Graphical Abstract

Viscosity and stability of ultra-high internal phase CO₂-in-water foams stabilized with surfactants and nanoparticles with or without polyelectrolytes

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Viscosity and stability of ultra-high internal phase CO₂-in-water foams stabilized with surfactants and nanoparticles with or without polyelectrolytes

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ABSTRACT

To date, relatively few examples of ultra-high internal phase supercritical CO₂-in-water foams (also referred to as macroemulsions) have been observed, despite interest in applications including “waterless” hydraulic fracturing in energy production. The viscosities and stabilities of foams up to 0.98 CO₂ volume fraction were investigated in terms of foam bubble size, interfacial tension, and bulk and surface viscosity. The foams were stabilized with laurylamidopropyl betaine (LAPB) surfactant and silica nanoparticles (NPs), with and without partially hydrolysed polyacrylamide (HPAM). For foams stabilized with mixture of LAPB and NPs, fine ~70 μm bubbles and high viscosities on the order of 100 cP at > 0.90 internal phase fraction were stabilized for hours to days. The surfactant reduces interfacial tension, and thus facilitates bubble generation and decreases the capillary pressure to reduce the drainage rate of the lamella. The LAPB, which is in the cationic protonated form, also attracts anionic NPs (and anionic HPAM in systems containing polymer) to the interface. The adsorbed NPs at the interface are shown to slow down Ostwald ripening (with or without polymer added) and increase foam stability. In systems with added HPAM, the increase in the bulk and surface viscosity of the aqueous phase further decreases the lamella drainage rate and inhibits coalescence of foams. Thus, the added polymer increases the foam viscosity by three-fold. Scaling law analysis shows the viscosity of 0.90 volume fraction foams is inversely proportional to the bubble size.

Key words: CO₂-in-water foam, high internal phase foam, nanoparticle-stabilized foam, foam stability, viscosity

1. INTRODUCTION

An aqueous dispersion of a gas in liquid, or foam, is thermodynamically unstable but can be kinetically stabilized with various amphiphiles including surfactants, solid particles, polymers, and biopolymers including proteins or combinations thereof.¹ Foams may coarsen and phase separate by a variety of mechanisms including Ostwald ripening and lamellae drainage followed by coalescence.²⁻⁶ Typically, the internal (dispersed) phase of foam is gas such as air or nitrogen in the ideal state. Foams formed with dense supercritical CO₂, which has an appreciable solvent strength between that of a gas and a hydrocarbon,⁷⁻¹² exhibit properties of both gas-in-liquid foams as well as liquid-in-liquid macroemulsions.^{11,13,14} CO₂-in-water (C/W) foams have been utilized for a variety of applications including enhanced oil recovery,¹⁰ hydraulic fracturing,^{15,16} fire retardants and synthesis of porous materials.¹⁷⁻¹⁹

High internal phase C/W foams with > 0.75 CO₂ have received relatively little attention and their properties are poorly understood due to the poor stability. Unlike the case for foams with nitrogen or other water insoluble gases, the high solubility of CO₂ in water²⁰ increases the rate of Ostwald ripening whereby CO₂ diffuses from smaller bubbles to larger ones. Also, as the CO₂ volume fraction (ϕ) increases, the lamella becomes more susceptible to drainage (film thinning) and eventually coalescence. The capillary pressure, or the pressure difference between the foam lamella and Plateau border that drives the lamella drainage, increases as ϕ increases.⁶ A better mechanistic understanding of the effects of surfactants, NPs and polymers on the morphology, viscosity and stability of high internal phase C/W foams would be beneficial for designing foams for a variety of practical applications including low water hydraulic fracturing fluids.

In an effort to achieve stable high CO₂ fraction foams, various surfactants with branched hydrocarbon tails^{8,9,11,21,22} and in some cases ethylene oxide groups^{8,9,22,23} have been explored. C/W foam with a $\phi = 0.90$, viscosity up to 60 cP and stability over 60 hours was reported.¹¹ In these foams, the viscosity of the continuous phase is as low as

that of water. Recently, quaternary ammonium surfactants that form wormlike micelles and viscoelastic aqueous phases were reported to stabilize $\phi = 0.75$ C/W foams up to 250 cP,²⁴ however, the long term stability and morphology of foams with viscoelastic continuous phases has received little attention. The stability of foams may also be raised by adding a viscoelastic polymer to the aqueous phase, especially when attractive interactions are formed between the polymer and a surfactant with opposite charge.²⁵ Here the electrostatic attraction induces formation of polymer-surfactant complexes in the bulk phase and at the fluid interface, which raise the stability of foam film against drainage and coalescence, due to an increase in the interfacial shear and dilatational viscoelasticity²⁶⁻²⁹ and structural forces³⁰⁻³². For C/W foams, mixtures of anionic surfactants and negatively charged guar- and cellulose-based biopolymers have been studied for application as energized hydraulic fracturing fluids.^{15,16} C/W foams with ϕ up to 0.8 were reported to have viscosities of tens to hundreds of centipoise at shear rate of 100 s^{-1} .^{15,16} For such like-charged polymer-surfactant systems, polymer may be expected to be depleted from the interface due to electrostatic repulsion and thus only slightly influence the interfacial rheological properties.^{26,27,33} The formation and long term stability of foams stabilized with polymer and surfactant with attractive interactions has rarely been studied.

Foams stabilized with colloidal particles may exhibit increased stability against Ostwald ripening and coalescence relative to surfactant stabilized foams.^{34,35} The enhanced stability may be attributed to enhanced structural forces³⁶ and a large desorption energy of the particles from the interface³⁵. The wettability of particles at the fluid/fluid interface, characterized by the contact angle, defines their interfacial activity and the preferred interfacial curvature. For example, fumed silica particles with decreasing surface coverage of hydrophobic dichlorodimethylsilane were reported to have the optimum wettability in terms of stabilizing air-water foams³⁷, C/W foams³⁸, and oil-water emulsions,³⁹ respectively. Here the cohesive energy density of the NP surfaces must match that of the internal phases. In addition to modifying the surface chemistry, the wettability of particles may be altered by adding salt. High salinity is also beneficial for the adsorption of charged particles towards fluid interface.^{35,40} The adsorption of anionic particles to a negatively charged oil-water interface increases with increasing salinity by

reducing electrostatic repulsion, both for equilibrium and kinetic reasons.^{35,40} However, too much salt may screen the charge to the extent that lack of repulsion results in aggregation of particles,⁴¹⁻⁴⁵ thereby breaking the foam.⁴⁶ Despite the efforts to facilitate the adsorption of particles to C/W interfaces, C/W foams stabilized with particles alone have had a maximum viscosity of ~ 16 cP up to $\phi = 0.9$.³⁸

The adsorption of relatively hydrophilic particles to fluid interface can be facilitated by mixing with oppositely charged surfactants, whereby surfactants adsorb to particles and increases their hydrophobicity (and thus amphiphilicity).⁴⁷ Such synergistic interactions between NPs and surfactants were studied in a number of air-water foams and oil-water emulsions.^{47,48} Mixtures of bare silica NPs and surfactant were also reported to stabilize C/W foams with a high viscosity of 80 cP up to $\phi = 0.75$.⁴⁹ However, the effect of NPs on the morphology, viscosity and long term stability of C/W foams remains to be investigated, particularly for ϕ above 0.75.

The objective of this work is to demonstrate the stabilization of $\phi = 0.90$ – 0.98 supercritical CO₂-in-water foams with high viscosity (on the order of 100 cP) and long lifetime (on the order of hours), by a judicious design of the interfacial and rheological properties. We examine two types of amphiphilic systems: (1) surfactant and NPs, and (2) surfactant and NPs and polymer. The addition of anionic silica NPs to very dilute surfactant (laurylamidopropyl betaine, LAPB) in the cationic protonated form produces viscous foams with ~ 70 μm fine bubbles and long-term stability against Ostwald ripening, as evaluated systematically with foam bubble size, change in bubble size with time, interfacial tension and surface viscosity. The LAPB surfactant reduces C/W interfacial tension, but by itself is too dilute to stabilize highly viscous foams. In addition, LAPB promotes the adsorption of NPs to the C/W interface and consequently increases the foam stability against coalescence and Ostwald ripening. In the second type of amphiphilic system, partially hydrolyzed polyacrylamide (HAPM) polymer is added to the mixture of LAPB and NPs to increase the continuous phase and surface viscosity. The polymer slows down the lamella drainage and inhibits coalescence, resulting in a 2-3 fold higher viscosity and finer bubbles of ~ 20 μm than in the case without polymer. The effects of bubble size and continuous phase viscosity on the C/W foam viscosity at high ϕ were characterized by scaling law analysis. The ability to stabilize viscous foams at

extreme CO₂ fractions ≥ 0.90 is expected to find utility in a broad range of applications, including low water hydraulic fracturing fluids that could potentially replace vast quantities of water used currently.

2. EXPERIMENTAL

2.1. Materials. Surface-modified colloidal silica NPs (EOR-5XS, Lot No. LB130204, Nissan Chemical America Corporation) were received as a 20 % w/v aqueous dispersion. The NPs had a proprietary, covalently attached non-ionic steric stabilizer on the surface as provided by the manufacturer. The purpose of the surface modification was to enable colloidal stability in presence of high salinity. Laurylamidopropyl betaine (LAPB) (Mackam DAB-ULS, Lot No. UP1J13X04) was from Rhodia (now Solvay). Alpha olefin sulfonate (AOS) (Bioterge AS-40) was from Stepan. Flopaam 3330S and 3630S were received from SNF Floerger. The Flopaam 3330S and 3630S were partially hydrolyzed polyacrylamide polymers with hydrolysis content of 25-30%. The molecular weight of FP 3330S and 3630S was 8 M and 20 M Dalton, respectively. The received powdered polymers were hydrated and filtered before use for subsequent studies (please see Supporting Information for the detailed description). The list of polymers and surfactants used in this study is tabulated in Table S1. Potassium chloride (KCl), hydrochloric acid (HCl) and sodium hydroxide (NaOH) were obtained from Fisher Scientific. All the chemicals were used as received unless otherwise noted.

2.2. Aqueous Phase Behavior in High Pressure CO₂ Saturated Brine. The phase behavior of mixtures of NPs, polymers and surfactants in high pressure CO₂ saturated 2% KCl brine solution were studied with an adjustable volume high pressure view cell as described in Figure S1. 2% KCl brine was used to mimic the salinity level in hydraulic fracturing fluids. The view cell is equipped with a piston inside for controlling the pressure and a sapphire glass window on the sides for visual observation. Mixtures of 4 g CO₂ and 4 g 2% KCl brine containing amphiphiles were loaded in the front part of the view cell to obtain CO₂ saturated brine condition. A cross-shaped magnetic stir bar was placed into the view cell for gentle mixing. The pressure on the rear side of the view cell was controlled by a high pressure syringe pump (Isco, model 260D) with CO₂ as the pressuring fluid. The temperature of the system was measured and controlled by thermocouples.

2.3. CO₂/Water Interfacial Tension Measurements. The interfacial tension between CO₂ and water under 3000 psia and 50 °C was determined from axisymmetric drop shape analysis of a CO₂ captive bubble method. The CO₂ bubble was equilibrated for 30 min in aqueous phase, which contained a known concentration of surfactants, NPs and polymers in 2% KCl brine. Before each measurement, the aqueous dispersion was equilibrated with pure CO₂ for 2 hrs. The drop shape profile was fitted with Young-Laplace equation using a commercial software package (CAM 200, KSV Ltd., Finland).

2.4. Shear Viscosity Measurements. The steady-state shear rheology of aqueous dispersions of polymers, NPs and surfactants at 50 °C were measured using AR G2 rotational rheometer (TA Instruments) with a cone-and-plate geometry (40 mm, 2°). Rheology measurements were conducted in 2 % KCl brine solution at pH 4 (to mimic the low pH of CO₂ saturated water) adjusted with 1N HCl. At least 3 scans of shear rates were conducted and the reported values are the average of these measurements.

2.5. Surface Shear Viscosity Measurements. Surface steady-state shear viscosity between air and 2% KCl aqueous dispersions containing polymer, surfactant and NPs at 50 °C and pH 4 was measured using AR G2 rotational rheometer (TA Instruments) with double wall ring (DWR) geometry. The DWR geometry works as a 2D analogue of a Couvette geometry and was designed to minimize the contribution of sub-phase drag to the apparent torque measured by the pressure transducer. To evaluate the contribution of surface drag relative to the sub-phase drag, a dimensionless number called the Boussinesq number (Bo) is defined under shear flow conditions:

$$Bo = \frac{\text{surface drag}}{\text{subphase drag}} = \frac{\mu_s \frac{V}{L_b} P_I}{\mu \frac{V}{L_s} A_S} = \frac{\mu_s}{\mu_b G} \quad (1)$$

where μ_s is the surface shear viscosity (Pa.s.m), μ_b is the viscosity of sub-phase (Pa.s), V is the characteristic velocity, L_b and L_s are the characteristic length scale over which the velocity decays at the bulk sub-phase and surface, respectively. P_I and A_S are the contact perimeter and area between the geometry and the surface, respectively. G is the characteristic length of the geometry, which is 0.7 mm for the DWR geometry.⁵⁰ The ring was carefully placed at the air-water interface by observing the appearance of capillary rise. The reported steady state torque at fixed angular velocities was the average of at

least 6 measurements. The detailed procedures are presented in the Supporting Information and the calculated velocity profiles are in Figure S2. The contribution of sub-phase drag to the measured steady state torque was evaluated with Boussinesq number and corrected with the iterative numerical procedures described by Vandebril et al..⁵⁰

2.6. C/W Foam Formation and Apparent Viscosity. The apparatus for measuring foam viscosity in high pressure is shown in Figure 1, which was adapted from previous studies.^{11,38,49} A water bath was used to control the temperature. Isco syringe pump with a Series D pump controller was used to inject CO₂. Aqueous formulations were injected by a second Isco syringe pump via a high pressure accumulator. Before co-injection of CO₂ and aqueous solution, the saturation of the porous media was achieved by running a sufficient volume of aqueous solutions (40 mL) through the beadpack (pore volume = 0.45 mL). The mixture of CO₂ and aqueous solution entered a glass bead pack with hydrophilic pores for foam generation. The glass bead pack has inner diameter of 0.38 cm and length of 11.3 cm, packed with 180 µm spherical glass beads (70-100 mesh soda-lime silica glass, stock number P-0080, Potters Industries Inc., Valley Forge, PA). The pore throat size in the glass bead pack ranges from 28 to 75 µm for hexagonal and cubic packing of 180 µm spheres, respectively. The foam then passes through a capillary tube viscometer and the apparent viscosity (μ_{app}) is calculated from the measured pressure drop (ΔP) with the Hagen–Poiseuille equation:

$$\mu_{app} = \frac{\pi \cdot \Delta P \cdot R^4}{8 \cdot q \cdot L} \quad (2)$$

where R is the capillary tube inner radius, q is the volumetric flow rate, and L is the length between the ΔP cells. The inner diameter of the capillary tube is 762 µm. During foam generation in the glass bead pack at 200 ft/day of superficial velocity, the shear rate in the capillary tube is 200 s⁻¹. The residence time in the glass bead pack is 54 s, and in the capillary tube is 107 s. The generated foam then flows into a high pressure view cell equipped with a sapphire glass window where the appearance of foams can be visually observed. Finally, the foam flows through the back pressure regulator where the system pressure at the outlet is controlled to be within ± 100 psia.

2.7. C/W Foam Microscopy and Stability. The foam bubble size and size distribution were measured at room temperature *in situ* with a high pressure microscopy

cell installed at the exit of the glass bead pack.¹¹ The microscopy cell was mounted onto a microscope (Nissan Eclipse ME600). The image from the microscope was captured with a Photometrics CoolSNAP CF CCD camera connected to a computer. Pictures at different time intervals were captured to show the foam stability over time. The images were analyzed with Image J software. Bubble size and size distribution were averaged over at least 100 bubbles. The Sauter mean diameter D_{sm} and the dimensionless polydispersity U_{poly} are calculated as follows:

$$D_{sm} = \frac{\sum_i D_i^3}{\sum_i D_i^2} \quad (3)$$

$$U_{poly} = \frac{1}{D_{med}} \frac{\sum_i D_i^3 |D_{med} - D_i|}{\sum_i D_i^3} \quad (4)$$

where D_i is the diameter of a foam bubble, D_{med} is the median of the volume averaged bubble diameter in the foam.

3. RESULTS AND DISCUSSION

3.1. Aqueous Phase Behavior for All Systems. The phase behavior of the various binary and ternary mixtures of solutes was measured with low shear stirring in CO₂ saturated 2% w/v KCl brine (Debye length = 0.56 nm) versus pressure at 50 °C to identify boundaries for one-phase transparent solutions (Figure S1). For CO₂ saturated brine at 3000 psia and ~ pH 4, the LAPB surfactant with pK_a of ~5 is positively charged, opposite to that of the anionic silica NPs and HPAM. Transparent aqueous dispersions were observed for each of the amphiphiles alone in CO₂ saturated 2% KCl brine from 0 to 5000 psia, indicating good solvation. For 1% NPs and LAPB, the aqueous dispersions remained transparent up to 0.08% surfactant concentrations and then became cloudy. Similarly, the mixture of 0.1% HPAM and LAPB, with and without NPs, remained transparent up to 0.08% surfactant and then underwent a transparent-to-cloudy transition as LAPB concentration increased. In contrast, mixtures of HPAM and AOS, with and without silica NPs, remained transparent at all tested conditions as expected. In the case of mixtures with oppositely charged species, the electrostatic and hydrophobic interactions produced turbid dispersions, and eventually precipitated as NP-surfactant or polymer-surfactant large aggregates.⁵¹ For the like-charged HPAM-AOS system, the

electrostatic repulsion did not result in phase separation into polymer-rich phase and surfactant-rich phase.^{52,53}

3.2. Systems Composed of Surfactant and NPs. In this section, the interfacial tension, surface viscosity, foam viscosity and foam stability with mixtures of oppositely charged NPs and LAPB surfactant were characterized. Synergistic interactions between the LAPB and NPs were shown to increase the foam viscosity and stability.

3.2.1. CO₂-Water Interfacial Tension. To probe the interfacial behavior, the interfacial tension (IFT) between CO₂ and 2% KCl brine was measured at 3000 psia and 50 °C in presence of surfactant alone, or with nanoparticles, or with nanoparticles and polymer as shown in Figure 2. Upon adding LAPB surfactant, the IFT was reduced from ~22 mN/m to ~5 mN/m above the CMC. The addition of NPs to the surfactant solution produced only a slight increase in the IFT. At 0.08% LAPB above the CMC, where the IFT reaches a plateau, the mixture was still soluble in the bulk aqueous phase (Figure S1).

The relatively low IFT of < 6 mN/m above the CMC indicates that the surfactant head group solvation was partially balanced by the solvation of the surfactant tail by CO₂. The slight increase in IFT upon addition of negatively charged NPs indicates that a significant amount of surfactant was present on the C/W interface, in addition to the amount adsorbed on the NP surfaces, due to electrostatic attraction. In this case, the adsorption of surfactant to the NPs surfaces must be weak as a large amount of surfactant remains available to adsorb at the CO₂-water interface and lower the IFT. This phenomena has been discussed in detail for weakly interacting systems of anionic silica NPs with zwitterionic caprylamido propyl betaine surfactant⁵⁴, as well as surface active fumed silica particles with nonionic alkylpoly(oxyethylene) surfactant at oil-water interfaces⁵⁵. The lack of strong adsorption of LAPB surfactant in the cationic protonated form on the anionic NP surface may be attributed to the presence of the non-ionic stabilizing ligands on NP surface.

3.2.2. Air-Water Surface Viscosity. The steady-state surface viscosity of 2% KCl brine (relative to air) containing LAPB surfactant, or silica NPs, and mixtures of the two at pH 4 and 50 °C were measured at an angular velocity of 1 rad/s. The results are given in Table 1. The surface viscosities of all systems were very low, ~ 10⁻⁶ Pa s m,

indicating a fluid-like surface as often seen for surfactant monolayers.⁵⁶ Thus, the adsorption of NPs did not significantly modify the surface viscosity.

3.2.3. C/W Foams Stabilized with NPs and Surfactants. The viscosity of $\phi = 0.75$ foams produced with either very dilute LAPB (0.01%), or 1% NPs, or a mixture of the two is shown in Figure 3a. By itself, the surfactant below the CMC was too dilute to stabilize foams. In DI water, the apparent viscosity measured with the NPs alone was very low (1.8 cP) and foam was not observed in the view cell. As the salinity increases, the viscosity increases, suggesting the NPs were “salted out” and migrated from the aqueous phase to the interface.³⁸ For 3% KCl brine, the viscosity reached 16 cP for a foam with fine opaque white texture.³⁸ We attributed this foam formation and stabilization to a decrease in the hydrophilicity of the NPs where the SiO^- charges are screened, thus driving the NPs to the interface, as seen by Binks et al. for silica NPs stabilized air-water foams.³⁷ Interestingly, the combination of surfactant and NPs resulted in synergy whereby the viscosities were much higher than expected from a combination of the values from each species alone. At all salinities tested, the opaque white foams had viscosities in the range of 20-27 cP at a salinity of 0 to 3% KCl. The LAPB surfactant in the cationic protonated form likely adsorbed on the silica NPs surfaces, lowering their hydrophilicity and raising the interfacial activity. The synergistic effect decreased as salinity increased, as the salt also made the NPs less hydrophilic.

Figure 3b shows the viscosity of C/W foams generated with 1% silica NPs and increasing concentrations of LAPB surfactant at 50 °C and 2% KCl brine. At only 0.01% surfactant below the CMC, the foam viscosity decreases monotonically as ϕ_C increases, and eventually above ϕ of 0.90, foam was not generated. At higher surfactant concentrations above the CMC, $\phi = 0.85$ -0.95 foams with much higher viscosities were generated. For example, for mixture of 1% silica NPs and 0.08 % LAPB where NPs starts to flocculate (Figure S1), foams with a viscosity of 70 cP and 36 cP at ϕ of 0.90 and 0.95, respectively, were stabilized. To our knowledge, highly viscous CO_2 foams at $\phi > 0.90$ are very rare. At higher surfactant concentrations, a large increase of foam viscosity was observed reaching 70 cP for 1% LAPB at a ϕ of 0.95 (Figure 3c). Surfactant with concentrations above 0.08% induces flocculation and precipitation of silica NPs, as shown in Figure S1. Similar results were also observed by Binks et al⁴⁶ whereby

emulsions stabilized with a mixture of anionic surfactant and cationic alumina-coated silica NPs were most stable at surfactant concentrations corresponding to flocculated NP dispersions.

The evolution of foam texture at $\phi = 0.95$ over time at room temperature is shown in Figure 4. Clearly, the initial bubble size was decreased by a factor of 3 upon addition of NPs at LAPB concentration of 0.08%. The Sauter mean diameter (D_{sm}) of bubbles stabilized with LAPB alone increased dramatically within hours, while that with the mixture of NPs and LAPB only increased slightly from 72 μm to 97 μm over 3 hours, indicating the NPs effectively stabilized foam against coalescence and Ostwald ripening.

The evolution of the mean bubble size is governed by the two competing processes of bubble generation and bubble destruction, both of which are influenced by the concentrations of the surface active agents.³⁵ The reduction in bubble size upon addition of silica NPs to the surfactant solution will now be explained in terms of various effects on lamella creation and stability as summarized in Table 3. The foam viscosities when generated with $> 0.08\%$ versus 0.01% LAPB are higher in part due to crossing the CMC, as shown in Figure 2, whereby the IFT was decreased to 6.6 mN/m. The lower IFT decreases the thermodynamic energy penalty for creation of bubbles. Furthermore, the presence of micelles above the CMC raises the availability of the surfactant for transporting to the expanding interfaces during lamella creation.⁵⁷ Another important manifestation of the lower IFT is the decrease of the capillary driving force for the drainage velocity V of the aqueous phase in the lamella to the plateau borders, as described by the relationship³

$$V = -\frac{dh_f}{dt} = \frac{h_f^2}{3\mu_e R_f^2} \Delta P_{film} \quad (5)$$

where $\Delta P_{film} = 2(P_c - \Pi_d)$. P_c is the capillary pressure originating from the curvature at the Plateau border. Π_d is the disjoining pressure. μ_e is the viscosity of the continuous phase, and R_f and h_f are the radius and thickness of the thin film, respectively. The reduction in IFT with surfactant also provides an opportunity to develop Marangoni interfacial tension gradients that slow down film drainage. Also, surfactant micelles may provide structural forces that influence the disjoining pressure.³⁶

The adsorption of relatively hydrophilic silica NPs onto negatively charged interfaces can be facilitated by the presence of salts.^{35,40} Also, in the current case, the electrostatic interactions with the LAPB in the cationic protonated form are attractive and favor adsorption. As LAPB surfactant adsorbs to silica NPs, the contact angle of the initially very hydrophilic NPs is shifted towards a more balanced state of 90° favoring adsorption at C/W interface.

Also, the ordering of NPs layers in the lamella could lead to large structural forces in the disjoining pressure and therefore slower drainage rates.³⁶ With slower drainage, the lamella remain thicker and are less prone to breakage by capillary wave instabilities and by nucleation of holes in the film.⁵⁸ The thermal activation energy barrier (W^*) for coalescence can be expressed as⁵⁸

$$W^* = \frac{\pi h_f^2 \sigma_h^2}{\gamma} \quad (6)$$

where h_f is the thickness of the lamella film, σ_h is the interfacial tension of the curved border of the hole, and γ is the interfacial tension of a planar interface. Clearly, increase of the film thickness greatly increases the lamella stability against rupture. Also, the strong capillary interactions between neighbouring particles at the liquid menisci may stabilize lamella against coalescence.³⁴ The reduction of particle charge with surfactant adsorption as shown in Figure S1 may result in particle flocculation, which is known to provide a greater steric barrier for lamella stability against coalescence, as well as raise the continuous phase viscosity to slow down drainage (Figure 3d), as seen for silica and hexadecyltrimethylammonium bromide,⁴⁶ as well as silica and caprylamidopropyl betaine⁵⁴.

The time evolution of D_{sm}^3 is shown in Figure 5. Ostwald ripening is driven by the Laplace pressure difference between bubbles of different curvature. The Lifshitz and Slyozov, followed by Wagner (LSW) theory for the Ostwald ripening rate for diffusion from a curved bubble to a flat interface is given by

$$\Omega_3 = \frac{dD_{sm}^3}{dt} = \frac{64\gamma D_{diff} S V_m}{9RT} F \quad (7)$$

where D_{diff} is the molecular diffusion coefficient, S is the bulk solubility, and V_m is the molar volume of the internal phase. F is a correction factor incorporated to account for the effects of a small diffusion length and nondilute conditions. In contrast to coalescence

where bubble polydispersity increases significantly over time, Ostwald ripening tends to even bubble sizes out. A significant increase of the D_{sm} and the bubble polydispersity was not observed for mixtures of NPs and LAPB (Figure S9), indicating that Ostwald ripening was more prevalent than coalescence. Similar decrease in Ostwald ripening rates upon addition of particles were also observed for air-water foams stabilized with fumed silica particles,⁵⁷ and was attributed to an increase in the interfacial dilatational elasticity. The dilatational elasticity (E) is defined as

$$E = -d\gamma/d\ln A \quad (8)$$

where A is the interfacial area. Due to the large desorption energy of particles at the interface and the slow mass transfer between the bulk phase and interface, the change in surface excess amount of NPs upon variations of interfacial area A is relatively small. Therefore, the dilatational elasticity of NP stabilized interfaces tends to be much higher than in the case of surfactant stabilizers.^{57,59,60} Higher surface dilatational elasticity may lead to lower Ostwald ripening rates, as expected from numerical simulations⁶¹ and experimentally observed for emulsions stabilized with surfactants^{62,63} and for air-water foams stabilized with particles.⁵⁷ Direct measurements of dilatational elasticity in high pressure systems are very rare and beyond the scope of this study. Also, the Ostwald ripening rate may be decreased due to the strong capillary effects between NPs at interface which modifies the curvature of the interface,³⁵ where compression of particle layers upon shrinking of drop/bubble diminishes the macroscopic interfacial tension by creating configurations with zero mean curvature of the fluid interfaces between particles.

3.3. Systems with Surfactant, NP and Polymer. In this section, the addition of viscoelastic polymer to a system with surfactant and NPs will be shown to raise the bulk viscosity and the surface viscosity, which enhances the foam stability relative to the case of only surfactant and NPs. The surfactant concentration was chosen to be 0.08% above the CMC, so that allows reduction of IFT and maintaining a transparent aqueous phase.

3.3.1. CO₂-Water Interfacial Tension. Upon addition of HPAM to the mixture of LAPB and NPs, the plot of IFT versus LAPB concentration in Figure 2 became more complex. A second plateau was observed at the critical aggregation concentration (CAC) for a LAPB concentration of $\sim 2 \times 10^{-4}$ %. In the presence of high pressure CO₂ the LAPB surfactant was positively charged, and thus highly solvated in the brine. The presence of a

CAC on the IFT isotherm below the CMC has been observed previously with other oppositely charged polymer-surfactant systems, such as mixtures of dodecyl trimethylammonium bromide with poly(styrene sulfonate)³³, polyacrylic acid²⁶ and poly(acrylamide-co-acrylamidomethylpropanesulfonate)⁶⁴. The plateau above the CAC indicates that the interactions of surfactant and polymer make less surfactant available to orient at the C-W interface to lower the IFT. This behavior may be caused by formation of polymer-surfactant complexes in the bulk or at the interface, which remove free surfactant.⁵¹ We will further discriminate between these two types of complexes below with surface viscosity measurements. At higher surfactant concentrations above the CMC, the interfacial tension decreased to similar values as seen for surfactant alone, consistent with the large activity of surfactant.⁵¹

3.3.2. Air-Water Surface Viscosity. The surface viscosities for systems with a sufficient concentration of added HPAM were shown to be much higher than for the systems with only NPs and surfactant (Table 1). The surface viscosity remained low for dilute HPAM at a concentration of 0.1% either with or without LAPB and NPs. However, for 0.88% HPAM alone or with NPs and either LAPB or AOS, it increased by 2- 3 orders of magnitude and reached $\sim 10^{-3}$ Pa s m, indicating polymer entanglement above the dilute-semidilute transition. Also, the surface viscosity in the plateau region at steady state (Figure 6) for the two cases with added LAPB was about 50% larger than that of HPAM alone, suggesting the surfactant raised adsorption of HPAM at the surface.²⁹ This surface adsorption may be facilitated by the electrostatic and hydrophobic interactions of HPAM with oppositely charged surfactant at the interface, as well by adsorption of HPAM-surfactant complexes formed in the bulk, consistent with the aforementioned CAC measurement.^{51,65}

From dynamic measurements of surface viscosity versus time, the viscous interfacial film was formed over ~ 80 min for HPAM with added LAPB, or LAPB and NPs (Figure 3). The slow mass transfer of polymer from the bulk to the interface can be attributed to the high aqueous phase viscosity, and electrosteric repulsion with the polymer already adsorbed at the interface. As a control, we substituted the anionic AOS surfactant for the LAPB surfactant, such that the charge of all three species was negative. Here the added surfactant and NPs did not raise the surface viscosity relative to HPAM

alone (Table 1), perhaps as a result of the electrostatic repulsion between all components. Similarly to our experiments with LAPB and HPAM, oppositely charged polyelectrolytes and surfactants such as mixtures of poly(styrene sulfonate)³³ or polyacrylic acid²⁶ with dodecyl trimethylammonium bromide also exhibited formation of viscoelastic interfacial films at air-water surface, as driven by the electrostatic and hydrophobic interactions.

3.3.3. Apparent Viscosities of Foams including HPAM Polymer. The viscosities of C/W foams stabilized with 1% silica NPs and LAPB surfactant increased with an increase in the HPAM concentration as shown in Figure 7. For only 0.01% LAPB surfactant below the CMC, the viscosity of $\phi = 0.90$ foam increased from 1 cP to 25 cP by addition of 0.1% HPAM polymer. However, at higher ϕ of 0.95-0.98, only very weak foam was present as seen in the view cell. In contrast, at higher LAPB concentrations above the CMC the foams at both ϕ values became highly viscous. For example, with 0.1% HPAM, 1% silica NPs and 0.08% LAPB, strong foams were formed with viscosities of 160, 68 and 24 cP at ϕ of 0.90, 0.95 and 0.98, respectively. With a further increase of polymer concentration to 0.88% they were 210, 100, and 34 cP at the same ϕ . The foams were also found to be shear thinning with power-law index of ~ 0.5 (Figure S6 and Table S3). The foam bubble size and the viscosity of the continuous phase were further characterized to shed light on the mechanisms of the increased foam viscosity. The D_{sm} of foam bubbles were determined from the micrographs of $\phi = 0.90$ foams stabilized with mixtures of 1% silica NPs, 0.08% LAPB and 0-0.88% HPAM at room temperature as shown in Figure 7 c-e. Whereas the bubble size was 72 μm and viscosity was 74 cP for foams stabilized with NPs and surfactant alone at room temperature, they became 23 μm and 274 cP, respectively, with the addition of 0.88% HPAM polymer.

It was also instructive to examine how the addition on NPs increases the viscosity for given concentrations of polymer and surfactant. The addition of 1% NPs to $\phi = 0.75$ -0.98 foams with HPAM and LAPB at 50 °C increased the viscosity significantly as shown in Figure 8. For example, while the mixture of 0.1% HPAM and 0.01% LAPB (below CMC) did not generate foam at $\phi = 0.95$, addition of 1% silica NPs yields white foam with a viscosity of 12 cP. For 0.08% LAPB above the CMC with 0.88% HPAM, the viscosity of $\phi = 0.95$ foam was enhanced from 42 cP to 98 cP. Similarly as shown in Table 2, the viscosity increased approximately two fold upon addition of 1% NPs at room

temperature. The addition of silica NPs at pH 4 and 50 °C to an aqueous dispersion of HPAM and LAPB did not significantly modify the apparent viscosity (Figure 8b). The D_{sm} was calculated from the micrographs of foams stabilized with mixtures of 0.88% HPAM and 0.08% LAPB, with and without 1% NPs at room temperature as shown in Figure 8 (c)-(f). As shown in table 2, adding 1% silica NPs decreased the bubble size by approximately one half, relative to the cases of foams stabilized without NPs. Also, the foam bubbles appear to be spherical with slight distortions at edges. The bubbles have a modest polydispersity of >0.29 as shown in Table 2. For relatively monodispersed foams, the bubble shape will transfer from Kepler cells to Kelvin cells as the internal phase volume fraction increases.⁶⁶ Transition to polyhedral Kelvin cells was not observed here, due to the relatively large polydispersity.⁶⁷

To understand the relative contributions of continuous phase viscosity and foam bubble size to foam viscosity, a superposition of viscosity curves has been performed following the approach used by Otsubo and Prudhomme.⁶⁸ Figure 9 shows the master curve for foams at $\phi = 0.90$, determined from the four foams listed in Table 2. The data can be superimposed in the form of $D_{sm}\mu_{foam}/\gamma\mu_e$ versus $\mu_e\dot{\gamma}$, where γ is the interfacial tension, μ_e is the continuous phase viscosity and $\dot{\gamma}$ is the shear rate. The scaling law analysis show the relation $\mu_{foam} \propto D_{sm}^{-1}\mu_e^{0.1}$. Clearly both the continuous phase viscosity and the foam bubble size contributed to the foam viscosity. The foam viscosity at $\phi = 0.90$ is inversely proportional to D_{sm} , and only weakly depends on the continuous phase viscosity. The scaling law determined by Prudhomme et al⁶⁸ for nine $\phi = 0.80$ oil-water emulsions is also plotted for comparison. The relation of $\mu_{emulsion} \propto D_{sm}^{-1}\mu_e^{0.32}$ was observed for oil-water emulsions.⁶⁸ In summary, the observed increase of foam viscosity upon increasing the concentrations of polymer and NPs may be attributed primarily to the decrease of bubble size. The role of the continuous phase viscosity is more of contributing to the stabilization of small bubbles than of directly affecting the foam viscosity.

The observed decrease of foam bubble size with added polymer was due in part to the enhanced stability of foam lamella against drainage and coalescence, given the larger continuous phase (Equation 5) and surface viscosities. For lamella with fluid surfaces, where the no-slip boundary condition was not present, a high surface viscosity obtained

with HPAM was beneficial for inhibiting lamella drainage.⁶⁹ In addition to the reduced drainage rates due to higher viscosity of the continuous phase and interface, the lamella were also stabilized by the adsorption of the high molecular weight polymer at the interface, which lead to stratification that adds structural forces to the disjoining pressure between bubbles.⁶⁵ The structure at the interface was complex, as the polymer may also interact with the surfactant modified NPs. These interactions possibly increased the disjoining pressure and consequently the stability of lamella against drainage (Equation 5).⁶⁵ Studies on oppositely charged polyelectrolyte-surfactant-stabilized aqueous thin films showed that such stratification effectively stabilized common black films with thickness of 10-100 nm, and prevented further thinning to ~5 nm Newton black films.^{30,31} Further, the adsorption of HPAM polymer at C/W interface could have also increased the shear and dilatational elasticity as reported for the O/W interface.²⁷ As indicated in a number of studies of air-in-water foams and oil-in-water emulsions stabilized with oppositely charged polyelectrolytes and surfactants,^{26,33} increased dilatational elasticity may also contribute to the stabilization of lamellae.²⁶ However, measurements of dilatational elasticity in high pressure systems are scarce in literature and beyond the scope of this study.

3.3.4. Effect of NPs on the Ostwald Ripening. The micrographs of bubbles as a function of time for $\phi = 0.95$ foams stabilized with mixture of 0.88% HPAM and 0.08% LAPB, with and without 1% NPs at 3000 psia and room temperature are presented in Figure 10. The plot of D_{sm}^3 as shown in Figure 5 for the two cases with HPAM is linear as expected from the LSW rate law over 10-fold increase of the volume of growing droplets. Furthermore, a significant increase of the polydispersity and mean bubble size was not observed (Figure S9 in Supporting Information), indicating a small role of coalescence relative to the dominant effect of Ostwald ripening.⁷⁰ A significant decrease of Ω_3 for systems containing NPs relative to those with only polymer and surfactant was observed. For mixture of 0.88% HPAM and 0.08% LAPB, the D_{sm} increased from 70 μm to 149 μm over 3 hrs (Figure 10). Interestingly, upon addition of 1% silica NPs, the foam became much more stable, with an increase in D_{sm} from only 42 μm to 55 μm . Even after 24 hrs, the D_{sm} only increased to 98 μm , as opposed to the heavily coarsened foam for the case without NPs, and Ω_3 was found to be unchanged for 24 hrs (Figure S9). Clearly, NPs

decrease the Ostwald ripening rates markedly by a factor of 30 (Figure 5). Also, the Ω_3 for mixture of NPs and LAPB without HPAM was in between that of the other two systems, indicating the NPs lower Ostwald ripening, in agreement with previous reports.^{35,63} The reduction in Ostwald ripening rates from the polymer is presumably due to the higher continuous phase viscosity and surface viscosity leading to less drainage and thus diffusion through thicker lamellae.⁷¹

4. CONCLUSIONS

The stabilization of ultra-high internal phase ($\phi = 0.90$ - 0.98) supercritical CO_2 -in-water foams with high viscosity of hundreds of centipoise and long lifetime in 2% KCl brine at 50°C is reported for the first time with either amphiphilic systems of NPs and surfactant, or NPs and surfactant and HPAM polymer. To our knowledge, previous studies have not examined ϕ above 0.90.^{11,38} LAPB surfactant in the cationic protonated form lowers the C/W interfacial tension to $\sim 5\text{mN/m}$ above the CMC and also attracts anionic NPs (and anionic HPAM in systems containing polymer) to the C/W interface. The NPs aid the formation of small CO_2 bubbles and markedly enhance the stability against Ostwald ripening. For systems including HPAM, as the concentration of HPAM increases, the resulting increase in continuous phase viscosity and surface viscosity slows down lamellae drainage rates and inhibits coalescence, as indicated by foams with smaller bubble size and thus increased viscosity. The increase in CO_2 foam viscosity and stability due to added polyelectrolyte is consistent with the behavior for air/water foams with oppositely charged polyelectrolyte-surfactant mixtures.^{25,72} Scaling law analysis shows that foam viscosity at ϕ of 0.90 is inversely proportional to the bubble size, and only weakly depends on the continuous phase viscosity. Ostwald ripening rates for systems containing NPs were 30-fold lower relative to those with only polymer and surfactant, perhaps due to the presence of thicker lamella and more elastic interface, as suggested for air/water foams.^{57,72} The adsorption of relatively hydrophilic NPs and polymer to C/W interface was likely facilitated by the interaction with oppositely charged surfactant as well as the presence of salt. The ability to stabilize viscous foams at ϕ above 0.90 with relatively low concentrations of NPs, surfactant and polymer is expected to find

utility in a broad range of applications, including low water hydraulic fracturing fluids and synthesis of porous materials.

Supporting Information

The aqueous phase behavior, foam viscosity, the evolution of foam bubble size and polydispersity over time, foam shear thinning behavior. Supporting information associated with this article can be found at the journal website.

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Notes

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All Figure Captions

Figure 1. Schematic of the apparatus used for foam viscosity and mean bubble size measurements. The glass bead pack was used as the foam generator.

Figure 2. Interfacial tension between CO₂ and 2% KCl brine at 3000 psia and 50 °C in presence of LAPB surfactants alone, binary mixture of 1% w/v silica NPs and LAPB surfactants, as well as tertiary mixtures of 0.1% w/v HPAM polymer (MW = 20 M), 1% w/v silica NPs and LAPB surfactants.

Figure 3. (a) Foam viscosity with LAPB alone, silica NPs alone, and mixtures of NPs and LAPB at varying salinities of 0-3% KCl. (b) Foam viscosity with mixtures of 1% silica NPs and 0-1% LAPB at ϕ of 0.75 to 0.98 in 2% KCl. (c) Foam viscosity as a function of LAPB concentrations while NP concentration is fixed at 1% in 2% KCl brine. Viscosities are measured at 3000 psia, 50 °C at a shear rate of 200 s⁻¹. (d) Aqueous phase viscosity of mixtures of NPs and LAPB at 50 °C. The concentrations in w/v % are specified in the legend. The lines are only to guide the eyes.

Figure 4. (a) Micrographs of $\phi = 0.95$ C/W foams stabilized with LAPB alone, and mixture of silica NPs and LAPB in 2% KCl at different time. Scale bar = 100 μ m. (b) Evolution of bubble size over time at 3000 psia and room temperature.

Figure 5. D_{sm}^3 as a function of time for $\phi = 0.95$ CO₂ foams in 2% KCl brine. Foams are maintained at 3000 psia and room temperature.

Figure 6. The evolution of surface viscosity over time between air and 2% KCl brine containing HPAM (diamond), mixtures of HPAM, and LAPB (triangles), and with silica NPs (squares) at 50 °C. The concentrations in w/v % are specified in the legend.

Figure 7. (a)-(b) Effect of HPAM concentrations on the foam viscosity in 2 % KCl brine at shear rate of 200 s⁻¹, 3000 psi and 50 °C. The concentrations in w/v % are specified in the legend. The lines are only to guide the eyes. (c)-(e) Micrographs of ϕ C/W foams stabilized with mixtures of 0.08% LAPB, 1% NP, and 0, 0.1% and 0.88% HPAM, respectively, at 3000 psia, 2% KCl brine and room temperature. Scale bar = 100 μ m.

Figure 8. (a) Effect of 1% NPs on the foam viscosity in 2% KCl brine at shear rates of 200 s⁻¹, 3000 psi and 50 °C. The concentrations in w/v % are specified in the legend. The lines are only to guide the eyes. (b) Viscosity of the aqueous phase containing mixtures of 0.88% HPAM and 0.08% LAPB, with and without 1% silica NPs at pH 4. (c)-(d) $\phi = 0.90$ foams stabilized with mixtures of 0.08% LAPB, 0.88% HPAM, with and without 1% silica NP. (e)-(f) $\phi = 0.95$ foams stabilized with mixtures of 0.88% HPAM, 0.08% LAPB, with and without 1% silica NP. Micrographs are collected at 3000 psia, 2% KCl brine and room temperature. Scale bar = 100 μ m.

Figure 9. Master curve for C/W foams at $\phi = 0.95$ compared with literature high internal phase oil-in-water emulsions rheology data (Otsubo et al. 1994, dashed line).

Figure 10. Micrographs of a $\phi = 0.95$ CO₂ foam stabilized with (a)-(d) mixtures of 0.88% HPAM and 0.08% LAPB, and (e)-(h) mixtures of 0.88% HPAM, 0.08% LAPB and 1% silica NPs in 2% KCl brine at room temperature and 3000 psia at 5 min, 30 min, 180 min and 24 hrs, respectively. Scale bar = 100 μm .

All Tables

Table 1. Torque measured with double wall geometry at the air-water interface, Boussinesq number ($\mu_s/\mu_b G$) and the air-water surface viscosity after correction of sub-phase drag.

Systems	Torque (mN.m)	Boussinesq number (Bo)	Surface viscosity (10^6 Pa s m)
1% NP	0.38 ± 0.02	6.0	2.3
0.08% LAPB	0.32 ± 0.02	5.2	2.0
0.1% AOS	0.42 ± 0.02	7.8	3.0
1% NP + 0.08% LAPB	0.40 ± 0.02	6.3	2.4
0.1% HPAM	0.64 ± 0.03	0.71	5.0
0.88% HPAM	93 ± 3	1.7	720
0.1% HPAM + 1% NP + 0.08% LAPB	0.77 ± 0.03	0.86	6.0
0.88% HPAM + 1% NP + 0.08% LAPB	138 ± 4	2.4	1000
0.88% HPAM + 1% NP + 0.1% AOS	87 ± 3	1.6	680

All the measurements were done at an angular velocity of 1 rad/s, 50 °C in 2% KCl brine.

Table 2. Sauter mean diameter and apparent viscosity of C/W foams at 3000 psia, 2% KCl brine and room temperature

Mixtures	CO ₂ volume fraction	D _{sm} (μm)	U _{poly}	μ _{continuous phase} (cP)	μ _{foam} (cP)
0.08% LAPB and 1% NP	0.90	72	0.98	1	74
0.1% HPAM, 0.08% LAPB and 1% NP	0.90	49	0.40	5	160
0.88% HPAM, 0.08% LAPB and 1% NP	0.90	23	0.41	80	274
0.88% HPAM, 0.08% LAPB	0.90	46	0.29	80	147
0.88% HPAM, 0.08% LAPB and 1% NP	0.95	36	0.36	80	105
0.88% HPAM, 0.08% LAPB	0.95	74	0.34	80	53

The viscosity of continuous phase and the C/W foam are measured at 200 s⁻¹.

Table 3. Summary of the effects of surfactant (S), polymer (P) and nanoparticle (N) on the lamella generation, and lamella stabilization against drainage and Ostwald ripening.

Mechanisms	N+S	N+P+S
Lamella creation		
Reduce IFT, lowers energy penalty to generate bubbles. Micelles raises surfactant concentration available to adsorb rapidly on interface	S	S
Lamella stabilization: increase disjoining pressure		
Electrosteric repulsion	N+S	P+S, N+S
Structural repulsion	N+S	P+S, N+S
Lamella stabilization: decrease drainage rates		
Reduce IFT, lowers capillary pressure driving force	S	S
Marangoni stabilization (interfacial tension driving force)	S	S
Increase surface viscosity, presumably C/W interfacial viscosity (agrees with wasan)		P, P+S
Increase continuous phase viscosity		P
Lamella stabilization: slow down Ostwald ripening		
Interfacial dilatational elasticity	N	N
Strong lateral capillary interaction, reduce local curvature difference and the driving force for Ostwald ripening	N	N

Note: P+S and N+S mean synergistic interaction.

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Figure 1. 2 columns

Figure 2. 1 column

Figure 3. 2 columns

Figure 4. 1.5 columns

Figure 5. 1 column

Figure 6. 1 column

Figure 7. 2 columns

Figure 8. 2 columns

Figure 9. 1 column

Figure 10. 1.5 columns