A Mechanistic Study of Surfactants, Particles, and Polymers on Foam Stabilization

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Abstract. Foam stabilization by mixtures of Bentonite, Xanthan Gum (XG) as stabilizers, and surfactants such as Sodium Dodecyl Sulfate (SDS) and Hexadecyltrimethyl Bromide (CTAB) were mechanistically investigated. Surface modification, adsorption properties and foaming characteristics of both surfactants were compared. Both possess dissimilar surface modification mechanisms namely the hydrophobic interaction mechanism for SDS and ion-pair mechanisms for CTAB. SDS generates foam of 21% longer half-life and 17% better foamability as compared to CTAB. Both Bentonite-stabilized and XG-stabilized SDS foam showed improvement of half-life of up to 10000 folds and 50000 folds. A reduction in foamability of up to 24% and 40% for Bentonite and XG respectively were observed. With increasing stabilizers concentration, viscosities across different shear rates and the elastic moduli (G’) across different frequencies increase due to the increasing particles adsorption density on the air/water interface. Bentonite acts as a better synergist to SDS in foam formation as it has less viscosifying tendencies as compared to XG. It is also able to sufficiently improve SDS foam properties.

1. Introduction
Several renowned Enhanced Oil Recovery (EOR) techniques such as gas flooding and water flooding face some technical challenges such as poor sweep efficiencies, gravity overriding, and high mobility ratio [1]. These are usually caused by the low apparent viscosity of injected phase such as gas and water that results in overriding of injected phase against displaced phase, thus causing early injected phase breakthrough [2]. Foam flooding has gained large attention recently due to its ability of reducing mobility ratio, producing slug that exhibits higher apparent viscosity as compared to its constituent phases, reducing the relative permeability of gas phase, and allowing a more piston-like displacement [3-5]. Due to the presence of gas bubbles in large number that traps pores and throats, foam blocks subsequent injected phase from flowing into the highly-permeable voids, thus rendering better displacement flood front. This is known as the Jamin effect [4]. Foams are versatile great performers that possess exceptionally amazing flexibility and properties. However, robust foam stability is of utmost importance for its extensive applicability in the field of EOR. Several foam destructive mechanisms such as bubble coalescence and coarsening, liquid evaporation drainage, and inter-bubble gas diffusion across foam film exist due to the intrinsic property of foam being thermodynamically
unstable and having large interfacial areas [6-8]. Nonetheless, in porous media, foam can be regenerated through three different mechanisms namely snap-off, lamella division, and leave-behind that occur during the advancement of foam fluid in pores and throats [9].

Surfactants are usually used for foam stabilization due to their excellent surface-active properties that can effectively reduce the surface tension at the air-liquid interface [10]. However, sole surfactant stabilization is not preferable due to the thermal susceptibility of surfactant molecules and possible high salinity condition present in the reservoir that retards surfactant’s efficiencies [2]. In light of this issue, several researches have been targeted on the usage of stabilizers in synergism with surfactants to create a stable foam. Polymer such as partially hydrolyzed polyacrylamide (HPAM) had been given wide attention recently due to its ability of increasing the bulk solution’s viscosity that retards foam drainage and hence produce synergism with surfactants. It was widely-known that increment in bulk solution’s viscosity improves foam stability [11]. However, polymers are plagued with shear-related problems. When the shear rate reaches the maximum associated straining stress, polymers strain start to deform as a result of their non-Newtonian and shear-thinning behavior, which results in bulk solution’s viscosity reduction [12-14]. This present work is designed to mechanistically study the surface modifications done by different surfactants such as Sodium Dodecyl Sulfate (SDS), an anionic surfactant and Hexadecyltrimethylammonium Bromide (CTAB), a cationic surfactant on the surface of Berea sandstone, and the influence of Xanthan Gum (XG) and Bentonite on surfactant-foam performance in terms of static stability. XG and Bentonite were chosen due to their cheap, easy availability, and their respective roles as viscosifiers. The effects of the two dissimilarly-charged surfactants on the surface modifying characteristics on Berea sandstone’s surface, and these surfactants’ individual foaming performance will be first investigated, followed by the selection of the best foaming candidate for subsequent tests.

2. Experimental Study

2.1. Materials
Sodium Dodecyl Sulfate (SDS) and Hexadecyltrimethylammonium Bromide (CTAB) were purchased from Sigma-Aldrich with a purity of 98.5 % and Acros Organics with a purity of 98 %, respectively. Bentonite and XG were obtained from MI-SWACO with a purity of >80% and >60% respectively. Cylindrical Berea sandstone cores of dimension 2 × 2 × 12 inches were used in the present study for the investigation of surface modification and wettability alteration properties. Crude oil sample was obtained from Miri Crude Oil Terminal (MCOT).

2.2. Critical Micelle Concentration Identification
Measurement of conductivity was used for Critical Micelle Concentration (CMC) determination. Different concentrations of surfactants solutions were prepared and measured for conductivity under room temperature. Plots of conductivity versus surfactants concentration were plotted and the inflexion points were deemed as CMC.

2.3. Preparation of Berea Sand Samples
Clean Berea core slices were grinded and sieved using a 75-micron sieve. The sieved Berea sands were washed with ultrapure water of 18.2 MΩ resistivity for several times including the process of decanting and settling to remove any possible impurities. The decanted sands were then vacuum filtered and dried overnight at 60 °C in conventional oven. To produce oil-aged Berea sand, the sands were dissolved in crude oil and aged at 60 °C for at least 8 hours before undergoing vacuum filtration and dried at 60 °C overnight. To prepare surfactant-treated oil-aged Berea sand, the sands were dispersed in different surfactant solutions at their respective CMC for 5 minutes by using the LSP-500 laboratory ultrasonic liquid processor, before proceed to drying at room temperature under vacuum for 5 days.
2.4. Preparation of Thin Sections
Berea Sandstone cores were trimmed to a thickness of 0.2 inches, polished in two stages with 45 microns and 15 microns diamond flat lap, washed with ultrapure water of 18.2 MΩ resistivity thoroughly, followed by drying at 80 °C for 3 days under vacuum. Dried Berea thin sections were saturated with formation brine of 70000 ppm under vacuum pressure of 0.05 MPa at 60 °C for 24 hours under vacuum to remove residual induced surface charges due to polishing and trimming actions. The saturated thin sections were then dried at 70 °C for two days under vacuum, followed by aging in crude oil for at least 7 days at temperature of 60 °C to render the surface oil-wet.

2.5. Preparation of Foam Solutions and Foam Static Stability Experiment
A two-step dispersion-generation method was for foam generation. A certain mass of stabilizers was dispersed in ultrapure water using the Fann multi-mixer 9B at 16000 rpm for 8 minutes to ensure well dispersion. The stabilizers dispersion was then left untouched for 1 hour to ensure similar shearing history. Next, the stabilized stabilizers dispersion was mixed with surfactant and homogenized at 6000 rpm for 2 minutes using the Thermo Scientific Silverson L5M Homogenizer to generate foam. The foam stability was assessed by two main parameters namely half-life and foamability. Half-life is defined as the time taken for half of the original liquid volume to be dewatered out of the foam while foamability is the initial foam volume right after foam formation. The setup of the experiment is depicted in Figure 1. ImageJ (NIH, ver. 2.0, USA) was used to precisely determine the occurrence of half-life and the foamability. The foamability is reported in terms of expanding factor as shown in equation (1).

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\text{Expanding Factor} = \frac{\text{Final Foam Volume}}{\text{Initial Foam Volume}}
\]

![Figure 1. Experimental setup for foam stability experiment.](image)

2.6. IR Determination
The identification of functional groups present on clean and aged Berea sands were carried out by determining peaks present across the IR-spectra using the Cary 630 Fourier Transform Infrared Resonance (FTIR) Spectroscope (Agilent, USA) in the range of 600-4000 cm⁻¹. The instrument operates on Microlab PC software supplied by Agilent. The transmittance module was used and the Potassium Bromide (KBr) pellet technique was employed. The ratio of dried sample to KBr was set at 2:100. Pure KBr was used as the zeroing sample.

2.7. Rheological Properties of Bulk Foam Solution
The viscosities and viscoelasticity properties were quantitatively represented using the AR-1500ex Rheometer (TA Instruments, USA). Viscosities of solution were measured across shear rate of 7.5 s⁻¹ and 200 s⁻¹. Frequency sweep across 0.2 Hz to 10 Hz at a constant shear stress of 0.1768 Pa was used.
for the determination of viscoelastic properties such as the elastic modulus (G') and the viscous modulus (G''), respectively. The bulk foam solutions generated from the previous section were left undisturbed for 24 hours before the test to obliterate any possible mechanical memory effects.

2.8. Contact Angle Measurement

The contact angle was measured using the sessile drop method under room temperature condition using the DSA-100B Drop Shape Analyser (Krüss, Germany). The instrument operates on Krüss Advance Software. Approximately 10 μL of sample was gently dripped onto the oil-wetted thin section. Contact angle alterations across time were determined.

3. Results and Discussions

3.1. IR spectra of the Berea sand surface

Figure 2(a) depicts the FTIR spectra of clean Berea sand as the control sample. It was found that Quartz is of vast presence in Berea sand. Peaks at 689 cm⁻¹, 800 cm⁻¹, and 916.93 cm⁻¹ which signifies bending and stretching vibrations of Si-O bonds, and deformation vibrations of Si-O-H bonds respectively, were observed. The peak at 3447.78 cm⁻¹ is attributed to the presence of remnant water adsorbed on clay minerals.

Figure 2(b) depicts the FTIR spectra of crude oil-aged Berea sand and it was found that several crude oil components such as carboxylic acid and aldehydes had adsorbed on the surface of Berea sand judging from the presence of peaks at 780.88 cm⁻¹, 1625 cm⁻¹, 1872.88 cm⁻¹, 1992.26 cm⁻¹, 2885.14 cm⁻¹, and 2924.10 cm⁻¹ which attribute to bending vibrations of C-H bond in a three-neighbouring substituted aromatic ring, aryl conjugated stretching vibration of C=C bonding, stretching vibration of –C-H group and stretching vibration of alkyl C-H bonds respectively.

Figure 2(c) depicts the FTIR spectra of CTAB-treated crude oil-aged Berea sand. Desorption of crude oil components from the surface of Berea by CTAB was confirmed by the disappearance of several transmittance peaks that attributes to the presence of carboxylic acid and aldehydes. The desorption is due to the strong electrostatic attraction between positively-charged CTAB molecules and negatively-charged crude oil components such as organic acids and aldehydes that results in the formation of ion-pair. The subsequent adsorption of CTAB on Berea’s surface was proven by the appearance of peaks at 1608.35 cm⁻¹, 2853.38 cm⁻¹, and 2918.51 cm⁻¹ which signify presence of –NH2 bonding that attributes to the alicyclic quaternary ammonium group of CTAB’s head group, and C-H stretching and deformation vibrations which signifies the methylene group of CTAB’s tail group [15].

Figure 2(d) shows the FTIR spectra of SDS-treated crude oil-aged Berea sand. By comparing Figure 2(b) and Figure 2(d), certain crude oil components are still adsorbed on Berea’s surface which was proven by the existence of peaks at 1621.39 cm⁻¹ and 1776.08 cm⁻¹ which attribute to C=O aryl conjugated stretching vibration and carboxyl group respectively. Furthermore, SDS adsorption on Berea’s surface is confirmed with presence of peak at 779.01 cm⁻¹ which attributes to the stretching vibration of S-O bonds, and peak at 1082.79 cm⁻¹ which signifies presence of sulf oxide SO₂ asymmetric stretching vibrations. Anionic SDS does adsorb on Berea’s surface due to the presence of weak capillary forces between SDS’s hydrophobic tail and the anionic crude oil components adsorbed on Berea’s surface as a result from hydrophobic interactions [16]. Both SDS molecules and anionic crude oil components form hydrophobic pairs with the negatively-charged hydrophilic SDS head molecules facing outwards from the surface. A water-wet bilayer that repels subsequent nearing surfactant molecules and crude oil components was formed and thus rendering the surface extremely water-wet.

3.2. Critical Micelle Concentration of Surfactants

Critical Micelle Concentration (CMC) is the concentration at when formation of surfactant micelles occurs. Figure 3 and Figure 4 depict the conductivity of SDS and CTAB solution across different surfactant concentration respectively. A change in conductivity increment rate was observed, which
signifies the CMC of the surfactant. The CMCs of SDS and CTAB are 0.203 wt% and 0.022 wt% respectively. At lower surfactant concentration prior to CMC, a steeper increment rate of conductivity was found due to a higher ionization degree of surfactant molecules as surfactant monomers act as a great electrolyte. At surfactant concentration beyond the CMC, the rate of conductivity increment slowed due to micelle formation. The electrostatic repulsion between each respective micelle and the encapsulation of surfactant molecules’ hydrophobic tails within micelles resulted in less binding site for electron movement. These reduced the net electrostatic charge and caused lowered ionization degree. Furthermore, micellar charge neutralization as a result from the electrostatic interaction between hydrophilic head and hydrophilic tail within a surfactant micelle also contributed to lower ionization degree [17].

Figure 2. FTIR spectra of (a) Berea sand particles (b) Oil-aged Berea sand particles (c) CTAB-treated oil-aged Berea sand particles (d) SDS-Treated Oil-Aged Berea sand particles.

3.3. Static Foam Stability and Wettability Alteration Properties of Different Surfactants
Figure 5 summarizes the comparisons between SDS and CTAB in terms of foam properties and wettability alteration properties. The surfactants’ concentrations were set at their respective CMC. In terms of foam properties, SDS formed foam with drainage velocity of 0.88 cm/min, a half-life of 6 minutes and a foamability of 2.25. CTAB formed foam with a drainage velocity of 1.22 cm/min, a half-life of 4.75 minutes, and a foamability of 1.88. The drained foam height versus time for SDS foam and CTAB foam are depicted in Figure 5(a) and Figure 5(b) respectively. The contact angle of distilled water on crude oil-aged Berea sandstone was 82.1° and it was deduced that the surface is of intermediate-wet to oil-wet. From Figure 5(c), it is shown that within 200 s, SDS altered the contact angle to 3.2° which shows extremely water-wet properties due to the formation of water-wet bilayer as stated previously where adsorbed SDS oleophobic head groups are facing upwards, thus facilitating the flattening of water droplet on Berea’s surface and renders the surface water-wet. On the other hand, CTAB altered the wettability to a more water-wet state at the beginning but the contact angle
rises after a short period of time as depicted in Figure 5(d). This can be explained further by the formation of ion-pairs, the micellar solubilization of ion-pairs, and the subsequent adsorption of CTAB molecules on Berea’s surface as stated previously. The rise in contact angle is due to the electrostatic repulsion between adsorbed CTAB molecules on Berea’s surface and the micelles formed in the bulk phase. This condition is known as autophobing in which a hydrophobic monolayer forms at the interface of oil/water/rock [18]. From these results, it was deduced that SDS is a better foaming agent that forms foam with better properties.

![Figure 3. Conductivity of SDS solution across different SDS concentrations.](image)

![Figure 4. Conductivity of CTAB solution across different CTAB concentrations.](image)

3.4. Effect of Stabilizers on Bulk Foam Stability
This section aims to study the stabilizing effect of stabilizers such as Bentonite and XG on SDS foam in terms of bulk foam stability where half-life and foamability are concerned. Bentonite and XG at varying concentrations were added into SDS solutions at its predetermined CMC. Figure 6 depicts the concentration of stabilizers added into SDS solution versus their respective foam properties such as half-life and foamability. It was shown that with increasing concentration of both Bentonite and XG, the half-life of SDS foam improves significantly by up to 50000 folds as compared to the half-life of foam formed by solely SDS at its CMC. Bentonite improves the half-life of SDS foam up to 10 hours without adversely affecting the foamability (with decrement of up to 24% as compared to pure SDS foam), while on the other hand XG sacrifices foamability (with decrement of up to 40%) albeit providing a long half-life of up to 2 days. This is due to the rheological properties improvement brought by two respective stabilizers, which will be further discussed in the next section.
3.5. Rheological Properties of Bulk Foam Solution

The rheological properties of Bentonite-stabilized SDS foam and XG-stabilized SDS foam were studied in terms of viscosities across different shear rates and the viscoelastic moduli in order to better characterize their stabilizing mechanisms. Figure 7(a) and Figure 7(b) depict the viscosities of Bentonite-stabilized SDS foam solution and XG-stabilized foam solution across different shear rates respectively. It is found that with increasing concentration of stabilizers added into SDS solution, the viscosities across different shear rates increase, which coincides with the increment in foam half-life [11]. XG is found to have a greater viscosifying effect as compared to Bentonite even at high shear rates. This can be attributed to XG’s special molecular structure which is made up of carbohydrate units that are side-chained grafted with polar groups which make them as branched rigid-rod structures that allow better shear resistance [3]. This in turn explains the low foamability that XG-stabilized SDS foam attain in the previous section as according to Reynolds number (Re) equation, high viscosity attributes to lower Re and thus lower turbulence for the dispersion of gas in liquid.

Figure 8(a) and Figure 8(b) depict the elastic modulus (G’) and viscous modulus (G”) against frequency for Bentonite-stabilized SDS foam solution and XG-stabilized SDS foam solution respectively. With increasing stabilizers concentration, both moduli increase due to the presence of stronger electrostatic interactions within the individual components in foam solution that in turn results in improved film strength and reduced film permeability [3]. In this present study, it is shown that Bentonite-stabilized SDS foam solution has a more elastic-dominant behavior as compared to XG-stabilized SDS foam as generally, Bentonite-stabilized SDS foam solution has higher values of G’, and a larger separation between G’ and G” at each Bentonite concentration. Furthermore, XG’s excellent viscosifying properties can be seen from the steep increment rate of XG-stabilized SDS foam’s G” at each XG concentration. On the other hand, Bentonite-stabilized SDS foam solution has a slower increment rate of G’ along with increasing Bentonite concentration, which signifies slower viscosities increment progression. From the results shown, Bentonite provides better synergism to
SDS due to its adequate foam stabilizing properties without excessively increasing the viscosities of bulk solution that affects the foamability adversely.

Figure 6. Half-life and foamability versus the concentration of (a) Bentonite and (b) XG added into SDS solution at CMC.

Figure 7. Viscosities across shear rates for (a) Bentonite-stabilized and (b) XG-stabilized SDS foam solution.

4. Conclusion
From the studies done, both SDS and CTAB alter wettability of oil-wetted Berea sandstone’s surface to water wet through hydrophobic interaction and ion-pair mechanism respectively. SDS molecules form hydrophobic pairs with adsorbed crude oil components on Berea’s surface with the hydrophilic head of SDS molecules facing outwards making the surface water-wet while on the other hand, CTAB molecules form ion-pairs with the adsorbed crude oil components on Berea’s surface, subsequently desorbing them from surface and thus attributing the surface hydrophilic. These were subsequently proven by the existence of evident functional groups on the surface of Berea sandstone after treatment, and their wettability alteration properties. At their respective CMC, SDS foam possesses half-life and foamability of 21% and 17% greater than CTAB foam. Foam stabilizers such as Bentonite and XG were able to improve SDS foam by up to 50000 folds as compared to pure SDS foam. Increasing stabilizer concentration results in increasing half-life and decreasing foamability due to the retardation of gas dispersion into liquid as a result of excessive viscosity increment; whilst longer half-life is simply attributed to the increased particles adsorption density on foam film and increased bulk solution viscosity. With increasing stabilizers concentration, bulk foam solution yields greater value of elastic modulus ($G'$) across frequencies of 0.2 Hz – 10 Hz, which can be attributed to the increasing particles adsorption density at the air/water interface that results in improved interfacial elasticity. XG has a more prominent viscosifying effect as compared to Bentonite judging from the viscosities across different shear rates and the higher value of $G''$ across different concentrations. This is due to the rigid rod and branched structure of XG where monomers are held together by strong hydrogen bonding that
renders great shear resistance. Bentonite on the other hand does not viscosify the bulk solution excessively while sufficiently improves SDS foam properties, making it a better synergist of SDS.

![Figure 8](image)

**Figure 8.** Viscoelastic properties of (a) Bentonite-stabilized and (b) XG-stabilized SDS foam solution.

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