Experimental Investigation of the Effect of Calcium Lignosulfonate on Adsorption Phenomenon in Surfactant Alternative Gas Injection

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Abstract
Fractional flow analysis confirms the advantages of surfactant alternative gas injection (SAG) in enhanced oil recovery, but an adsorption phenomenon that has been affected by several factors, weakens the effectiveness of SAG injection. In this study, the effects of sacrificial agent, gas phase, and surfactant concentration on adsorption density on silica mineral were investigated by static and dynamic adsorption experiments. A series of SAG tests were performed to examine the effect of injection rates and presence of Calcium Lignosulfonate (CLS) on oil recovery. Also, variation of effluent sodium dodecyl sulfate (SDS) concentration during SAG test was examined. Spectrophotometric method based on the formation of an ion-pair was used in all experiments for determination of SDS concentration. The results of adsorption experiments show that SDS adsorption density on silica was reduced when nitrogen was imposed instead of using methane. It can be reduced with addition of CLS as sacrificial agents and amount of adsorption reduction increases as concentration increases. Flooding experiment results show that SAG injection increase ultimate recovery up to 10% in comparison with water alternative gas (WAG) injection. Increasing viscosity of gas phase and its trapping in porous media results a decrease in the mobility of gas and an increase in oil recovery. Stability of formed foam in porous media is rate-dependent and higher SDS adsorption was observed at first cycle of SAG injection due to high solid/liquid interaction. Using CLS slightly increases the ultimate oil recovery, while it decreases the adsorption density of SDS about 22 percent during the SAG test.

Keywords: Surfactant alternative gas (SAG), Oil recovery, Adsorption, Ion pair, Sodium Dodecyl Sulfate, Calcium Lignosulfonate (CLS), Mobility control

Introduction
With the decline in oil production, oil price augmentation during the last decades and a large amount of oil which is still trapped in reservoirs after applying the common EOR method, it is reasonable to use profitable method with higher initial operational cost. Because of having huge sources of gas, Iran has a high potential in the field of gas injection. In principle, miscible gas injection can nearly displace all of the oil from the portions of a reservoir swept by gas. Hence, the process of gas injection has been paid more attention [1]. But gas injection has major problems with poor sweep efficiency, and inefficient displacement of oil in low pressure reservoir [2]. Processes such as the injection of water alternating gas (WAG) and direct gas thickeners are being used to enhance the sweep efficiency and control the mobility of gas injection. In spite of satisfying result of thickeners, it has a few usages because of being too costly. The process of alternating injection of water and gas helps to control the gas mobility [2,3]. Unfortunately WAG effectiveness is reduced by the reduction of oil-gas contact in the presence of water. Gravity segregation tends to impair the advantages of this injection strategy and is amplified by permeability differences. It should be noted that the injectivity of WAG was reduced in carbonate reservoirs [4].

According to Austad and Milter, chemical flooding of oil reservoirs is one of the most successful methods to enhance oil recovery from depleted reservoirs at low pressure [5]. Effective oil recovery by surfactant was not a question of technical probability but rather a question of economics. The low oil prices in past (before 2000) provided little stimulus for research on chemical enhanced oil recovery. Nowadays, a broad selection
of surfactant structures is available to use in EOR. Zaitoun et al. conducted a series of experiments on surfactant screening and evaluation for surfactant flooding in the Chihuindo de la Sierra Negra field in Argentina. They developed a new anionic surfactant that provides good solubility in high salinities and low interfacial tension at low concentrations [5]. Cationic surfactants have less usage in EOR, in some situations they can be used as a mixture with anionic type.

The use of foam for gas mobility control was first proposed in 1958 by Bond and Helbrook [3,7]. Aqueous foam is a dispersed gaseous phase within a continuous aqueous phase mainly comprised of films known as lamellae. The lamellae are stabilized by adsorption of surfactant at the gas/liquid interfaces. When foam is generated and propagated in the porous media, the foam bubbles are as large as pore bodies and the lamellae span the pores that reduce the gas mobility [6]. At the presence of foam, the relative permeability of gas will decrease and this amount of reduction will aggravate in high permeability zones. The same trends in foam behavior are observed in sandpacks as in consolidated core, but at lower pressure gradient (Khatib et al., 1988; Alvarez et al., 2001; Gauglitz et al., 2002, Rossen, 2005).

The formation of foam in porous media is performed in different ways. Shi and Rossen showed that SAG injection has several advantages over other foam injection methods. It minimizes the contact between gas and water in the injection facilities in comparison with co-injection method which can help reduce corrosion. Moreover, overcoming gravity override with continuous pre-formed foam injection requires raising injection-well pressure, possibly risking fracturing the formation [7,8,9]. While pre-formed and co-injection foams, under certain conditions can completely block the porous medium, SAG injection never does [10]. SAG injection also improves injectivity; as water is displaced from the near-well region during gas injection, foam weakens there, gas mobility rises, and injectivity increases while, stronger and wetter foam further from the well maintains mobility control [11].

One of the factors affecting the economics of SAG is the loss of the foaming agent by adsorption onto reservoir rocks, precipitation, and resultant changes in rock wettability [5,12]. In all mentioned above the adsorption phenomenon in liquid-solid contact is of great importance. In a chemical process in a reservoir, it is not uncommon to have over 90% of a component required to satisfy adsorption onto the rock. Thus, understanding adsorption process is critical in evaluation of transport of chemicals and in order to accurately assessing the volume of chemicals required for a successful SAG operation [13]. Surfactant retention by adsorption and phase trapping determines the amount of surfactant required for a surfactant enhanced oil recovery process [14]. 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 an adsorption isotherm. This will reveal lots of characteristics of surfactant. Soluble minerals, which occur in many reservoirs, can cause further changes in interaction of surfactants with rocks and their wettability [15]. Due to the different mineralogy, most solid surfaces, including reservoir rocks, are charged. The most important cause of ionic surfactants adsorbing onto a solid is often the electrical interaction between the charged solid surface and surfactant ions, which can be explained by electrical double layer theory. 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 and negatively charged at higher pH [16]. For simple solutes, adsorption behavior is generally uncomplicated, and can be modeled accurately on the basis of the interactions between the adsorbing species and the surface of the substrate. This type of adsorption is generally interpreted using the
Langmuir isotherm, which adequately describes adsorption behavior up to a monolayer level of coverage. The Langmuir equation was used in simulating adsorption and desorption of some chemical flooding in enhanced oil recovery. Both nonionic and ionic surfactants are found to comply with the Langmuir adsorption isotherm. For a thermodynamically consistent study, the surface excess theory is more suitable to model surfactant adsorption and desorption at the solid/liquid interface [13].

Choosing the type of gas used in EOR process depends on different factors like economics and accessibility of injected gas. By knowing the fact that there are lots of huge nitrogen resources with high percentage like Kabir – kooch gas reservoir (Dahrom formation with 21 trillion cubic feet gas in place) and Milaton gas reservoir (Sormeh formation with 24 trillion cubic feet gas in place) and Samand reservoir (upper Dalam formation with 75 trillion cubic feet gas in place) in Iran, it seems reasonable to use this gas as a proper substitute for natural gas, of course after conducting necessary experiments. Nitrogen is usually cheaper than CO₂ or a hydrocarbon derived gas for displacement in EOR applications and has the further benefit of being non-corrosive. It does not cause asphaltene deposition and has a higher compressibility factor in comparison with CO₂ and natural gas. It means that in equal pressure and temperature conditions there will be more nitrogen in specific volume [17].

Frequently, to overcome the problems of surfactant loss, a sufficient amount of surfactant is pre-injected into the reservoir to satisfy the surfactant adsorption prior to injection of gas or pre-generated foam. Such an approach may not be very economically when an expensive foaming agent is used. It is reasonable to use sacrificial agent such as Lignosulfonate [18]. It could reduce surfactant loss and surfactant concentration for foam that was rock type and injection scheme-dependent [2]. CLS has stronger affinity to the solid surface. It competes with SDS for the adsorption on surface area and therefore reduces the overall adsorption amount of SDS at the solid-liquid interface.

In this study, the effects of gas phase, surfactant concentration, and sacrificial agent on adsorption were investigated by static and dynamic adsorption experiments and surfactant alternative gas injection was designed. A series of flooding experiment was performed to examine the effect of injection rates and sacrificial agent. Also, variation of effluent SDS concentration during SAG test was examined. Water alternative gas injection was conducted to compare some parameters.

**Experimental procedure**

Adsorption (static and dynamic) and flooding experiments were performed to evaluate the adsorption phenomenon, oil recovery and injection pressure. Fast spectrophotometric method was used for determination of SDS concentration.

**Chemical materials, Rock and fluids**

The type of surfactant, sacrificial agent, organic solvent, cationic dye, and their basic properties are shown in table 1. Silica was used as an adsorbents in all experiments. Bangestan crude oil with 28 API and purified gases (Nitrogen and Methane) were used.

<table>
<thead>
<tr>
<th>Material</th>
<th>Type</th>
<th>Mw</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 g/L,H2o, 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 g/LH2o, 20 °C)</td>
</tr>
<tr>
<td>Organic solvent</td>
<td>Ethyl acetate</td>
<td>88.105</td>
<td>-</td>
</tr>
</tbody>
</table>
Table 2: Summary of flooding experiments and conditions

<table>
<thead>
<tr>
<th>Test No.</th>
<th>Injection Mode</th>
<th>Injection rate (cc/min)</th>
<th>Additive</th>
<th>Perm (md)</th>
<th>Porosity (%)</th>
</tr>
</thead>
<tbody>
<tr>
<td>1</td>
<td>SAG</td>
<td>0.15</td>
<td>SDS</td>
<td>242</td>
<td>29.76</td>
</tr>
<tr>
<td>2</td>
<td>SAG</td>
<td>0.20</td>
<td>SDS</td>
<td>301</td>
<td>29.89</td>
</tr>
<tr>
<td>3</td>
<td>SAG</td>
<td>0.25</td>
<td>SDS</td>
<td>267</td>
<td>30.36</td>
</tr>
<tr>
<td>4</td>
<td>WAG</td>
<td>0.20</td>
<td>-</td>
<td>263</td>
<td></td>
</tr>
<tr>
<td>5</td>
<td>SAG</td>
<td>0.20</td>
<td>SDS+CLS</td>
<td>303</td>
<td>29.33</td>
</tr>
</tbody>
</table>

Table 3: Effect of gas phase on adsorption density of SDS on silica

<table>
<thead>
<tr>
<th>Initial SDS Concentration</th>
<th>Adsorption density-No Gas (baseline)</th>
<th>Adsorption density in presence of N₂</th>
<th>Adsorption density in presence of 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>

Analytical method to detect SDS concentration

Since SDS is a multi-component colorless material, a clean and relatively fast spectrophotometric method was performed for determination of sodium dodecyl sulfate based on the formation of an ion-pair, surfactant-Safranin O (SDS-SO). For the possibility of disturbance in determining the concentration of SDS in the presence of CLS using the method of spectrophotometric was suggested. Different organic solvents like Choloform and Dichloro methane are used for liquid – liquid extraction but unfortunately they are toxic. In this study, 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 [19]. The procedure was conducted at 10 °C and in case of necessity to dilution, Ethyl acetate solution was used. The method exhibited a wide linear range (1–20 µM). The absorption spectra of SO-SDS and CLS are shown in Figure 1.

The maximum amount of CLS adsorption is achieved at the wave length of 232 nm and 279nm, which is at proper distance from SDS maximum adsorption (529 nm) and reduces the possibility of any disturbance in the amount of SDS adsorption from spectrophotometry to the least value, in presence of CLS. To calculate SDS concentration, the standard calibration curve of SDS was established (Figure 2).

![Figure 1: Absorption spectra of SDS and CLS](image1.png)

The achieved calibration curve is almost linear (R²=0.999). So using the Safranin with Ethyl acetate has proper accuracy for measuring the concentration of SDS.

Static adsorption method

In each experiment, 15 grams of SDS solution and 5 grams of the Silica mineral was 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 for 24 hours and then left undisturbed for another 48 hours.

![Figure 2: Calibration curve of SDS at 529 nm](image2.png)
Thereafter, a sample was taken and centrifuged at 2000 RPM for 15 min. Finally, 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. Tests were performed at a temperature of 70° C and different pressures.

**Dynamic adsorption method**

Two dynamic methods, circulation and flow through experiment, are employed to study surfactant adsorption and desorption.

![Figure 3: Schematic diagram of dynamic adsorption test](image)

Flow-through method was used to study SDS adsorption/desorption onto porous media. Figure 3 shows the schematic diagram of the flow-through method apparatus. The test procedure is as follows:

i. Porosity and permeability measurement and saturating of the model with aqueous phase.
ii. Injection of one pore volume (PV) of surfactant solution.
iii. Injection of about 5 PV of aqueous phase.
iv. Sample collection at different times to measure the concentration of the SDS.

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

**Flooding experiments**

According to the achieved results from researchers in the case of foam’s same behavior in sand pack model and cores, all flooding experiments were conducted in sandpacks (15cm in length and 5cm in diameter). Tests were performed at a temperature and pressure of 70° C and 2200 psig, respectively. Summary and conditions of flooding tests are shown in table 2.

The apparatus used in this study are consisted of HPLC pump, four accumulators (with maximum working pressure of 15000 psig), backpressure regulator, and digital pressure transducers (Figure 4). A Digital HPCL Pump with maximum working pressure of 6000 psi was used to directly inject oil, brine, SDS solution or nitrogen. These fluids were injected at constant rates through floating-piston accumulators. A backpressure regulator was used to maintain a constant pressure during the flooding experiments. The regulator was set at 2200 psi on the outlet of the system. The sample was collected for quantifying oil recovery and SDS concentration. The UV-VIS spectrophotometer Spectroquant® Pharo 300, equipped with 1 cm quartz cell was used for all spectrophotometric measurements. The pH measurements were made with a 780-pH meter equipped with an Ag/AgCl electrode.

![Figure 4: Schematic diagram of flooding apparatus](image)

The flooding procedure is as follows:

i. Porosity and permeability measurement.
ii. Saturating of the model with aqueous phase.
iii. Saturating of the model with oil.
iv. Alternating injection of SDS solution and gas in SAG injection
and, water and gas in WAG injection.

v. Sample collection at different times and injection pressure recording.

**Results and discussion**

**Mixture interference on concentration determination**

The absorbance of SDS-SO solution had its maximum value at 529 nm (Figure 1), which created minimum interference with the CLS absorption at 279 nm, when mixed with CLS. Figure 5 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 $R^2$ more than 0.9902. Results show that the presence of CLS has a minimal effect on the method of determination of SDS concentration.

![Figure 5: SDS calibration curve at different concentration of CLS](image)

**Static adsorption – Effect of sacrificial agent on adsorption density**

Static experiments were run to study the effect of calcium lignosulfonate on SDS adsorption density of silica. Experiments with different initial concentration of SDS (1000 and 2000 ppm) were performed at 70 °C and atmospheric pressure. The final concentrations were 948 and 1937 ppm, respectively. Figure 6 compares SDS adsorption density of silica with and without CLS. The results indicate that the adsorption of surfactant can be reduced with addition of CLS as sacrificial agents. The amount of pH for these experiment is 5.5 while the point of zero charge is pH 2 for Silica and it is positively charged at lower pH and negatively charged at higher pH. The reason for low adsorption of SDS on silica is that under these pH values, the negative charge on the silica has an electrostatic repulsion for the negatively charged surfactant anion. Because CLS carries anionic charges in solution, it can reduce SDS adsorption sites of reservoir rock and act to protect the primary surfactants from adsorption in surfactant flooding process.

![Figure 6: Effect of CLS on SDS adsorption density on silica](image)

**Static adsorption – Effect of gas phase on adsorption density**

Two series of experiments, in presence of different gases, with different initial concentration of SDS (1000 and 2000 ppm) were performed. An experiment was performed as a baseline at atmospheric pressure. The adsorption density of SDS in the presence of CH₄ and N₂ are shown in table 3.

Results represents that the adsorption of SDS onto silica in the presence of N₂ is lower than CH₄ (Figure 7). All experiments were performed at 70 °C and 2200 psig. Since flooding operation of reservoirs takes a lot of time, the possibility of gas phase and surfactant coming together will increase and adsorption of surfactant in gas phase and rock surface will be more. Then nitrogen was used for flooding experiment. however, as mentioned before, choosing the
type of gas in EOR process depends on different factors such as economic and accessibility of injection gas.

**Figure 7:** Incremental percentage of SDS adsorption density in presence of gas

**Dynamic adsorption – Effect of different SDS concentration**

Flows through experiments were carried out to measure the adsorption isotherm and optimum SDS concentration. SDS retention by adsorption and phase trapping determines the amount of surfactant required for a surfactant enhanced oil recovery process. Different SDS concentration of 100, 500, 1000, 2000, 3000 and 4000 ppm were used to obtain the optimum concentration at 70 °C and 2200 psig. Figure 8 shows the adsorption isotherm for SDS on silica.

The reason for low adsorption of SDS on silica is the pH value of solution (pH\textsubscript{Solution} = 5.5). The adsorption isotherm of SDS was S shape and adsorption rises sharply as the concentration increases and then levels off to a nearly constant value of 1000 ppm. SDS concentration of 1500 ppm was used in all surfactant alternative gas injection experiments.

**Figure 8:** Adsorption isotherm for SDS on silica at 70 °C and 2200 psig

**Flooding Experiment**

According to the results of previous experiment, a series of experiments were performed to examine the effect of injection rate and presence of CLS on recovery. Also, variation of effluent SDS concentration and the effect of CLS on SDS adsorption density during the test were examined. Finally, in order to compare the results, WAG injection process was performed. Gas injection in all experiments was immiscible.

**Surfactant alternative gas injection**

SAG flooding, including 4 cycles, at the optimum cycle ratio (1:1) with a total injection pore volume of 1.2 was performed. The optimized value of injection is achieved according to the recovery amount. Each cycle includes 0.15 pore volume surfactant injected in the aqueous solution (1500 ppm) followed by 0.15 pore volume of gas.

The amount of critical injection rate is 0.42 cc/min. The oil recovery profiles of three injection rates are shown in figure 9.

**Figure 9:** Effect of injection rate on oil recovery

The injection pressure at the rate of 0.15 cc/min increased which is a sign of foam formation, but the formed foam cannot completely move the oil in place and at the end caused the media to be plugged. The ultimate recovery at 0.15 cc/min will be 81 percent. The formed lamella in porous media has caused the plugging some ways. The injection rate of 0.2 cc/min shows the highest amount (87 percent) of recovery in
the performed experiments. Sudden increase of injection pressure in the third cycle shows that foam has formed in this cycle, which causes reduction in gas mobility and sudden increase in oil production. The amount of injection rate is such that it causes the formation of stable foam and proper movement of oil in porous media. At the injection rate of 0.25 cc/min, early break through occurred due to fingering phenomenon, hence, the proper foaming did not happen. Increase in injection rate has caused a reduction in the amount of foam in media. Using high injection rate causes less possibility of facing the gas and surfactant. So, Recovery efficiency of SAG is a function of rate. The amount of ultimate recovery of oil at this rate was about 77 percent. Injection rate of 0.2 cc/min was selected as an optimized rate.

Water alternative gas injection

The alternating injection process of water and gas at optimized rate was conducted to compare the amount of oil recovery and injection pressure. Figure 10 compares the amount of oil recovery versus injected pore volume in two methods of alternating injection. The amount of ultimate recovery in WAG process is about 76 percent, which is 10 percent less in comparison to SAG process. The changes in injection pressure in two methods are shown in figure 11. The injection pressure during the WAG process is steady while in the SAG it is not and this indicates the possibility of foaming in porous media. Pressure variations of alternating injection of gas and water are the same as the process of surfactant and gas injection in the first cycle and the only difference is the viscosity of the SDS solution which is higher than water viscosity. It is clear that at the absence of foam, the amount of injection pressure increases during gas injection and it decreases, when water is injected while in the process of surfactant injection and gas in some cases, this is not observed because of the existence of foam.

![Figure 10: Trend of recovery changes at optimized injection rate](image)

![Figure 11: Injection pressure in SAG and WAG processes](image)

![Figure 12: Effluent SDS concentration profiles of SDS for the injection rate of 0.25 (cc/min) of SAG](image)
An experiment at optimized rate of injection is conducted, using CLS with concentration of 4000 ppm to reduce adsorption of SDS during SAG test (figure 13). The amount of recovery in the presence of CLS was increased by only two percent (89 percent) while the amount of effluent SDS concentration is also increased which shows the reduction of adsorption density of SDS (22 percent) during test and confirms the result of adsorption experiment on CLS. Figure 14 compares the produced SDS concentration of SAG test with and without CLS.

**Figure 13: The amount of oil recovery in the presence and absence of CLS**

Using CLS in SAG injection does not have any effect on the break through time and the profile of recovery was steadier. Higher recovery was observed at the end of second cycle of injection in comparison to SAG without CLS.

**Conclusion**

The main goal in the present article was to evaluate the effect of CLS on adsorption density and oil recovery using SAG flooding. Parameters such as gas phase, concentration and sacrificial agent type have affected the adsorption phenomena. The results of adsorption experiments show that SDS adsorption density on silica was reduced when nitrogen was imposed in comparison with using methane. It can be reduced with addition of CLS as sacrificial agents and amount of reduction increases as concentration increases. Flooding experiment results show that SAG injection increase ultimate recovery up to 10% in comparison with water alternative gas (WAG) injection. Increasing the viscosity of gas phase and it’s trapping in porous media results in a decrease in mobility of gas and an increase in oil recovery. Stability of formed foam in porous media is rate depended and higher SDS adsorption was observed at first cycle of SAG injection due to high solid/liquid interaction. The amount of recovery in the presence of CLS was increased by only two percent (89 percent) while it decreases the adsorption density of SDS about 22 percent during the SAG test.

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**References:**


