zeta potentials of fumed silica suspensions made in surfactant solutions at concentrations relevant for our experiments. Figure 3.3 shows zeta potentials of fumed silica particles after they are added to a SDS solution. We observed an increase in zeta potential (less negative) of the particles with an increase in particle concentration. We observed a similar behavior when NaCl is added to the fumed silica suspensions, suggesting that the rise in zeta potential is due to reduced overall dissociation of silanol groups at higher particle concentrations, followed by Na^+ (counterion) binding on silica surfaces. There is little or no adsorption of the anionic surfactant moiety on silica particles. We observe no change to the zeta potential of fumed silica particles in the presence of Triton X-100

(beyond the change observed when fumed silica is added to water). Fumed silica particles attain a negative charge through the dissociation of silanol groups on the silica surfaces. Triton X-100 interacts with the particles through the formation of hydrogen bonds with undissociated silanol groups, and therefore does not alter the zeta potential of silica particles.²⁷ Silica particles are positively charged in the presence of CTAB due to the formation of surfactant bilayers on the surface of the particles.

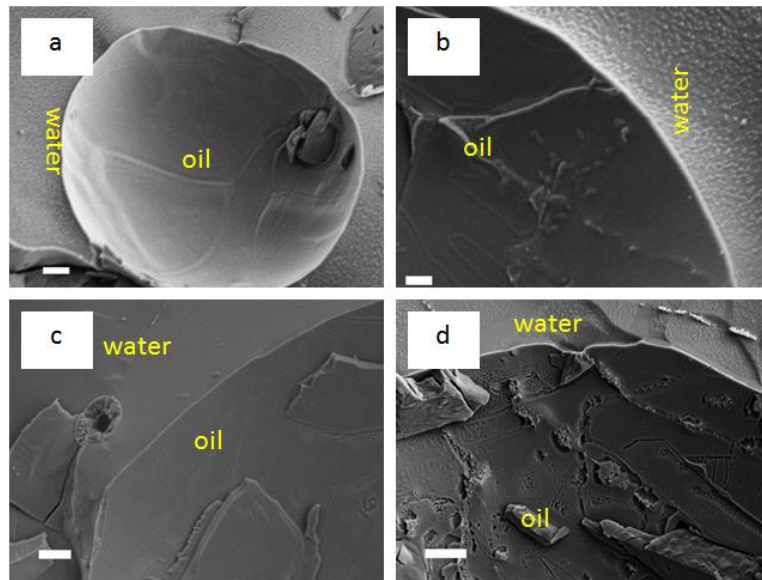


Figure 3.4: Cryo-SEM images of surfactant-stabilized emulsion droplets obtained after gently mixing with different concentrations of fumed silica suspensions. SDS-stabilized emulsion drops in the presence of (a) 0.05 wt% fumed silica. Scale bar= $3\mu\text{m}$ (b) 0.5 wt% fumed silica. Scale bar = $1\mu\text{m}$. Triton X-100-stabilized emulsion drops in presence of (c) 0.05wt% fumed silica; and (d) 0.5wt% fumed silica. Scale bars for (c) and (d) = $3\mu\text{m}$. Particles do not breach the oil-water interfaces in any of these cases.

Under these gentle mixing conditions, cryo-SEM images shown in Figs. 3.4(a)-(d) reveal no particles breaching the oil-water interfaces for all of the cases we studied. This observation confirms that for weak or no particle-surfactant interactions and gentle mixing, there is a rather insignificant effect of the addition of particles to a surfactant-stabilized emulsion.

Since CTAB can adsorb strongly on fumed silica, we further examined this system under gentle mixing conditions visually as well as with confocal microscopy, and show results in Fig. 3.5.

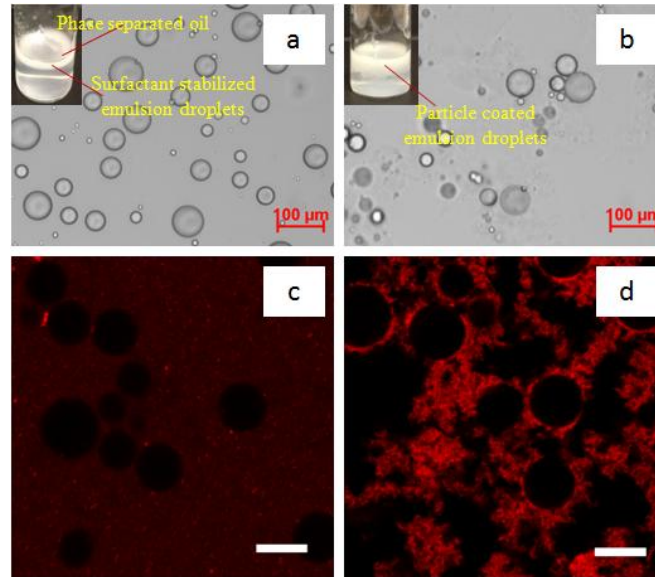


Figure 3.5: Optical microscopic images of CTAB-stabilized emulsion droplets after gentle mixing with fumed silica suspensions (a) 0.05 wt% fumed silica particles; inset showing partial phase separation of oil and water phase after the addition of fumed silica particles b) 0.5 wt% fumed silica particles; inset showing particle-coated emulsion droplets. Confocal fluorescence microscope images of the CTAB-stabilized emulsion droplets after gentle mixing with (c) 0.05 wt% fumed silica particles. The particles do not adsorb at oil water interfaces, but distribute uniformly in the aqueous phase d) 0.5 wt% fumed silica particles, showing the formation of particle coated droplets along with the particle networks between droplets. Scale bars = 50 μ m.

At low particle concentrations, surfactants get depleted from the oil-water interfaces and the emulsion partially destabilizes (Fig. 3.5(a)). As the concentration of particles increases, more particles get attached to the droplet surfaces leading to the formation of particle-coated droplets (Fig. 3.5(b)). The particle layers on the droplet surfaces hinder droplet coalescence. Fig. 3.5(c) is a confocal microscope image of the emulsion at low particle concentrations. The particles are distributed quite uniformly in the aqueous phase. The presence of alkyl chains on the silica surfaces increases the

particle hydrophobicity¹⁷ and creates hydrophobic patches on the silica surface. Exposure of these silica particles to water is not energetically favorable and the attractive van der Waals interactions then cause particle chaining in the bulk at high particle concentrations²⁸ and connections with particles located at the droplet surfaces. This results in particle networks between the emulsion droplets (Fig. 3.5(d)).

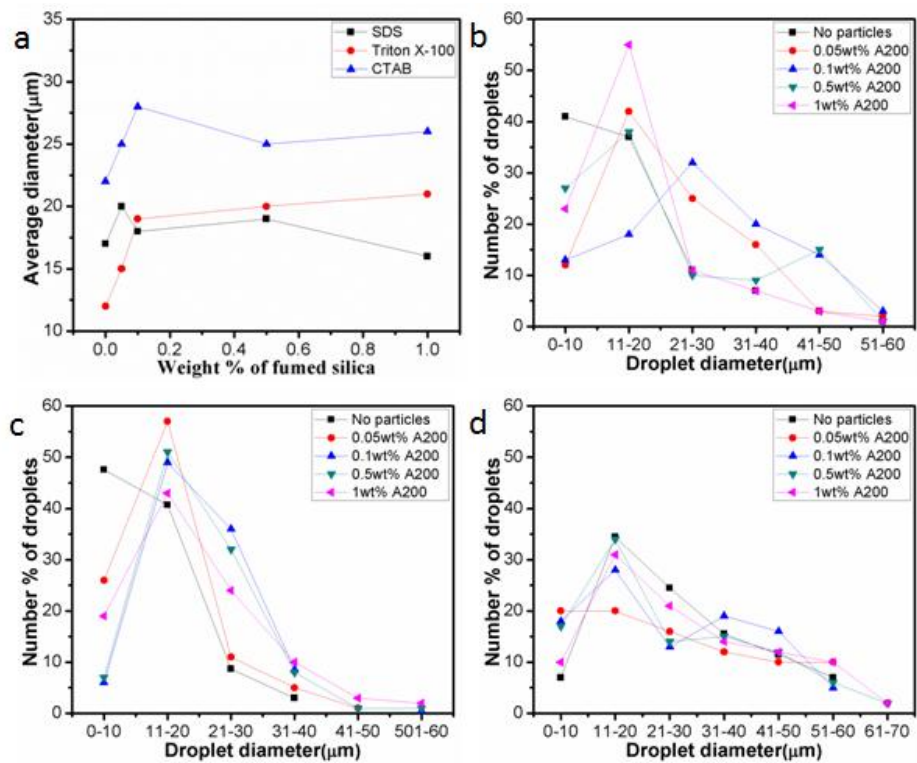


Figure 3.6: (a) Average diameter of the surfactant stabilized emulsions following vortex mixing with fumed silica suspensions. Droplet size distributions of (b) SDS, (c) Triton X-100 and (d) CTAB-stabilized emulsions after vortex mixing with fumed silica suspensions

We reexamined our systems under condition of vortex mixing, which allows particles to breach the oil-water interfaces. Figure 3.6 shows the average diameter of the droplets and droplet size distributions following the addition of the fumed silica suspension to surfactant-stabilized emulsions. For SDS and CTAB stabilized emulsions, we observed an increase in population of the smaller droplets with an

increase in silica concentration. The size distribution shifted towards the higher droplet size when fumed silica is added to the Triton X-100 emulsions. There will be competitive adsorption of silica particles and surfactant molecules on droplet interfaces. The relative concentration of particles on the droplet interfaces increases with an increase in particle concentration in the bulk. The presence of both particles and surfactants at interfaces further enhances the stability of oil droplets.

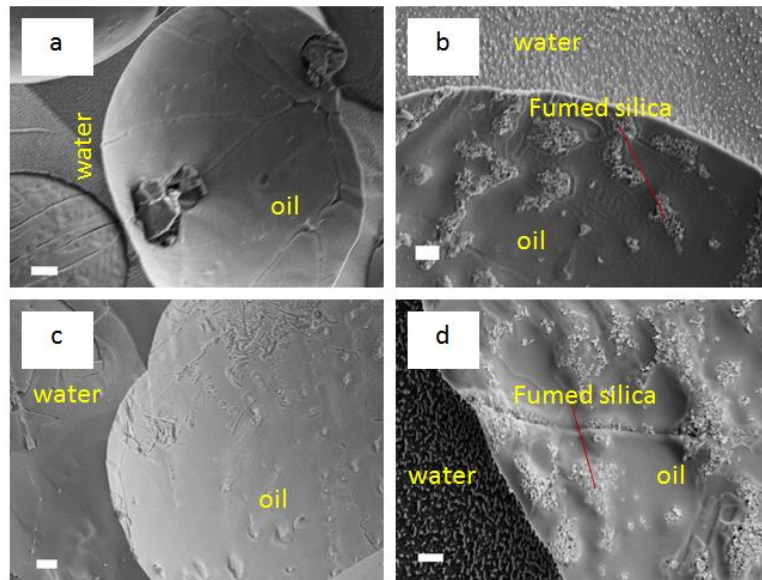


Figure 3.7: Cryo-SEM images of surfactant-stabilized emulsion droplets obtained after vortex mixing with fumed silica suspensions showing the position of fumed silica particles at oil-water interfaces. SDS-stabilized emulsion drops in presence of (a) 0.05 wt% fumed silica; no particles at oil-water interface. Scale bar = $3\mu\text{m}$ (b) 0.5 wt% fumed silica. Particles at oil-water interface. Scale bar = $1\mu\text{m}$. Triton X-100-stabilized emulsion drops in presence of (c) 0.05 wt% fumed silica; no particles at oil-water interface. Scale bar = $3\mu\text{m}$ and (d) 0.5 wt% fumed silica; the emulsion droplet is stabilized by both particles and surfactant. Scale bar = $1\mu\text{m}$.

Cryo-SEM images of the emulsion droplets are shown in Fig. 3.7. At low particle concentrations, we do not see particles at the oil water interface (Fig. 3.7(a)).

However, we see silica at the oil-water interfaces as the particle concentration is increased (Fig. 3.7(b)). For emulsions stabilized with Triton X-100, no particles are observed at the oil-water interfaces at low particle concentration (Fig 3.7(c)). As the

particle concentration increases, more particles stabilize the emulsion (Fig 3.7(d)). Depletion of surfactant in the bulk and a change in particle wettability due to surfactant adsorption enhances particle adsorption at the dodecane-water interface.

Fig. 3.8(a) and 3.8(b) show optical microscope images of a CTAB-stabilized emulsion in the presence of fumed silica particles, after vortex mixing. We observe the formation of particle-stabilized emulsions. Figs 3.8(c) and (d) are corresponding confocal microscope images. The adsorption of CTAB on fumed silica particles modifies the wettability of particles.

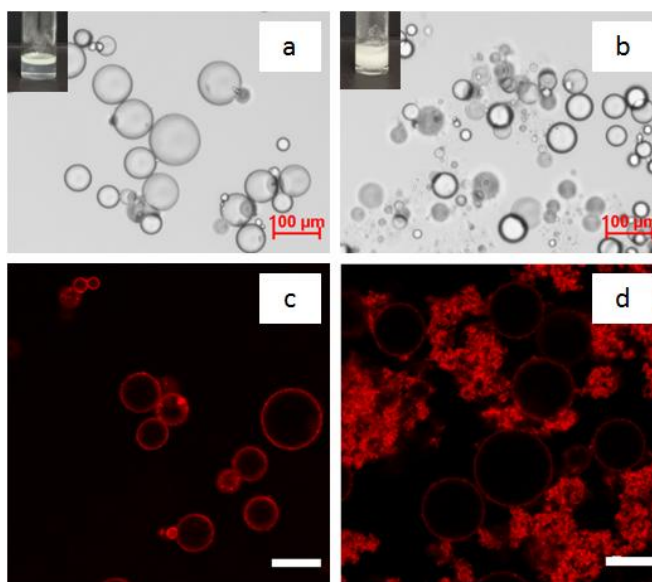


Figure 3.8: Optical microscopic images of CTAB-stabilized emulsion droplets after vortex mixing with fumed silica suspensions (a) 0.05 wt% fumed silica particles; inset shows vial containing the sample. b) 0.5 wt% fumed silica particles; inset shows a larger amount of the emulsion phase. Confocal microscope image of the CTAB-stabilized emulsion droplets after vortex mixing with (c) 0.05 wt% fumed silica. Particle-stabilized emulsion droplets are visible (d) 0.5 wt% fumed silica. Particle-stabilized emulsion droplets are trapped between fumed silica networks. Scale bars = 50 μ m

As the concentration of the particles increases, more particles locate at the interface (Fig. 3.8(c)). The attractive interactions between the silica particles in the bulk and particles around the emulsion droplets lead to the formation of three-dimensional

networks between the emulsion droplets at high particle concentrations (Fig. 3.8(d)). All the excess particles in the continuous phase get incorporated in these networks resulting in an increased viscosity and thickness of the emulsion phase.²⁹

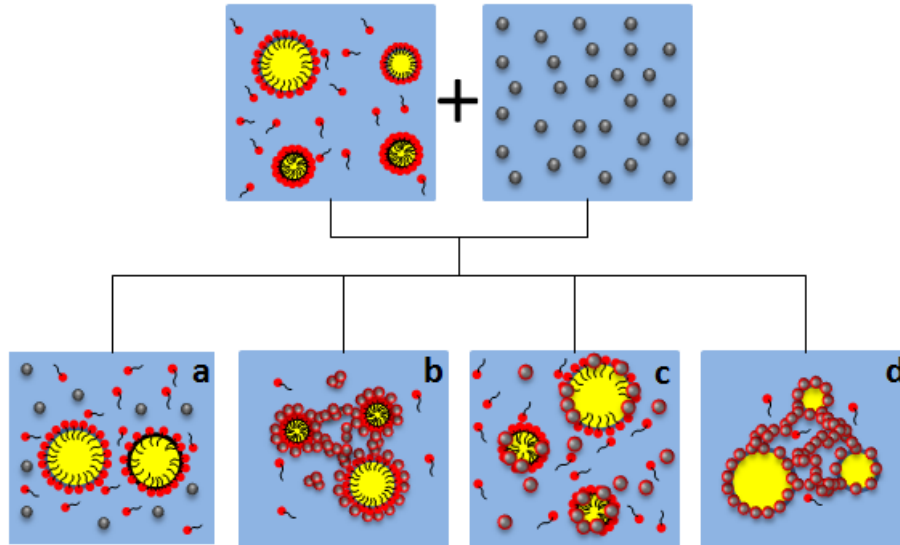


Figure 3.9: Possible end states that can be observed after the addition of colloidal particles to surfactant stabilized emulsions. (a) Weak or no particle-surfactant interactions, emulsion remains stabilized by surfactant (b) Strong particle-surfactant interaction, gentle mixing; Particle-coated surfactant-stabilized emulsion droplets (c) vortex mixing; Surfactants and particles at oil-water interfaces. (d) Strong particle-surfactant interaction, high concentration of particles; Particle-stabilized emulsions, particle network in continuous aqueous phase.

There are four different end states for emulsion droplets depending on surfactant-particle interactions, particle concentration and mixing conditions (Figure 3.9). Weak interactions (hydrophobic and hydrogen bonding) between surfactants and colloidal particles lead to the formation of surfactant-stabilized emulsions (Fig. 3.9(a)).

Attractive interactions between the particles and surfactants lead to the coalescence of emulsion droplets or formation of particle coated droplets depending on the surfactant-to-particle concentration when there is no mixing in the system (Fig. 3.9(b)).

Vortexing results in formation of particle-stabilized emulsions or emulsions stabilized

with both surfactants and particles depending on the relative concentration of the particles and surfactant molecules (Figs. 3.9(c), (d)).

3.6 Conclusions:

We studied the effect of the addition of negatively charged fumed silica particles on surfactant-stabilized emulsions. Depending on surfactant-particle interactions and mixing conditions, we observed four different end states for the emulsion. Addition of these fumed silica particles had no effect on the emulsion stability when the interactions between surfactants and particles were repulsive. We observed a phase separation and the formation of particles coated droplets when the interactions between surfactants and colloidal particles were attractive. Weak adsorption of surfactant on particles (in case of Triton X-100) resulted in coalescence of emulsion droplets. Finally, vigorous mixing resulted in the formation of emulsions stabilized with both surfactants and colloidal particles. These results highlight the importance of surfactant-particle interactions and different mixing conditions on the stability and reformation of surfactant-stabilized emulsions in the presence of colloidal particles.

3.7 Acknowledgements:

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CHAPTER 4

Microstructure and Rheology of Particle Stabilized Emulsions: Effect of Particle Shape

In preparation for *Colloids and Surfaces A: Physicochemical and Engineering Aspects*

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4.1 Abstract:

Here, we studied the effect of particle shape and inter-particle interaction on the formation and stability of bromohexadecane-in-water emulsions stabilized with spherical and fumed silica particles with similar hydrodynamic diameter. Emulsions were prepared at two different NaCl concentrations 0.1mM and 50mM. We found that the particle shape and inter-particle interactions have strong influence on the creaming behavior and microstructure of the emulsions. At 0.1mM NaCl, there is sedimentation of emulsion droplets stabilized with spherical silica particles and creaming of emulsion droplets stabilized with fumed silica particles. Increasing salt concentration to 50mM lead to the flocculation of emulsion droplets stabilized with spherical silica particles whereas, emulsions stabilized with fumed silica formed a gel like structure. All the emulsions have shown shear thinning behavior. The emulsions stabilized with fumed silica particles have higher viscosity and were yielding at higher strains when compared with emulsions stabilized with spherical silica particles. The degree of shear thinning and yielding has increased with an increase in salt concentration.

4.2 Introduction:

The ability of the colloidal particles to get strongly adsorb at oil-water interfaces makes them potential alternatives to surfactants for stabilizing emulsions.¹ Unlike surfactants, the adsorption of colloidal particles onto the oil-water interfaces is not spontaneous.^{2, 3} However, once a partially wettable particle is placed at the oil-water interface, it gets kinetically trapped and thermal fluctuations will be insufficient to displace it from the oil-water interface. With sufficient coverage at the interface,

these particles act as electrostatic, steric or mechanical barriers against droplet coalescence.^{4,5}

Particle shape and inter-particle interactions also play significant role in determining the micro-structure and stability of particle stabilized emulsions.⁶ Madivala et. al.⁷ showed that ellipsoidal polystyrene particles above a critical aspect ratio are capable of forming stable emulsion, even when spherical and lower aspect ratio particles with the same wetting properties do not produce an emulsion. San-Miguel et. al.⁸ showed that roughness on the colloidal particle surface enhance the stability of the emulsions as long as there is a homogeneous wetting of particle surface by oil and water phases. It is argued that anisotropic and rough particles gets pinned at the oil-water interfaces and lead to a significant deformation of the oil-water interface when compared with smooth spherical particles.⁶ This results in strong adsorption of these particles at oil-water interfaces when compared with smooth spherical particles of same size⁹ which leads to an increase in emulsion stability. Interfacial coverage of the particles on the emulsion droplet interface also dependon particle shape.^{7, 10, 11} Particle shape and inter-particle interactions also influence the microstructure and the viscosity of the particle suspension, which in turn affect the structure and properties of the emulsions. Silanized fumed silica particle can form volume filling networks at concentrations much lower than the spherical silica particles of same hydrodynamic size when the interactions between the particles are attractive.¹² These networks will have a huge influence on the creaming behavior and stability of the emulsion droplets.¹³

Here we formed Pickering emulsions using colloidal particles with repulsive and attractive interactions and systematically compared the effect of particle shape on the formation and microstructure of the emulsions. The combination of optical, cryogenic scanning electron microscopy (Cryo-SEM), and rheological measurements were used to determine the microstructure and stability of the emulsions.

4.3 Materials and methods:

Mono-dispersed spherical silica particles (210 ± 10 nm) were purchased from Fiber Optics Inc. Fumed silica particles (Aerosil 816) were provided by Evonik Corporation, which were fractal in nature with a primary particle size of ~ 12 nm. They were surface modified with hexadecyltrimethoxysilane, which makes the particles hydrophobic enough to stabilize oil-in-water emulsions. Fumed silica particles form aggregated structures when suspended in water with an average hydrodynamic diameter of 204 ± 20 nm. The particles attain negative charge when suspended in water due to the dissociation of surface hydroxyl groups. Spherical silica particles were surface modified with 0.06 mM Hexylamine (Fisher Scientific) to make the particles hydrophobic enough to emulsify all the oil phase. Bromohexadecane (97%, Fisher Scientific) was used for emulsion formation. Emulsions were prepared at two different salt concentrations 0.1 mM and 50 mM NaCl. The salt concentrations were chosen in such way that the interactions between particles are repulsive at 0.1 mM NaCl and attractive at 50 mM NaCl concentration. The zeta potential of the spherical and fumed silica particles were -48.2 mV and -45.6 mV respectively at 0.1 mM NaCl. At 50 mM NaCl, there is a rapid flocculation of spherical silica particles and a rise in viscosity for fumed silica suspensions, suggesting attractive interactions between

particles. Bromohexadecane in water (1:1) emulsions were prepared by vortex mixing the oil and water phase at 3000 rpm for 2min. 2 wt% silica dispersions were used to prepare the emulsions. The volume fraction of the oil phase separated due to coalescence was less than 0.5% in all the cases. The emulsions were analyzed with bright field optical microscopy and the images were processed with Image-J to obtain average droplet size and size distributions. Cryogenic Scanning Electron Microscopy (Gatan Alto 2500 cryo-system attached to a Zeiss Sigma field emission scanning electron microscope) is used to look at the fine structure around the emulsion droplets. An AR2000ex rheometer with concentric double wall cylindrical geometry is used for doing rheological measurements. The samples were pre-sheared at 1s^{-1} for 30seconds to remove any shearing history before doing the measurements.

4.4 Results and discussion:

Figure 4.1 shows the optical microscopic images of the emulsion droplets stabilized with spherical and fumed silica particles at two different salt concentrations. The average diameters of the emulsion droplets were $27\pm 18\mu\text{m}$ and $22\pm 16\mu\text{m}$ for emulsions stabilized with fumed silica particles, $32\pm 17\mu\text{m}$ and $35\pm 18\mu\text{m}$ for emulsions stabilized with spherical silica particles at 0.1mM and 50mM NaCl respectively. There is sedimentation of emulsion droplets that are stabilized with spherical silica particles (insets in figure 4.1(a) and 4.1(b)). The diameter of the neutrally buoyant droplet can be estimated using the following equation,

$$D = 4\phi d_p \frac{\rho_p - \rho_w}{\rho_w - \rho_o} \quad (1)$$

Where, D and d_p are the diameter of the droplet and particle, respectively, ϕ is the fractional coverage of the particles at the droplet interface, and ρ_p , ρ_w , and ρ_o are the

densities of the particles, water, and oil respectively. For spherical silica particles, the calculated diameter of the neutrally buoyant droplet is $\sim 576\mu\text{m}$. The average diameter of the emulsion droplets formed after vortex mixing was less than the calculated diameter of the neutrally buoyant droplet. Therefore, the effective density of the emulsions droplets will be higher than the continuous phase,^{14, 15} which explains the sedimentation of the emulsion droplets. Increase in salt concentration lead to the flocculation of the emulsion droplets. Interaction between colloidal particles also dictate the interactions between emulsion droplets.¹⁶ At 50mM NaCl there are attractive interactions between silica particles which explain the flocculation of the emulsion droplets.

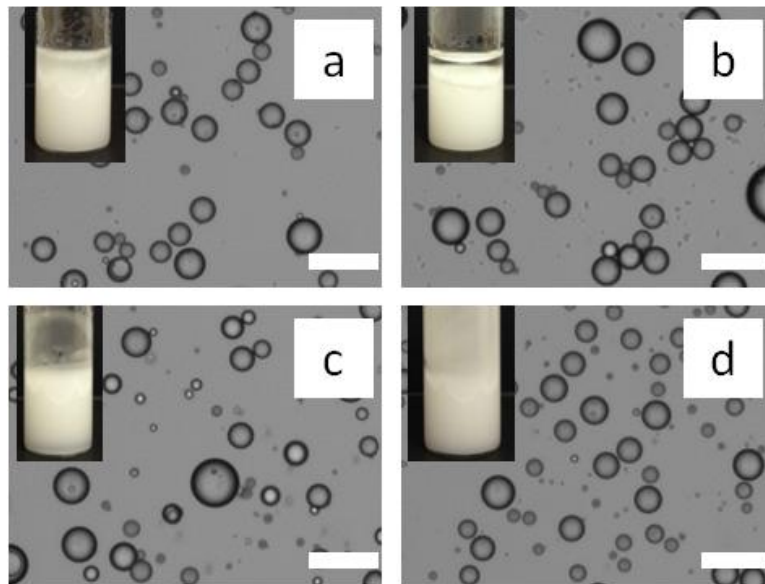


Figure 4.1: Optical microscopic images of the emulsion droplets stabilized with (a) spherical silica at 0.1mM NaCl; insight showing the sedimentation of emulsion droplets. (b) spherical silica at 50mM NaCl; insight showing the sedimentation of emulsion droplets. (c) fumed silica at 0.1mM NaCl; insight showing the creaming of emulsion droplets. (d) fumed silica at 50mM NaCl; insight showing the gel like emulsion phase. Scale bars: $100\mu\text{m}$.

Fumed silica particles have a similar hydrodynamic size as spherical silica particles, but we observed creaming of the emulsion phase at 0.1mM NaCl (inset in

figure 4.1(c)). The size of the primary particle is 12nm for fumed silica particles and the corresponding diameter for the neutrally buoyant droplet is $\sim 34\mu\text{m}$ and is calculated by assuming hexagonal packing of fumed silica particles on the droplet interface. Owing to their fractal nature, the actual packing fraction of fumed silica particles on the droplet interface will be less than 0.9 which might result in much small diameter for a neutrally buoyant droplet. This explains the creaming of the emulsion droplets and highlights the importance of the primary particle size in determining the properties for emulsions stabilized with fumed silica particles. There is no creaming or sedimentation observed for fumed silica stabilized emulsions at 50mM NaCl (inset in figure 4.1(d)).

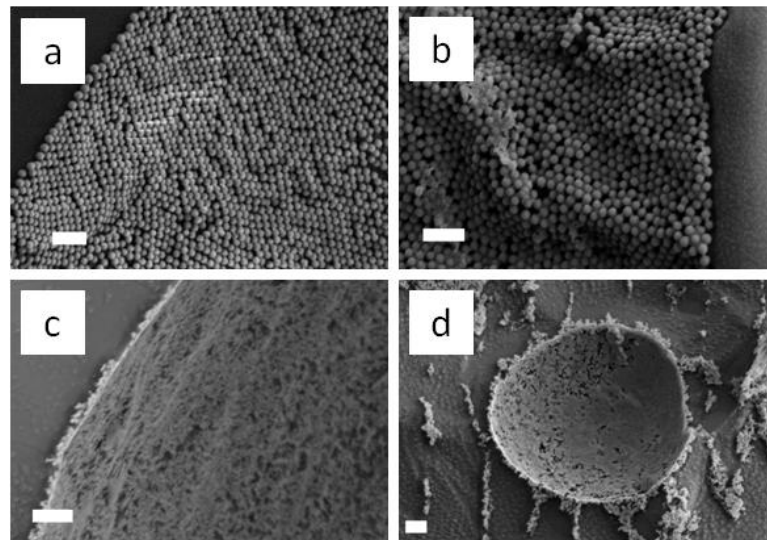


Figure 4.2: Cryo-SEM images of the emulsion droplets stabilized with (a) spherical silica at 0.1mM NaCl, shows hexagonal packing of particles on droplet interface. (b) spherical silica at 50mM NaCl, shows hexagonal packing of particles on droplet interface. (c) fumed silica at 0.1mM NaCl, shows the complete coverage of fumed silica particles on droplet interface. (d) fumed silica at 50mM NaCl, shows networks fumed silica particles in bulk and closely packed silica particles on droplet interface. Scale Bars = 1 μm .

Fumed silica particles forms networks of particles at higher salt concentration due to attractive inter-particle interactions. The emulsion droplets gets trapped in

between these networks resulting in a gel like structure, which might have resulted in no observable creaming of the emulsion phase. Cryo-SEM images were used to determine the structure of the emulsion droplets. Figure 2 shows the Cryo-SEM images of the emulsions stabilized with spherical and fumed silica particles at two different salt concentrations 0.1mM and 50mM NaCl. The droplets were coated with a close packed (Hexagonal) monolayer of particles for emulsions stabilized with spherical silica particles (figure 4.2(a), (b)). For fumed silica stabilized emulsions packing of particles on the droplet surface was no longer hexagonal in nature, instead there were multiple layers of fumed silica particles on the droplet surfaces (figure 4.2(c)). As we know fumed silica particles were fractal in nature, so the coverage of the particles on the droplet surfaces will be different when compared to smooth spherical silica particles.¹⁷ At higher salt concentrations, we observed the networks of fumed silica particles in the bulk and an increase in thickness of particle layers around the droplet surface (figure 4.2(d)), suggesting the aggregation of fumed silica particles on the droplet surface and in the bulk due to attractive inter-particle interactions.

4.4.1 Rheology measurements:

Figure 4.3 show the rheology of silica particle suspensions and emulsion droplets . Suspensions of spherical silica particles showed Newtonian behavior at both the salt concentrations (figure 4.3(a)). As mentioned before interactions between particle dictates the interactions between emulsion droplets. Therefore, emulsions stabilized at low salt concentrations will have repulsive interactions between the droplets, whereas emulsions stabilized at high salt concentrations will have attractive interactions between the emulsion droplets. Repulsive emulsions behave as disordered

elastic solids¹⁸ and show shear thinning behavior. We observed similar behavior for emulsions stabilized with spherical silica particles at 0.1mM NaCl and there is a monotonic decrease in viscosity with increased shear rate (figure 4.3(a)). At higher salt concentrations, there was a discontinuity in the flow curve for emulsions stabilized with spherical silica particles at a shear rate of 1s^{-1} (figure 4.3(a)). This is due to the progressive breakdown of aggregated emulsion droplets which results in a low viscosity continuous phase.¹⁹ Fumed silica suspensions showed Newtonian behavior at low salt concentration and shear thinning behavior at high salt concentration. There is a monotonic decrease in viscosity with an increase in shear rate in case of emulsions stabilized with fumed silica particles at both the salt concentrations.

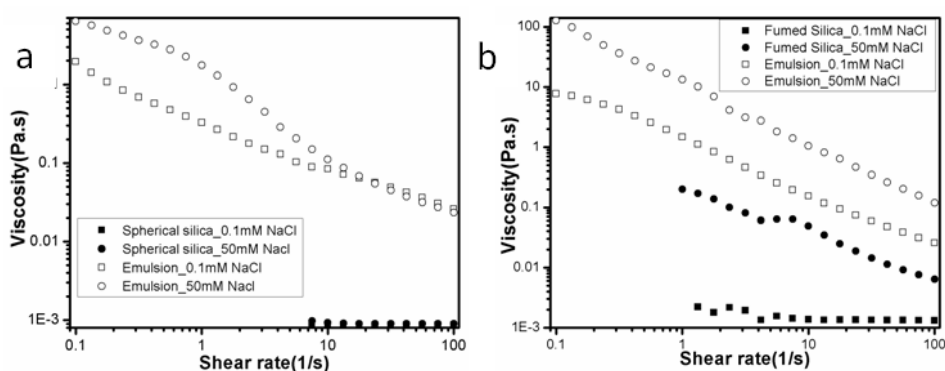


Figure 4.3: A plot of viscosity vs. shear rate (a) Spherical silica suspensions (solid symbols) and emulsions stabilized with spherical silica particles (open symbols) (b) fumed silica suspensions (solid symbols) and emulsions stabilized with fumed silica particles (open symbols).

The formation of gel like structure at high salt concentration results in more ordered structure and increased the viscosity of the particle suspensions and emulsions. This is due to the fact that the effective volume fraction occupied by the fumed silica particles in the suspension is more when compared to spherical silica

particles with similar hydrodynamic size. The effective volume fraction occupied by fractal particles can be estimated using following equation,

$$\frac{\phi_{\text{eff}}}{\phi_o} = \left(\frac{R}{R_o}\right)^{3-D_f} \quad (2)$$

Where, ϕ_{eff} and ϕ_o are the effective and actual volume fraction of the silica particles in the suspension. R is the diameter of the fractal particle and R_o is radius of the primary particle. D_f is the mass fractal dimension of the particles. D_f for fumed silica particles is 2.17.²⁰ The effective volume fraction occupied by the fumed silica particles is ~11 times higher than that of the spherical silica particles with similar size, which results in higher viscosity and the attractive interactions between fumed silica particles results in the formation of the particle networks in the suspension resulting in shear thinning behavior at 50mM NaCl concentration.

Oscillatory strain experiments were performed at an oscillatory frequency of 1Hz to understand the yielding behavior of the emulsions. Particle suspensions did not showed any yielding and viscoelastic behavior. At 0.1mM NaCl, emulsion stabilized with spherical silica particles, did not show any linear viscoelastic region (LVR) and started to yield from 0.1% strain (figure 4.4(a)). However, the emulsion retained solid like behavior until 6% strain with $G' > G''$. Fumed silica stabilized emulsions responded purely elastically until 0.4% strain, further increase in strain resulted in yielding of the emulsion phase. The emulsion retained solid like behavior until 50% strain before there is a crossover.

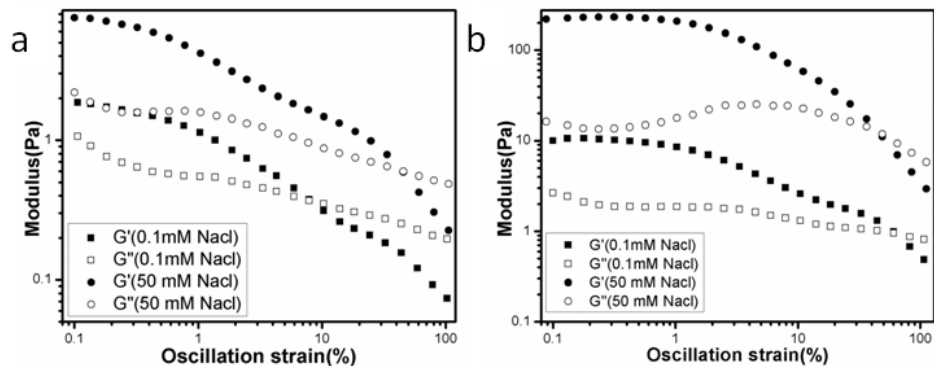


Figure 4.4: Elastic (G' , solid symbols) and viscous (G'' , open symbols) moduli for Bromohexadecane-in-water emulsions stabilized with (a) spherical silica particles, (b) fumed silica particles.

This behavior suggests that fumed silica stabilized emulsions have much resistance to deformation when compared with emulsions stabilized with spherical particles. This is due to the fact that the fumed silica particles are fractal in nature and the edges of these particles gets pinned to the oil-water interface which resulted in strong adsorption at the interface when compared with spherical silica particles.⁹ At 50mM NaCl, emulsion stabilized with spherical silica particles have a small region of LVR up to strain amplitudes $\gamma < 0.2\%$. The emulsion started to yield above 0.2% strain with a crossover at 50% strain amplitude (figure 4.4(a)). Flocculation of emulsion droplets gives some structure to the emulsions stabilized with spherical silica particles at 50mM NaCl. Therefore, the emulsion retains solid like character until the flocks get broken which results in a crossover at higher strains. For fumed silica stabilized emulsions, there is a significant increase in elastic and shear module and the LVR goes up to strain amplitudes $\gamma < 1\%$ at higher salt concentration (figure 4.4(b)). The gel like structure formed due to the formation of three dimensional particle networks between the emulsion droplets results in such behavior.

4.5 Conclusions:

We studied the effect of particle shape and inter-particle interactions on the microstructure and rheology of Pickering emulsions using spherical and fumed silica particles as emulsifiers. Attractive and repulsive emulsions were prepared by controlling the interactions between the silica particles in the bulk. The shape of the particles and inter-particle interactions strongly affect the creaming and rheological properties of the emulsions. We observed sedimentation and creaming for emulsion droplets stabilized with spherical and fumed silica particles respectively at 0.1mM NaCl. At 50mM NaCl, we observed flocculation in spherical silica stabilized emulsions, whereas emulsions stabilized with fumed silica particles formed a gel like structure. All the emulsions showed shear thinning behavior. The emulsions stabilized with fumed silica particles yielded at higher strains when compared with emulsions stabilized with spherical silica particles. The degree of shear thinning and yielding has increased with an increase in salt concentration.

4.6 Acknowledgement:

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SOME CAVEATS:

Droplet size distributions were used to support some of the observations that were presented in this dissertation. However, the reproducibility of these distributions depends on many parameters. The mixing conditions, type of mixer and vial used for emulsion formation and the extent of mixing will influence the final distribution of the emulsion droplets. Therefore, the reproducibility of these measurements will be very sensitive to the conditions used during the emulsion formation. However, most of these observations are qualitative and are reproducible phenomenon.