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Experimental Investigation of the Effects of Partially Hydrolyzed Polyacrylamide (PHPA) and Xanthan on Foam Stability

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Abstract

In this study the feasibility of improving foam stability by polymer addition is investigated. Alkyl Ethoxy Sulfate (AES) surfactant as the anionic surfactant and Cetyl Trimethyl Ammonium Bromide (CTAB) as the cationic surfactant are used as the foaming agents. The effects of polymer addition on foam stability is determined by the addition of different concentrations (0-3000 ppm) of PHPA and xanthan to foam solution and finally foam stability as the time taken for 80% of the foam to collapse was determined accordingly. The experimental results showed that CTAB performed better than AES as the foaming agent. Foam stability was enhanced by the addition of both PHPA and xanthan to foam solutions. Xanthan was more compatible with formation brine and PHPA was more compatible with fresh water to enhance foam stability.

Keywords: PHPA; Xanthan; Polymer; Surfactant; Foam stability

Abbreviations: AES: Alkyl Ethoxy Sulfate; CTAB: Cetyl Trimethyl Ammonium Bromide; PHPA: **Partially** Hydrolyzed Polyacrylamide Polymer; PAM: Polyacrylamide; AMPS: Polyacrylamide Sulfonated Copolymer: PAHM: Hydrophobically Modified Polyacrylamide

Introduction

Foam has been widely used in many disciplines of petroleum industry over decades. One of these applications of foam is during enhanced oil recovery, where foam plays an important role in controlling the mobility of the injected gas and increasing the sweep efficiency [1-4]. Foam is defined as the dispersion of gas phase in a continues liquid phase. The gas phase is

discontinued by a thin liquid phase called lamellae. The stability of foam is directly related to the stability of these lamellas, where the higher the lamellas stability, the higher the foam stability. One of the major controlling parameters is viscosity of liquids locating in these lamellas. Thus, the addition of a thickening agent to improve the viscosity of bulk liquid phase could be beneficial to improve the lamellas stability [5-9]. Polymers are the most widely used materials to increase the solution viscosity and consequently increasing the lamellae characteristics. PHPA and xanthan are two of the most widely used polymers ton increase solution viscosity [9-11].

One of the earliest works on the application of polymers to enhance foam stability was conducted by Sydansk

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[12,13]. This researcher added different concentrations of PHPA to the foams prepared by AOS surfactant. He concluded that polymer addition is very effective in improving foam stability. Conventional foam stability made by AOS surfactant was improved by increasing the concentration of PHPA. He also concluded that polymer molecular weight is very effective in this process. While the higher the molecular weight of the polymer, the higher the stability of the produce foam.

In another study conducted by Wang et al [14], the feasibility of PHPA addition to foam was investigated. Polymer concentrations of 0.05%, 0.1%, 0.15%, 0.2% and 0.25% were used to find the effect of polymer concentration of foam performance. Polyacrylamide polymers with different MW of 6000000, 10000000, 15000000 and 27000000 were used accordingly. Their results showed that polymer addition, even with the minimum concentration of 0.05 wt% is effective in improving the stability of foam. Moreover, molecular weight of the polymer found to have direct effects on foam stability where the most stable foam was found when PHPA with the molecular weight of 27000000 was used.

Zhu et al. [15] investigated the effects of salt presence on the overall performance of polymer enhanced foam stability. They used a low molecular weight polyacrylamide polymer (FP 1230) in conjunction with AOS surfactant. High salinity and low salinity brines were prepared using NaCl and CaCl₂. They concluded that polyacrylamide polymer addition increased foam stability in both fresh water saline brine, however, the presence of salts decreased foam stability as compared to fresh water.

Romero et al. [16] investigated the performance of PEF made by AOS surfactant and five different kinds of polyacrylamide polymer with different molecular weight and hydrolysis content including two partially hydrolyzed polyacrylamides (PHPA). non-hydrolyzed polyacrylamide (PAM), a sulfonated polyacrylamide copolymer (AMPS) and a hydrophobically modified polyacrylamide (PAHM) and Nitrogen in a micromodel system. They concluded that all the tested polymers are capable of improving the foam stability. Also the molecular weight of polymer found to have significant effect on foam stability. Polymers with higher molecular weight resulted in a more stable foam as compared to low molecular weight polymers.

In this study, the effects of two different polymers including a partially hydrolyzed polyacrylamide polymer (PHPA) and xanthan on foam stability is investigated. Two different surfactants including CTAB and AES surfactants

are used as the foaming agents. In addition, CO_2 is used to produce foam in graduate cylinder. Formation brine and fresh water are also used to investigate the effects of salt presence on foam stability. Moreover, foam stability as the time required for 80% of the foam to collapse is determined for each solution.

Experimental Section

Materials

In this study two different surfactants including CTAB and AES were used. The effects of polymer concentration on foam stability were investigated by the addition of PHPA and xanthan to foam solutions. Pure analytical CO_2 with the purity of 99% was used to prepare foam solutions. In addition, formation brine from one of oil fields in Iran is used.

Solution preparation

In order to prepare surfactant and polymer solutions, magnetic stirrer method was used as shown in Figure 1. Initially, polymers with the desired concentration were prepared and poured in a 1L volumetric flask. Depending on the experiment, either fresh water of formation brine was used as the solution. Then, magnetic stirrer was used to create vortex in the flask. Each solution was given 24 hours of stirring time to generate a uniform solution. After this stage, surfactant with the desired concentration was added to each solution and stirred for another 1 hour. In case of sole surfactant solution, the desired concentrations of each surfactant was added to 1L formation brine or fresh water and stirred for 1 hour. Then, the solutions were ready for foam stability measurements tests.



Figure 1: Magnetic stirrer for solution preparation.

Apparatus and methods

The foam stability apparatus consists of a $1000\,$ mL graduate cylinder named as foam column. A CO_2 cylinder, an HPLC pump and a solution container is also used. A spherical stone gas diffuser is mounted to the bottom of the graduate cylinder to produce foam in the foam column. CO_2 is injected from the bottom of the column, containing solution and foam is produced in the column. Figure 2 represents the schematic diagram of foam stability apparatus used in this study.

After filling the column with desired solution, CO_2 with the injection pressure of two bar was injected to the column. Once injection started, CO_2 created bubbles in the column and injection continued until the whole column was filled with foam. Once the whole column was filled time recording was started. Then, the time taken for 80% of the foam to collapse was measured. In other words, when only 20% of the foam was remained in the column, time recording was stopped and foam stability was measured. In addition, CMC was determined using ring method by a Krüss tensiometer (Krüss GmbH, Hamburg, Instrument Nr, K6) with a platinum-iridium ring as shown in Figure 3.



Figure 2: Schematic diagram of foam stability apparatus.



Figure 3: Krüss tensiometer to measure surface tension.

Results and Discussions

CMC measurement of the surfactants in fresh water and formation brine

In order to identify the CMC of each surfactant, different concentrations of each surfactant was prepared in fresh water and formation brine and surface tension was determined accordingly. Table 1 and Figure 1 summarize the surface tension results based on different surfactant concentrations. As it is shown in this table, increasing surfactant concentration has direct effect on reducing the surface tension. The maximum surface tension is achieved at surfactant concertation of zero, while the minimum surface tension is achieved at the maximum concertation of 5000 ppm. This trend is true for both tested surfactants in both formation brine and fresh water. However, surface tension achieved in formation brine is always higher than the surface tension achieved in fresh water. In addition, CTAB is more effective than the AES in reducing the surface tension. As it is shown in Figure 4, while using CTAB in fresh water, surface tension sharply decreases with increasing concertation to about 1000 ppm and then the decreasing trend is almost smooth with minimal changes. On the other hand, the decreasing trend in surface tension with AES continues up to 2000 ppm and then reaches a steady state.

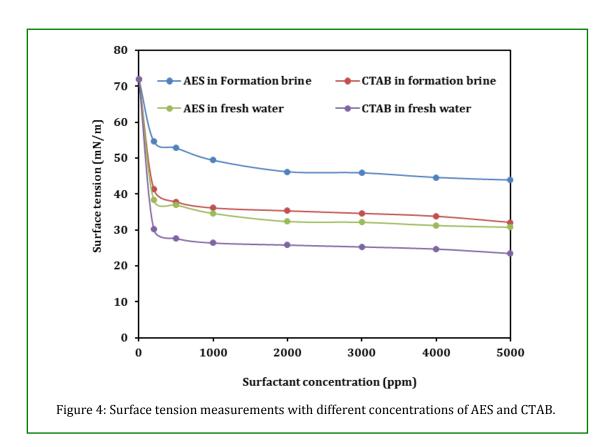
This suggests that CMC value of CTAB is 1000 ppm and CMC value of AES is 2000 ppm in fresh water and formation brine. The surface tensions of 26.4 and 32.3 mN/m are achieved at CMC values of CTAB and AES surfactant in fresh water, respectively. In addition, the surface tensions of 36.1 mN/m and 46.2 mN/m are achieved for both CTAB and AES at CMC values. Cationic

surfactants such as CTAB, with increasing the number of carbon atoms in the non-polar part (tail) of the surfactant its length is increased accordingly and are more effective

than anionic surfactants in reducing the surface tension. In addition, the presence of salts decreases the efficiency of surfactants in reducing the surface tension (17-19).

| Surfactant | Surface tension, mN/m | | | |
|---------------------|---------------------------|---------------------|-------------------------------|-------------------------|
| Concentration (ppm) | AES in fresh water | CTAB in fresh water | AES in formation brine | CTAB in formation brine |
| 0 | 72 | 72 | 72 | 72 |
| 200 | 38.3 | 30.2 | 54.7 | 41.4 |
| 500 | 37 | 27.6 | 52.8 | 37.8 |
| 1000 | 34.6 | 26.4 (CMC) | 49.4 | 36.1 (CMC) |
| 2000 | 32.3 (CMC) | 25.8 | 46.2 (CMC) | 35.3 |
| 3000 | 32.1 | 25.3 | 45.9 | 34.6 |
| 4000 | 31.2 | 24.7 | 44.6 | 33.8 |
| 5000 | 30.7 | 23.4 | 43.9 | 32.1 |

Table 1: Surface tension measurements for different concentrations of CTAB and AES in fresh water.



Foam stability in the absence of Polymer

In order to investigate the effects of polymer on foam stability, the control experiments were performed without any polymer addition. Thus, CMC values of each surfactant was selected and foam solution was prepared in both fresh water and formation brine. Then, foam stability of each solution was determined as shown in in Table 2. Foam stability was defined as the time required

for 80% of the foam to collapse. The time was measured after stopping the gas injection to the column. As shown in Table 2, foam prepared in fresh water is always more stable than the foam in formation brine. In addition, foam prepared by CTAB surfactant is more stable than the foam prepared by AES surfactant. The most stable foam is the one prepared by CTAB in fresh water (foam stability of 89 min) and the least stable foam is the one prepared by AES

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surfactant (foam stability of 52 min) in formation brine. This clearly suggests that CTAB is more effective than AES surfactant in producing stable foams. In addition, the

presence of salts in formation brine still have negative impact on surfactant efficiency and foam stability.

| Solution | Time required for 80% of foam to collapse (min) | |
|----------------------------------|---|--|
| 2000 ppm AES in fresh water | 63 | |
| 2000 ppm AES in formation brine | 52 | |
| 1000 ppm CTAB in fresh water | 89 | |
| 1000 ppm CTAB in formation brine | 64 | |

Table 2: Foam stability for the control case experiments without polymer addition.

Polymer enhanced foam stability by PHPA

In order to investigate the effects of polymer on foam stability, different concentrations of PHPA were added to foams prepared by CTAB and AES surfactant. Table 3 represents the foam stability data prepared by CTAB surfactant prepared in fresh water and formation brine with variable PHPA concentration. As shown in this table, PHPA addition has significant effect on foam stability. Foam stability or in other words, the time taken for 80% of the foam to collapse was significantly improved by PHPA addition to foam solutions. The minimum foam

stability was achieved by the addition of 500 ppm PHPA and the maximum foam stability was achieved by the addition of 3000 ppm PHPA to foam solution. Again, the presence of salt gad detrimental effect on foam stability and the polymer enhanced foam stability was always higher with fresh water rather than formation brine. As shown in this table, for the solutions prepared in fresh water, the most and the least stable foams are 198 and 91 min by the addition of 3000 and 5000 ppm PHPA, respectively. These values are 102 and 65 min for the solutions prepared in formation brine, respectively.

| PHPA concentration (ppm) | Foam stability prepared in fresh water (min) | Foam stability prepared in formation brine (min) |
|--------------------------|--|--|
| 0 | 89 | 64 |
| 500 | 91 | 65 |
| 700 | 96 | 69 |
| 1000 | 104 | 78 |
| 2000 | 148 | 91 |
| 3000 | 198 | 102 |

Table 3: Polymer (PHPA) enhanced foam stability prepared by CTAB surfactant.

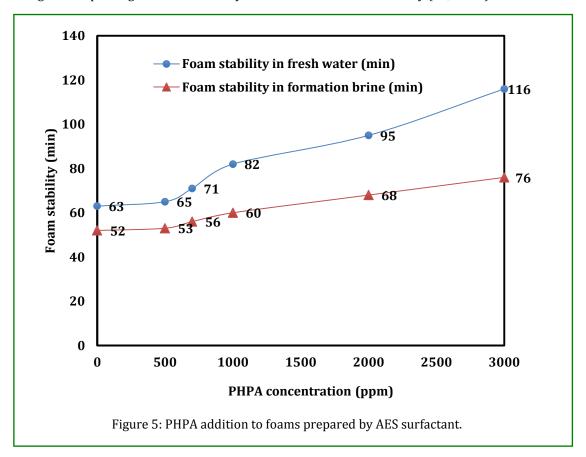
In addition, the effects of PHPA on foams prepared by AES surfactant were also investigated. Foam stability of each solution was determined and the results are shown in Figure 5. As shown in this figure, foam stability is in direct relationship with polymer concentration. Increasing the PHPA concentration increases foam stability significantly. The minimum foam stability is achieved with 500 ppm PHPA addition and the maximum foam stability is achieved by the addition of 3000 ppm PHPA. The values are 65 and 116 min with fresh water and 53 and 76 for formation brine, respectively.

Immediately after foam generation, there will always be a tendency for liquid to drain due to the force of gravity. This liquid will drain by flowing downward through the existing liquid-films, the interior of the lamellae. Eventually the gas bubbles will no longer be even approximately spherical, and relatively planar lamellae

will separate polyhedral-shaped bubbles. At this point, the capillary forces will become competitive with the forces of gravity. At the Plateau borders the gas-liquid interface is quite curved, and this curve generates a low pressure region in the plateau area and because the interface is flat along the thin-film region, a higher pressure resides here.

This pressure difference forces liquid to flow toward the plateau borders and causes thinning of the films and motion in the foam. Bulk viscosity is one of the main important issues in controlling the foam stability and it can be said that, the foam stability is a function of solution bulk viscosity; therefore the higher bulk viscosity will give the more stable foam. Polymer addition to the solution is a way to increase solution viscosity in which the higher polymer concentrations exhibit higher viscosities. PHPA can increase the bulk viscosity, thus decrease the film

drainage thinning and improving the foam stability as it occurred in this study (17,19-21).



Polymer enhanced foam stability by Xanthan

To investigate the effects of xanthan on foam stability, different concentrations of xanthan were added to foams prepared in formation brine and fresh water. The time required for 80% of the foam to collapse was determined and foam stability was measured. Table 4 presents the foam stability results prepared by CTAB surfactant in fresh water and formation brine. As shown in this table, xanthan was able to improve foam stability very effectively. The addition of small amount of xanthan to foam was able to increase foam stability significantly. The minimum foam stability was achieved by 500 ppm

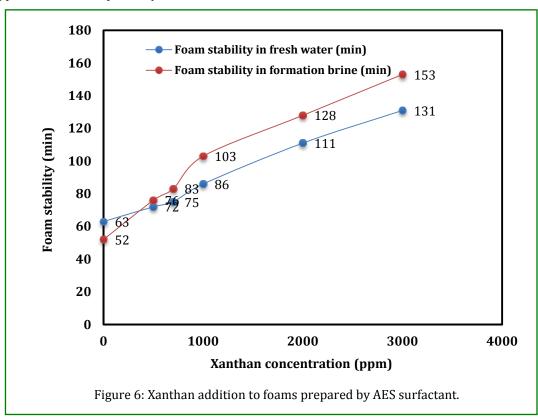
xanthan addition and the maximum foam stability was achieved by the addition of 3000 ppm xanthan to foams prepared by CTAB surfactant. Another observation was that foam stability was always higher in formation brine compared to fresh water. Foam solutions prepared in formation brine always exhibited more stable foams as compares to foams prepared in fresh water. In case of fresh water, the most and the least stable foams of 221 and 103 min are produced by the addition of 3000 and 500 ppm xanthan, respectively. On the other hand, in case of formation brine, these values are 274 and 123 min by the addition of 3000 and 500 ppm xanthan, respectively.

| Xanthan concentration (ppm) | Foam stability prepared in fresh water (min) | Foam stability in formation brine (min) |
|-----------------------------|--|---|
| 0 | 89 | 64 |
| 500 | 103 | 123 |
| 700 | 118 | 146 |
| 1000 | 131 | 178 |
| 2000 | 165 | 215 |
| 3000 | 221 | 274 |

Table 4: Polymer (xanthan) enhanced foam stability prepared by CTAB surfactant.

On the other hand, foam stability results of the addition of different concentrations of xanthan to solutions prepared by AES surfactant are shown in Figure 6. As shown in this figure, foam stability is influenced by xanthan concentration, in which the minimum foam stability is achieved by 500 ppm xanthan addition and the maximum foam stability is achieved by 3000 ppm xanthan addition. When fresh water was used, the minimum and maximum foams stability 72 and 131 min was achieved by the addition of 500 and 3000 ppm xanthan, respectively. These values were 76 and 153 min by the addition of 500 and 3000 ppm xanthan, respectively when formation

brine was used. Comparing the results of foam stability for different xanthan concentrations in the presence and absence of salt in the solution showed that, since the xanthan viscosity was greatly increased by the addition of salt, this increasing in the solution viscosity directly affected the foam stability and lead to have more stable foam. When formation brine was used, the lamellae and plateau boarders become more stable, then the produced foam was more stable in the case of salt in the solution and this increase in the foam stability was more emphasized in high xanthan concentrations (17,22-24).



Conclusions

In this study, the stability of different foam solutions prepared by AES and CTAB surfactants were investigated. PHPA and xanthan with different concentrations were used to improve foam stability. The following conclusions could be extracted from the studies performed:

- a) Surface tension is reduced by increasing the concentration of surfactant. The CMC values of CTAB and AES surfactants are 1000 and 2000 ppm, respectively.
- b) In general, CTAB performed better than AES in reducing the surface tension and improving foam stability.
- c) The maximum stability of conventional foams without any polymer addition is 89 and 63 min for CTAB and AES surfactants prepared in fresh water.
- d) PHPA addition to foam increased foam stability significantly. The higher the PHPA concentration, the higher the foam stability. The maximum foam stability of 198 min was achieved when 3000 ppm PHPA was added to fresh water and CTAB surfactant.
- e) PHPA performed better in fresh water compared to formation brine.

f) Xanthan was more compatible with formation brine rather than fresh water. The maximum foam stability of 274 min was achieved when 3000 ppm xanthan was added to formation brine and CTAB surfactant.

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