An Experimental Examination of Adsorption Phenomenon in Foam-assisted Water Alternative Gas: The Effect of Injection Rate

Mohammad Amin Safarzadeh¹, Seyyed Alireza Tabatabaei Nezhad²*, Eghbal Sahraei², and Mehdi Mohammad Salehi²

¹Reservoir Studies and Field Development Division, Research Institute of Petroleum Industry, Tehran, Iran
²Department of Chemical Engineering, Sahand University of Technology, Tabriz, Iran

Received: February 24, 2014; revised: May 27, 2014; accepted: June 17, 2014

Abstract
The main factor affecting the economics of foam-assisted water alternative gas (FAWAG) process is the loss of foaming agent by adsorption onto reservoir rocks. In this study, the effects of phases, surfactant concentration, salinity, adsorbents, and sacrificial agent on adsorption density were investigated by special adsorption experiments. Moreover, a series of FAWAG tests were performed to examine the effect of injection rates on final adsorption density and adsorption variation during the test. A clean and fast spectrophotometric method was used for the determination of sodium dodecyl sulfate (SDS) concentration based on the formation of an ion-pair, SDS-Safranin O. Higher SDS adsorption was observed at the first cycle of FAWAG flooding. FAWAG injection rate had no noticeable effect on the adsorption density. However, using high injection rate decreased the possibility that gas faces surfactant, and thereby reducing the ultimate oil recovery. The presence of CLS increases the ultimate oil recovery slightly, while it decreases the adsorption density of SDS by 22%.

Keywords: Foam-assisted Water Alternative Gas, Adsorption, Sacrificial Agent, Mixture Interference Concentration, Oil Recovery

1. Introduction
In gas injection, early breakthrough occurs due to high mobility (Syahputra et al., 2000). Processes such as the injection of water alternating gas (WAG), and direct gas thickeners have been used to mitigate these problems (Syahputra et al., 2000; Grigg et al., 2004). While, uses of gas thickeners are so costly and not applicable on field scale, the effectiveness of WAG process is reduced by gravity segregation between water and gas, which is amplified by permeability differences (Grigg et al., 2004).

Foam-assisted water alternative gas (FAWAG) flooding, where the surfactant is introduced in the aqueous phase, can improve the effectiveness of WAG in controlling mobility. Chemical flooding is one of the most successful methods to enhance oil recovery especially from depleted reservoirs (Gogoi et al., 2009). Nowadays, a broad selection of surfactant structures is available to use in enhanced oil recovery (EOR). The surfactant slug lowers oil-water interfacial tension, promotes oil-water miscibility, and reduces residual oil saturation (Lawson et al., 1980). The alternating

* Corresponding Author:
Email: tabatabaei@sut.ac.ir
imbibition/drainage cycles of gas and surfactant in FAWAG injection can help to create foam in the reservoir (Syahputra et al., 2000; Liave et al., 1989; Kibodeaux et al., 1997). However, such unfavorable conditions, including the dilution and adsorption of the surfactant slug can occur (Le et al., 2008).

Surfactant adsorption is a process in which surfactant molecule transfer from bulk solution phase to the surface/interface (Paria et al., 2004). The adsorption of surfactants on media was first studied by mineralogists trying to maximize the recovery of ores (Somasundaran et al., 2006). For a FAWAG displacement, however, one of the factors affecting the economics of the process is the loss of foaming agent by adsorption onto reservoir rocks, which makes it quite uneconomic (Tsau et al., 1999). Since surfactant is adsorbed on the rock surface, the loss of surfactant due to adsorption affects the propagation of surfactant and its effectiveness in stabilizing the lamellae (Tsau et al., 2000). The most important outcome of ionic surfactants adsorbing onto a solid is often the electrical interaction between the charged solid surface and surfactant ions. The point of zero charge of a mineral is the pH at which the net surface charge vanishes. The mineral is positively charged at lower pH values, while it becomes negatively charged at higher pH values. The relationship between the amount of surfactant adsorbed per unit mass or unit area of the solid and the bulk solution concentration of the adsorbate is called adsorption isotherm. This gives some useful information. Three approaches may be used to minimize surfactant adsorption:

1. Matching surfactant type to specific reservoir rock by surface charge;
2. Use of surfactant mixtures;
3. Sacrificial adsorbate (Song et al., 1994).

Use of a low-cost sacrificial agent is economically necessary to minimize the loss of costly foaming agent and to ensure a satisfactory foam displacement (Chiwetelu et al., 1979). Lignosulfonates are commercially available and used as sodium and calcium salts (Cecilia et al., 2008), which are weak foam formers; however, they become a good foaming agent when mixed with other surfactants. Calcium lignosulfonate (CLS) is a by-product of the paper industry (Grigg et al., 2002).

Choosing the type of gas used in FAWAG process depends on different factors like economic and the accessibility of the injected gas. Nitrogen is usually cheaper than CO$_2$ or a hydrocarbon gas for displacement in EOR applications and has the added benefit of being non-corrosive. It does not cause asphaltene deposition either and has a higher compressibility factor in comparison with CO$_2$ and natural gas.

In this work, static and dynamic adsorption tests were performed at the pressure and temperature of FAWAG flooding to design FAWAG injection strategy. The effects of adsorbent, sacrificial agent, gas phase, oil, salinity, and surfactant concentration on adsorption were evaluated by adsorption tests. Furthermore, FAWAG injection experiments were conducted to examine the effect of injection rates on adsorption density and oil recovery. Finally, the variations of effluent SDS concentration were evaluated.

2. Experimental procedure

Three series of experiments, namely static, dynamic, and flooding were performed to evaluate the adsorption phenomenon. A spectrophotometric method was used in all the experiments for the determination of sodium dodecyl sulfate concentration.

2.1. Chemical materials, rock, and fluids

The type of surfactant, sacrificial agent, organic solvent, cationic dye, and their basic properties are
shown in Table 1. Three formation stone types of Asmari (sandstone), Asmari (dolomite) and Kazhdumi (shale), and one lithology type of silica as adsorbents with a mesh size between 60 to 120 were used during all the tests. Bangestan and Asmari crude oils (dead oil) were used with 28 and 36 API respectively.

<table>
<thead>
<tr>
<th>Material Type</th>
<th>Chemical Material</th>
<th>$M_w$</th>
<th>pH</th>
</tr>
</thead>
<tbody>
<tr>
<td>Surfactant</td>
<td>Sodium dodecyl sulfate (SDS)</td>
<td>288.37</td>
<td>6-9 (10 gr/l, H$_2$O, 20 °C)</td>
</tr>
<tr>
<td>Lignosulfonate</td>
<td>Lignosite 100</td>
<td>18000</td>
<td>-</td>
</tr>
<tr>
<td>Cationic dye</td>
<td>Safranin o</td>
<td>350.85</td>
<td>10 (10 gr/l, H$_2$O, 20 °C)</td>
</tr>
<tr>
<td>Organic solvent</td>
<td>Ethyl acetate</td>
<td>88.105</td>
<td>-</td>
</tr>
</tbody>
</table>

2.2. Analytical method to detect SDS concentration

Since SDS is a multi-component colorless formulation, the spectrophotometric method was performed for the determination of sodium dodecyl sulfate based on the formation of an ion-pair, surfactant-Safranin O (SDS-SO). Ethyl acetate was used as the organic solvent for ion-pair extraction. Safranin O was chosen due to its efficiency as extractor and its low solubility in organic phases (Daneshfar et al., 2009). The procedure was conducted at 10 °C and the method exhibited a wide linear range (1-20 µM). The absorption spectra of SO-SDS and CLS are shown in Figure 1. To calculate SDS and CLS concentrations, standard calibration curves were established (Figure 2). The calibration curves obtained are almost linear ($R^2$=0.999 for SDS and $R^2$=0.9998 for CLS). Therefore, using Safranin with ethyl acetate for SDS and the direct spectrophotometric measurement of CLS have the proper accuracy.

![Absorption spectra of SDS and CLS.](image)

Figure 1
Absorption spectra of SDS and CLS.
2.3. Static adsorption method

In each experiment, 15 grams of SDS or CLS solution and 5 grams of the selected mineral or crushed core were mixed in the bottle and shaken for about 3 minutes. The bottle was then placed in the shaker bath, where it was being shaken continuously. A sample was taken after 24 hours and then left undisturbed for another 48 hours. Thereafter, the sample was centrifuged at 2000 rpm for 15 minutes and the supernatant solutions were separated from the vial of the solids after gravity sedimentation. The concentration difference between stock and the sample was used to evaluate the adsorption density. For the evaluation of the effect of oil, before the execution of the above procedure, the adsorbent was mixed with 10 cm$^3$ oil (for 7 days) and then was washed for 2 days until no oil remained on the surface.

2.4. Dynamic adsorption method

Two dynamic methods, i.e. circulation and flow through experiment, have been employed to study surfactant adsorption and desorption. In this study, flow-through method was used to evaluate surfactant adsorption/desorption onto porous media. The amount of surfactant adsorbed is expressed as the mass of SDS adsorbed per bulk volume of rock (mg/cm$^3$). Figure 3 (a) shows the schematic diagram of the flow-through method apparatus. General equipment used in this process includes:

a) A fluid injection system: during the experiments a pump with high performance liquid chromatography was used to displace fluids in the sand pack.

b) Accumulators: they were used to provide a high pressure for the injection. The distilled water was transported from the pump to the bottom of the accumulator to move the piston upward and compact the contained fluid.

c) A heating system and air bath chamber: all the systems were placed in an air bath capable of controlling temperature.

d) A pressure differential gauge which was used to measure the pressure drop along the porous media.
e) A back pressure regulator (BPR) and effluent collector: a backpressure regulator (BPR) was used to produce a constant backpressure during flood experiments.

f) A spectrophotometer: the UV-VIS spectrophotometer Spectroquant® Pharo 300, equipped with 1 cm quartz cell was used for all the spectrophotometric measurements.

The test procedure is described as follows:

1. The porosity and permeability measurement and saturating of the porous media with aqueous phase;
2. The injection of one pore volume of SDS solution;
3. The injection of about five pore volumes of aqueous phase;
4. Sample collection at different times to measure the concentration of the SDS and breakthrough time.

Tests were performed using the above procedure for six concentrations of SDS at 70 °C and 2200 psig.

![Figure 3](image)

(a) A schematic diagram of dynamic adsorption test and (b) a schematic diagram of FAWAG and WAG tests.

### 2.5. Flooding experiments

The same trends in foam behavior are observed in sand packs as in consolidated core, but at a lower pressure gradient (Khatib et al., 1988; Alvarez et al., 2001; Gauglitz et al., 2002, Rossen, 2005). Therefore, all the flooding experiments were conducted in sand packs (15 cm in length and 5 cm in diameter). Tests were performed at a temperature and pressure of 70 °C and 2200 psig respectively. The summary and conditions of flooding tests are shown in Table 2. In order to qualify the results of adsorption experiments, FAWAG injection tests were conducted. FAWAG and WAG injection, including 4 cycles with a total injection pore volume of 1.2, were performed (Figure 3 (b)). Each
cycle of FAWAG includes 0.15 pore volume surfactant injected in the aqueous solution followed by 0.15 pore volume of gas (WAG ratio=1:1). The apparatus consisted of an HPLC pump, four accumulators (with maximum working pressure of 15000 psig for the injection of gas, brine, oil, and surfactant), a backpressure regulator, and digital pressure transducers. At first, the effect of injection rate on adsorption was evaluated. Next, after saturating the model with oil, FAWAG injection was conducted to examine the effect of injection rate on oil recovery.

<table>
<thead>
<tr>
<th>Test No.</th>
<th>Injection mode</th>
<th>Injection rate (cc/min)</th>
<th>Additive</th>
<th>Absolute Permeability (mD)</th>
<th>Porosity (%)</th>
<th>Initial SWi (%)</th>
</tr>
</thead>
<tbody>
<tr>
<td>1</td>
<td>FAWAG</td>
<td>0.10</td>
<td>SDS</td>
<td>281</td>
<td>30.26</td>
<td>22.55</td>
</tr>
<tr>
<td>2</td>
<td>FAWAG</td>
<td>0.15</td>
<td>SDS</td>
<td>242</td>
<td>29.76</td>
<td>20.09</td>
</tr>
<tr>
<td>3</td>
<td>FAWAG</td>
<td>0.20</td>
<td>SDS</td>
<td>301</td>
<td>29.89</td>
<td>20.45</td>
</tr>
<tr>
<td>4</td>
<td>FAWAG</td>
<td>0.25</td>
<td>SDS</td>
<td>267</td>
<td>29.96</td>
<td>22.36</td>
</tr>
<tr>
<td>5</td>
<td>FAWAG</td>
<td>0.30</td>
<td>SDS</td>
<td>245</td>
<td>30.2</td>
<td>21.26</td>
</tr>
</tbody>
</table>

3. Results and discussion

3.1. Mixture interference in concentration determination

The absorbance of SDS-SO solution had its maximum value at 529 nm, which created minimum interference with the CLS absorption at 279 nm, when mixed with SDS (Figure 1). Figure 4 shows the influence of CLS on SDS absorbance at 529 nm. For each system of CLS concentration, the plot of SDS concentration versus absorbance was linear, with the corresponding $R^2$ value more than 0.9902. The results show that the presence of CLS has a minimal effect on the analytic method of determination of SDS concentration.

![Figure 4](image_url)

Effect of different CLS concentrations on SDS calibration curve.
3.2. Static adsorption onto three crushed cores

Static experiments were run to study SDS adsorption onto three different Iranian cores. The initial concentration of SDS for each crushed core was 1000 ppm. The final concentration for Asmari (sandstone), Asmari (dolomite), and Kazhdumi were 845, 702, and 632 ppm respectively. The fact that under these conditions (pH=6), the negative charge on the silica has an electrostatic repulsion for the negatively charged SDS anion is the main reason for the low adsorption of SDS on sandstone. While sandstone is negatively charged, dolomite and Kazhdumi have positive charge on their surfaces at this pH. Figure 5 compares the SDS adsorption density of cores with and without CLS. The adsorption of SDS decreases in order of Kazhdumi > Asmari (dolomite) > Asmari (sandstone). The results also indicate that the adsorption of surfactant can be reduced with the addition of CLS as sacrificial agents. The relative reduction in SDS adsorption due to the presence of CLS was 28%, 22%, and 30% respectively. Because CLS carries anionic charges in solution, it can reduce SDS adsorption sites of reservoir rock and protect the primary surfactants from adsorption in surfactant flooding processes. Adsorption density without CLS and adsorption reduction in the presence of CLS were greater for the Kazhdumi, which was due to its structure. Experiments were performed at 70 °C, atmospheric pressure, and using 100000 ppm of a brine solution.

![Figure 5](image)

**Figure 5**
Adsorption density of three crushed cores with and without CLS.

3.3. Static adsorption onto silica in the presence of gases

Silica mineral was used to analyze the effect of gas on the adsorption of SDS. Two series of experiments, in the presence of different gases, with different initial concentrations of SDS (1000 and 2000 ppm) were performed; the volume of vessel was 29 cm$^3$ and an experiment was performed as a baseline at atmospheric pressure. The adsorption density of SDS in the presence of $CH_4$ and $N_2$ are shown in Table 3. To avoid foam formation in the presence of surfactant solution, the process of injection and the emission of gas from the vessel were performed too slowly. Although no foamy bubbles were observed at end of tests, mass transfer may occur between gas and surfactant solution. All the experiments were performed at 70 °C and 2200 psig.

The results show that the adsorption of SDS onto silica in the presence of $N_2$ is 9% lower than $CH_4$ (Figure 6). Moreover, as mentioned above, choosing the type of gas in EOR processes depends on different factors such as economic and accessibility of injection gas.
Table 3
Effect of gas phase on the adsorption density of SDS on silica.

<table>
<thead>
<tr>
<th>Initial concentration</th>
<th>No Gas (baseline)</th>
<th>N₂</th>
<th>CH₄</th>
</tr>
</thead>
<tbody>
<tr>
<td>1000 PPM</td>
<td>0.237</td>
<td>0.297</td>
<td>0.318</td>
</tr>
<tr>
<td>2000 PPM</td>
<td>0.306</td>
<td>0.363</td>
<td>0.405</td>
</tr>
</tbody>
</table>

Figure 6
Incremental percentage of SDS adsorption density in the presence of gas.

a) Static adsorption-CLS adsorption on silica
Figure 7 shows that CLS adsorption density is a function of CLS solution concentration. Similar to surfactants, it increases as CLS solution concentration increases. The increment rate of CLS adsorption density is reduced after a concentration of 3000 ppm. In addition, the result confirms that using CLS as a sacrificial agent is reasonable. In fact, inexpensive CLS competes with SDS for the adsorption on surface area and therefore reduces the overall adsorption amount of SDS at the solid-liquid interface.

Figure 7
Variation of CLS adsorption density with CLS concentration.

b) Static adsorption-effect of salinity on SDS adsorption density
Figure 8 shows the variation of SDS adsorption density with aqueous phase concentration. Adsorption
density of SDS increases as salinity rises. Surfactant adsorption mechanisms suggested for minerals include salt formation at the solid surface, surfactant binding to lattice ions, ion exchange of surfactant with lattice ions, and surface precipitation. By increasing NaCl concentration, the electrical double layer on the surface of adsorbent is compressed and the electrostatic repulsion between the adsorbed surfactant species decreases, which results in an increase in adsorption capacity. The adsorption of surfactants generally rises as divalent ion content increases. However, some studies reveal a small dependence of adsorption on salt concentration; it may decrease the adsorption of surfactant by competing with the surfactant for the surface or by shielding the surface charge on the solid.

![Figure 8](image1)

Variation of SDS adsorption density with salinity.

### 3.4. Effect of oil type on adsorption density of silica

Asmari and Bangestan crude oil were used for the evaluation of the effect of oil phase on adsorption density of SDS. All the experiments were performed at 70 °C and atmospheric pressure. Figure 9 shows that SDS adsorption density on silica was reduced about 7% in the presence of oil. Similar to the mechanism of CLS in the presence of SDS, the primary adsorption of oil onto the silica is a main reason for low SDS adsorption onto silica. On the other hand, the reaction of SDS with trapped oil in pores may cause the degradation of SDS. The static experiment results confirm that loss of SDS due to adsorption on surface is more important than the effects of salinity and hydrocarbon phases.

![Figure 9](image2)

The decrease in SDS adsorption density in the presence of oil.
4. Dynamic adsorption onto porous media

Flows through experiments were carried out to measure the adsorption isotherm and optimum SDS concentration. The optimization was performed with regard to the amount of the SDS adsorbed onto surface. Different SDS concentrations of 100, 500, 1000, 2000, 3000, and 4000 ppm were used to obtain the optimum concentration at 70 °C and 2200 psig. Figure 10 shows the adsorption isotherm for SDS on silica. Adsorption density rises sharply as the concentration increases and then levels off to a nearly constant value of 1000 ppm.

![Figure 10](image1.png)

**Figure 10**
Adsorption isotherm for SDS on silica at 70 °C and 2200 psig.

A slight increase in SDS adsorption density is observed at 4000 ppm, which is because at SDS concentration more than 3500 ppm SDS is not fully dissolved and solution is not well homogenized. The SDS concentration of more than 1000 ppm (1500 ppm) was used in all the foam-assisted water alternative gas injection experiments. The effluent normalized concentration (effluent concentration per injection concentration) profiles of SDS for 100, 1000 (with and without 4000 ppm CLS), and 3000 ppm are shown in Figure 11.

![Figure 11](image2.png)

**Figure 11**
Effluent normalized concentration profiles of SDS.

By increasing the SDS concentration, the breakthrough time decreases, which is due to an increase in the dispersion coefficient of surfactant. CLS has a stronger affinity to the solid surface and competes with SDS during experiments for the adsorption on surface area; therefore, it reduces the overall
adsorption amount of SDS at the solid-liquid interface. The area between two curves for the SDS concentration of 1000 ppm represents the amount of SDS that is not adsorbed in the presence of CLS. The decrement of SDS adsorption is 34%. Dynamic tests confirm that, even at high pressure and in the presence of 100000 ppm brine water, CLS can reduce the adsorption of SDS.

5. Flooding experiments

According to the results of the previous experiments, a series of FAWAG experiments were performed in order to compare SDS adsorption under different combinations of SDS and CLS (initial condition of 70 °C and 2200 psig). Figure 12 shows the effluent SDS concentration at different FAWAG injection rates.

![Figure 12](image1.png)

**Figure 12**

Effluent SDS concentration at different injection rates of FAWAG.

The contact time of SDS solution and silica surface increases with decreasing injection rate. However, in spite of the uncertainty, a noticeable increasing trend in effluent SDS concentration cannot be seen as FAWAG injection rate rises. Thus the overall injection rate is not considered a significant factor in adsorption density using FAWAG. Effluent SDS concentration profiles during SAG at the injection rates of 0.20 and 0.25 cc/min are shown in Figure 13. A higher adsorption was observed at first due to solid/liquid interaction. Therefore, to increase the efficiency of FAWAG flooding, the injection of higher concentrations of sacrificial agents at the first cycle is recommended.

![Figure 13](image2.png)

**Figure 13**

Effluent SDS concentration profiles during FAWAG; injection rates of 0.2 and 0.25 cc/min.
Finally, different injection modes (WAG and FAWAG with and without CLS at different injection rates) were conducted and cumulative oil recoveries were compared (Figure 14). Due to the high porosity and permeability of porous media, the ultimate recovery of WAG is high. However, the early breakthrough of gas leads to a decrease in the efficiency of WAG process.

The results confirm that FAWAG injection improves ultimate oil recovery (by about 10% in comparison with WAG injection). Increasing the viscosity of gas phase and trapping gas in porous media result in a decrease in the mobility of gas and thereby increasing oil recovery during FAWAG tests. The CLS minimizes the loss of surfactant and leads to the earlier formation of foam in media. Maximum oil recovery is observed in FAWAG injection with CLS at an injection rate of 0.2 cc/min (89%). Using CLS increases the ultimate oil recovery slightly, while it decreases the adsorption density of SDS about 22% during the FAWAG test. With an increase in injection rate, injection fluids flow in channels with higher permeability and undesirable early breakthrough is occurred. Finally, there is a probability that foam dries out.

6. Conclusions

The main goal of the present work was to evaluate the effect of injection rate on adsorption using FAWAG flooding. The absorbance of SDS-SO solution had a maximum value at 529 nm, which created minimum interference with the CLS absorption at 279 nm in SDS concentration determination, when mixed with SDS. Parameters such as gas phase, oil, salinity, absorbent, and sacrificial agent type affected the adsorption phenomena. The adsorption of SDS in a decreasing order was: Kazhdumi (shale) > Asmari (dolomite) > Asmari (sandstone). The results also indicated that the adsorption of surfactant could be reduced with the addition of CLS as a sacrificial agent. Adsorption reduction with the addition of CLS was greater for Kazhdumi. The results also confirmed that adsorption density dropped when N₂ was imposed in comparison with CH₄. Both Asmari and Bangestan crude oil due to primary adsorption on rock decreased the SDS adsorption. Foam-assisted water alternative gas flooding showed that CLS could reduce the SDS adsorption, while the injection rate was not considered a significant factor in adsorption. Higher adsorption was observed for FAWAG injection at first due to high solid/liquid interaction. The results showed that FAWAG injection improved ultimate oil recovery by about 10% with WAG injection (87%); the amount of recovery in the presence of CLS was increased by only 2% (89%), while it decreased the adsorption...
density of SDS by about 22% during the SAG test. Using a high injection rate in FAWAG injection decreased the possibility that gas faces surfactant and thereby reducing ultimate oil recovery.

**Nomenclature**

<table>
<thead>
<tr>
<th>Acronym</th>
<th>Definition</th>
</tr>
</thead>
<tbody>
<tr>
<td>WAG</td>
<td>Water alternating gas</td>
</tr>
<tr>
<td>FAWAG</td>
<td>Foam-assisted water alternative gas</td>
</tr>
<tr>
<td>CLS</td>
<td>Calcium lignosulfonate</td>
</tr>
<tr>
<td>SDS</td>
<td>Sodium dodecyl sulfate</td>
</tr>
<tr>
<td>SO</td>
<td>Safranin O</td>
</tr>
</tbody>
</table>

**References**


Lawson, J. B. and Reisberg, J., Alternate Slugs of Gas and Dilute Surfactant for Mobility Control during Chemical Flooding, SPE/DOE Improved Oil Recovery Symposium, Tulsa, Oklahoma, 1980.


Cecilia, M., Toledo, F., and Kuznesof, P. M., Calcium Lignosulfonate, for the 69th JECFA, 2008.


Grigg, R. B., Tsau, J. S., Martin F. D., and Martin D., Cost Reduction and Injectivity Improvements for CO$_2$ Foams for Mobility Control, SPE/DOE Symposium, Tulsa, Oklahoma, 2002.
