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Sacrificial Agent for Reducing Adsorption of Anionic Surfactants
Hadi ShamsiJazeyi, George J. Hirasaki, Rafael Verduzco, Rice University

Abstract

An important economical factor affecting Enhanced Oil Recovery (EOR) is the adsorption of surfactants on the rocks. Sacrificial agents may be used to reduce the adsorption of surfactants. An alkali (traditionally, sodium carbonate or sodium hydroxide) is often used as sacrificial adsorption agent; however, sodium carbonate is not an effective sacrificial agent in the presence of anhydrite in the rocks due to the reaction between sodium carbonate and sparingly-soluble anhydrite. Therefore, it is essential to develop a sacrificial adsorption agent that can act effectively in the presence of anhydrite.

In this work, sodium polyacrylate is evaluated as a sacrificial agent, and is compared to many other conventional or recently-recommended sacrificial agents, and has shown advantage over all of them for the case of presence of anhydrite. Some experiments have been conducted to demonstrate the ineffectiveness of sodium carbonate as sacrificial agent in the presence of anhydrite. Effect of molecular weight of sodium polyacrylate is tested, and it is found that increase in molecular weight results in decrease in adsorption of surfactant until a certain molecular weight of polyacrylate is reached after which molecular weight has no further effect on reducing adsorption of surfactant. Addition of polyacrylate was shown to reduce adsorption of a selected anionic surfactant on different outcrop minerals, including Carpool dolomite, industrial calcite, kaolinite, Berea sandstone, and Indiana limestone. To prove the point further, application of polyacrylate was tested with two different anionic surfactants. Adsorption of polyacrylate itself is measured in the presence and absence of surfactant and showed to be independent of the presence of surfactant. The effect of concentration of divalent ions and salinity in the brine on effectiveness of sodium polyacrylate as sacrificial agent has been evaluated on different minerals/rocks. Finally, dynamic adsorption data has been presented in different concentrations of sodium polyacrylate.

All these experiments demonstrate the advantage of using sodium polyacrylate as sacrificial adsorption agent for anionic surfactants even in the presence of anhydrite in the rock.

Introduction

With the increasing demand of energy around the world and diminishing amount of conventional oil, Enhanced Oil Recovery (EOR) methods have attracted significant attention for production of oil, especially in recent years. Chemical EOR (ASP, SP) is a process in which alkali, surfactants and polymers are being used to lower interfacial tension, change the wettability and control mobility, respectively [1-3] in order to increase the amount of oil recovered from a previously water-flooded reservoir. In spite of significant potential increase in the production of oil using SP or ASP methods, there are still some big challenges that make the application of chemical EOR slow.

One of the main challenges facing EOR processes is the adsorption of surfactants on the formation rock, which increases the cost of EOR processes involving surfactants [4, 5]. In other words, high adsorption of surfactant can make the chemical EOR processes economically-unfeasible.

It is well-known that the adsorption of ionic surfactants on charged surfaces is primarily governed by electrostatic forces [17]. It is also known that net charge of typical rock/mineral surfaces is strongly dependent in pH; that is, above a certain pH known as pH of point of zero charge (pHpzc), the net charge of the surface is negative and vice versa [18]. Figure 1-a schematically illustrates the adsorption of an anionic surfactant on a positively charged surface. The first adsorbed layer of surfactant is mostly governed by electrostatic attraction. Once this first adsorbed patch formed on the surface, a second layer of surfactant may be adsorbed by surfactant tail-tail hydrophobic interactions at high anionic surfactant concentrations [17, 19]. Adsorption of this second layer helps to change the net surface charge to negative; therefore, repelling other anionic surfactant molecules and saturating the adsorption.
Traditionally, alkali has been used to decrease the adsorption of anionic surfactants on the rock mineral as a sacrificial agent [2]. Alkali acts as a sacrificial agent for anionic surfactants by fixing the surface charge to negative values (pH>pH_{pzc}); The negative charge of the surface causes electrostatic repulsion between the rock/mineral surface and anionic surfactant, leading to a significant decrease in adsorption of anionic surfactant Figure 1-b.

However, in the presence of even small amounts of anhydrite in the formation rock, alkali reacts with the anhydrite [6-9]. Equation 1 shows the reaction between anhydrite and sodium carbonate. Due to this reaction, the alkali is an inefficient sacrificial agent in the case of presence of anhydrite in the formation rock.

\[
\text{CaSO}_4 + \text{Na}_2\text{CO}_3 \rightarrow \text{Na}_2\text{SO}_4 + \text{CaCO}_3 \downarrow \quad \text{(Equation 1)}
\]

As Figure 1-c schematically represents, a negatively-charged polyelectrolyte can also effectively change the net charge of the surface just by being adsorbed on the surface. There are at least two advantages over using a polyelectrolyte as sacrificial agent over a Monomeric one:

1) The multiple adsorption sites on the polyelectrolyte add an exclusive advantage of low rate of desorption of polyelectrolyte comparing to an anionic monomer adsorbed on the surface. For the small molecules with limited adsorption sites, the rate of attachment-detachment is very rapid, which makes the adsorption of monomeric molecules completely reversible [20]. Polyelectrolytes, however, have effectively zero rate of desorption; that is, multiple adsorption sites on the polyelectrolytes anchors on the surface by many points of attachment. In other words, once polyelectrolyte adsorbs on the surface, it is very less probable to detach from the surface [21-23].

2) If polyelectrolyte lies flat on the surface, it will be a very efficient sacrificial agent due to the fact that it covers the surface with a very high charge/area ratio [24].

Figure 1-a) Schematic illustration of adsorption of anionic surfactant on positively charged surface

Figure 1-b) Schematic illustration of electrostatic repulsion when alkali is used to change the surface charge

Figure 1-c) Schematic illustration of adsorbed negatively-charged polyelectrolyte on a positively charged surface causing repulsion with bulk surfactant and reducing the adsorption of anionic surfactant
This study extensively evaluates the application of sodium polyacrylate as an alternative to the traditional sacrificial agents at least in the presence of anhydrite in the formation rock. Static and dynamic adsorption studies have been carried on to demonstrate the benefits of using sodium polyacrylate as sacrificial agent and the disadvantages of using sodium carbonate in the case of presence of anhydrite. Some experimental data has been presented to support that in the presence of anhydrite, sodium carbonate (a traditionally-used alkali) is not an effective sacrificial agent. As for sodium polyacrylate, effect of molecular weight, different rock minerals, different anionic surfactants, different salinities, and added divalent ion concentrations have been examined. Effectiveness of sodium polyacrylate is compared with other chemical candidates. Adsorption of sodium polyacrylate is evaluated in the presence and absence of anionic surfactants and is compared with the adsorption of a selected anionic surfactant. Dynamic adsorption studies have also been performed.

Materials and Methods

Table 1 and 2 summarize the surfactants and polyacrylates used in this study, respectively. Two anionic surfactants (or blend of anionic surfactants) were selected for this study including NI-Blend and S13B. A 0.5 wt% solutions of these surfactants in a 3.5% NaCl brine were used as an initial solution for adsorption experiments unless otherwise is stated. Before carrying on the adsorption experiments, solutions of these surfactants were made in the desired conditions and the solubility and clarity of the surfactant solutions were monitored so that any precipitation of large micelles during experiments may be eliminated. This is important to obtain reproducible and sensible adsorption data.

Table 1) Summary of the properties of surfactants used

<table>
<thead>
<tr>
<th>Trade or descriptive name</th>
<th>Chemical structure</th>
<th>Activity (%)</th>
<th>Supplier</th>
</tr>
</thead>
<tbody>
<tr>
<td>Neodol-67 (N)</td>
<td>( bC_{16,17}(\text{CH}_3-\text{CH}_2-\text{O})_7\text{SO}_4\text{Na} )</td>
<td>22.88</td>
<td>STEPAN</td>
</tr>
<tr>
<td>IOS15-18 (I)</td>
<td>R-\text{CH(OH)}-\text{CH}_2\text{CH(SO}_3\text{)-R} (\sim 75%) \nR-\text{CH=CH-SO}<em>3\text{)-R} (\sim 25%) \where R+R' = C</em>{12,15}</td>
<td>21.29</td>
<td>STEPAN</td>
</tr>
<tr>
<td>NI-Blend</td>
<td>A Blend of Neodol-67-7PO-Sulfate and IOS15-18 (N:I)=4:1</td>
<td>--</td>
<td>--</td>
</tr>
<tr>
<td>Petro-step S13B</td>
<td>i-C_{13}(\text{PO})_7\text{SO}_4\text{Na}</td>
<td>85.50</td>
<td>TIORCO</td>
</tr>
</tbody>
</table>

Table 2) Summary of the properties of the polyacrylates used

<table>
<thead>
<tr>
<th>Trade or descriptive name</th>
<th>Chemical structure</th>
<th>Activity (%)</th>
<th>Supplier</th>
</tr>
</thead>
<tbody>
<tr>
<td>FLOSPERSE 1000</td>
<td>sodium polyacrylate (Mw=2200 Da)</td>
<td>44</td>
<td>SNF</td>
</tr>
<tr>
<td>FLOSPERSE 3000</td>
<td>sodium polyacrylate (Mw=4500 Da)</td>
<td>44</td>
<td>SNF</td>
</tr>
<tr>
<td>FLOSPERSE 15000</td>
<td>sodium polyacrylate (Mw=150 KDa)</td>
<td>30</td>
<td>SNF</td>
</tr>
<tr>
<td>FLOPAM AN 995 BPM</td>
<td>sodium polyacrylate (Mw~3 MDa)</td>
<td>100</td>
<td>SNF</td>
</tr>
<tr>
<td>ACUMER 1100</td>
<td>sodium polyacrylate (Mw=4500 Da)</td>
<td>47-49</td>
<td>DOW Chemical</td>
</tr>
<tr>
<td>Poly(acrylic sodium salt)</td>
<td>sodium polyacrylate (Mw= 5100 Da)</td>
<td>100</td>
<td>Sigma-Aldrich</td>
</tr>
</tbody>
</table>

Table 3 shows some of the characteristics of the used rocks/minerals as adsorbents for this study. The received outcrop rock plugs were first crushed to smaller pieces and then powdered using a shatterbox for 2 min. The powders were sieved and mesh of 100-200 was used for adsorption tests. These powders were not washed due to the care taken for not dissolving the possibly existing anhydrite in the mineral/rock powders.
The BET surface area of this adsorbent was measured using a surface analyzer based on nitrogen adsorption (Quantachrome instruments Autosorb-3B). The samples were degassed at 200°C at vacuum pressure of 10 mtorr for 12 hrs. The temperature of the liquid nitrogen bath, used during the BET test, was 77.4 K, and an equilibrium time of 3 hrs was used for each point. This is a common procedure followed by many researchers [10, 11].

### Table 3) Properties of the powdered rocks and minerals used

<table>
<thead>
<tr>
<th>Adsorbent (Powdered Rock/Mineral)</th>
<th>Multi-point BET Surface Area* (m²/g)</th>
<th>T-Method External Surface Area (m²/g)</th>
<th>T-Method Micro-Porous Pore Volume (cc/g)</th>
<th>Average Pore Diameter (nm)</th>
<th>Other Notes</th>
</tr>
</thead>
<tbody>
<tr>
<td>purified calcite</td>
<td>1.318</td>
<td>1.222</td>
<td>5.008E-5</td>
<td>1.820</td>
<td>(99.5 wt% CaCO₃) Alfa Aesar [Lot # C270009]</td>
</tr>
<tr>
<td>industrial calcite</td>
<td>1.608</td>
<td>1.297</td>
<td>1.617E-5</td>
<td>1.780</td>
<td>97.00 wt% CaCO₃ (38.80 wt% Ca) Franklin Industrial Minerals</td>
</tr>
<tr>
<td>Carlpool dolomite</td>
<td>0.7846</td>
<td>0.7426</td>
<td>1.726E-5</td>
<td>4.181</td>
<td>(20.00 wt% Ca) (10.00 wt% Mg) Earthsafe Organics Carlpool Products</td>
</tr>
<tr>
<td>Indiana limestone</td>
<td>0.9851</td>
<td>0.9850</td>
<td>1.421E-7</td>
<td>4.363</td>
<td>Kocurek Industries</td>
</tr>
<tr>
<td>purified kaolinite</td>
<td>20.8655</td>
<td>19.5626</td>
<td>5.832E-4</td>
<td>4.969</td>
<td>Sigma-Aldrich [Lot # 048K0046]</td>
</tr>
<tr>
<td>powdered Berea sandstone</td>
<td>2.6750</td>
<td>2.6730</td>
<td>3.341E-4</td>
<td>1.149</td>
<td>Kocurek Industries</td>
</tr>
</tbody>
</table>

* 11 points were used for calculation of BET

In order to measure adsorption, some volume of surfactant solution (usually, 5 ml of 0.5 wt% at 3.5% NaCl brine in the case of no sacrificial agent) is contacted with some weight of the powdered rock or mineral, and mixed on a rotary mixer (4-5 rpm) at room temperature for 24 hrs. The concentration of anionic surfactant is measured using potentiometric titration. The surfactant solution after centrifuge at 8000 rpm for 4 min is diluted with DI-water, and the concentration is measured using 1 mM TEGO solution and potentiometric titration device (Metrohm 716 DMS Titrino). To insure that presence of sodium polyacrylate does not affect measurement of anionic surfactant, the pH of the solution is set to 3. Some unpublished data proves that sodium polyacrylate has no effect on the measurement of anionic surfactants if the pH is set to 3. The concentration of sodium polyacrylate is measured in accordance with previous publications through a colorimetric method [12, 13].

Adsorption is measured by measuring the difference between the concentrations of the anionic surfactant in the bulk before and after contact with the rock. Equation 2 quantifies the relationship between the different variables and amount of adsorption per unit weight of adsorbent:

\[
\text{Adsorption} = \frac{(C_0-C_e)VM_a}{g} \quad \text{(Equation 2)}
\]

C₀ and Cₑ are the initial and equilibrium concentrations of the adsorbate. V is the volume of the adsorbate solution in contact with adsorbent. Mₑ is the molecular weight of the adsorbate, and g is the weight of the adsorbent used.

A significant amount of care has been taken to insure that all the measured adsorption data are indeed located on the plateau region of the adsorption isotherm corresponding to that particular experimental condition. For this reason, each adsorption data point shown in this study is the median of at least 3 points on plateau region of the adsorption isotherm. Usually, five data points is measured by changing the weight of the adsorbent in contact with the same amount and initial concentration of surfactant, and only those which seemed to be on the plateau region were taken into account for calculation of adsorption.

### Results and Discussions

**Effect of Presence of Anhydrite on Alkali as Sacrificial Agent**

Traditionally, alkali is used as sacrificial agent for anionic surfactants. Alkali increases the pH to high values (around 10-12 depending on type of alkali and concentration). This makes the charge of the mineral surface negative; thus repulsing the anionic surfactant from the surface resulting in lowering the adsorption.

Anhydrite and gypsum are the calcium sulfate minerals that are present in some types of rocks, especially in dolomites. Divalent ions can be dissolved in the aqueous phase in the reservoir due to the dissolution of sparingly soluble anhydrite. These hard ions can react with the alkali and/or surfactant, and cause a significant increase in adsorption of anionic surfactants. Many authors have studied the effect of anhydrite in the ASP processes, and have observed that even a low percentage of
anhydrite can have an important effect on adsorption of surfactant on the rocks [6, 9]. A work recently done by our research group showed that presence of only 0.1 wt % anhydrite in the rock causes retardation of surfactant to about 0.7 pore volume, which is considered a huge amount of adsorption [7]. Recently, some researchers have claimed that sodium hydroxide is a better alkali to be used comparing to sodium carbonate in the presence of anhydrite [8].

The adsorption of a surfactant (NI-Blend, initial Conc. = 0.5 %wt) was measured in the case of adding different amounts of sodium carbonate to a mixture of pure calcite and calcium sulfate (anhydrite). By changing the concentration of sodium carbonate, the stochiometric ratio between sodium carbonate and anhydrite (STR) was varied from 0.6 to 2.5, resulting in a change in adsorption of the surfactant used.

Figure 2 represents the result of this experiment. The red curve shows adsorption of NI-Blend on pure calcite with addition of 1wt% sodium carbonate without presence of anhydrite. It can be observed that this adsorption isotherm is on the plateau region. The blue curve is the adsorption of NI-Blend (without sodium carbonate) on pure calcite when 5 wt% of the adsorbent is anhydrite. The green and purple curves are adsorption isotherm for NI-Blend on pure calcite when different molar stochiometric ratios of anhydrite and sodium carbonate are present (ranging from 0.6 – 2.5 molar ratio) after 24 and 72 hr mixing time, respectively.

The first thing to notice in this figure is that the purple and green curves (at different equilibrium times of 24 and 72 hours) do not have much difference. This means that 24 hr mixing time is enough for equilibrium of these types of samples. The most important point Figure 2 is that the adsorption of NI-Blend on Pure Calcite changes increases if the molar ratio of anhydride to sodium carbonate increases. In other words, the result of Figure 2 demonstrates how presence of anhydrite affects the adsorption of surfactant, and causes sodium carbonate to be an inefficient sacrificial agent.

STR ratio seems to play a key role on the adsorption of surfactant. Once the STR ratio is more than 2.5, the adsorption of surfactant seems to be approximately the same as the adsorption of surfactant in the case of an infinite STR ratio (red curve). Similarly, by decreasing the STR ratio, the adsorption increases until it approaches the adsorption corresponding to zero STR ratios (blue curve). In a reservoir, the value of STR depends on the concentration of alkali used and the concentration of anhydrite in the rock.

Figure 2) Experimental data for the effect of presence of anhydrite on adsorption of anionic surfactant (NI-Blend)

Comparison of Sodium Polyacrylate with other Traditionally-Used Sacrificial Agents and Other Candidates

A list of potential candidates was selected: Glycolic acid, Glyceric acid, Sodium EDTA, Pectin, sodium Algae, and sodium polyacrylate. The criteria for choosing these chemicals as possible sacrificial agent candidates are as follows:

- Presence of Carboxylic functionality
- To be bio-compatible
- To be reasonably-priced (not much more expensive than surfactants)
- To be commercially-available
A very common plot in this study is the adsorption of a surfactant vs. the initial concentration of sacrificial agent, which is introduced in this section. Figure 3 shows the result of the experiment on adsorption of NI-Blend (0.5 wt% initial concentration) on Carlpool Dolomite in 3.5 wt% NaCl salinity after addition of different initial concentration of different chemicals. Clearly, a chemical can be selected as a better sacrificial adsorption agent if it can reduce the adsorption of surfactant to a lower value just by using less of that sacrificial agent. In Figure 3, it seems sodium polycarboxylate with an average molecular weight of 4500 Da shows the most promise as a sacrificial agent. Sodium alginate and pectin are in second place, and other monomer compounds were not that effective in reducing the adsorption of NI-Blend on dolomite in this experimental condition.

Also, these results show that addition of 1 wt% sodium carbonate has reduced the adsorption only by about 20% comparing to the case that sodium carbonate is not used. This can be explained by the presence of anhydrite in dolomites, which reacts with the sodium carbonate as discussed in previous section.

In addition, sodium polycarboxylate has been obtained and tested from two different vendors with a similar molecular weight. This is a test to investigate if the result is specific to a product from a particular vendor due to the presence of some potential impurities. However, one can see that sodium polycarboxylates of similar molecular weight from two different vendors have shown similar effect on reducing the adsorption of NI-Blend on dolomite in this experimental condition.

![Figure 3](image)

**Figure 3** Comparison of sodium polycarboxylate with some monomer and polymeric candidates as sacrificial agent

In addition to comparing sodium polycarboxylate with other candidate chemicals, a comparison has been performed between sodium polycarboxylate and some recently introduced sacrificial agents in recent publications (sodium metaborate and poly(ethyleneglycol) methyl ether) [14-16]. Figure 4 represents the result of this comparison. It can be seen that sodium polycarboxylate reduces adsorption on dolomite in the presence of anhydrite of anionic surfactant (NI-Blend) to very low values at a much lower concentration; therefore, sodium polycarboxylate shows stronger character as sacrificial agent comparing to the ones recently introduced in publications.
Effect of Molecular Weight of Sodium Polyacrylate in Reducing Adsorption of Anionic Surfactants

One of the first basic questions about application of sodium polyacrylate as sacrificial adsorption agent is to verify the effect of molecular weight on reducing adsorption of anionic surfactants. The importance of this question is that higher molecular weight polyacrylate tends to precipitate in the presence of divalent ions.

In this section, the following questions are answered for the tested experimental conditions:

- Does molecular weight of sodium polyacrylate have an effect on reducing adsorption of anionic surfactants?
- If yes, what is that effect, and which molecular weight of sodium polyacrylate is best to be used as sacrificial agent?

To answer these questions, Batch adsorption experiments have been done varying the initial concentration of added polyacrylate for each different molecular weight.

As it can be seen in Figure 5, increase in molecular weight of polyacrylate from that of the repeating unit (sodium propionate) to that of polyacrylate ($M_w = 4,500$ Da) decreases the adsorption of surfactant to a significantly lower value; therefore, increase in the molecular weight of sodium polyacrylate up to 4,500 (Da) benefits reducing surfactant adsorption. However, all the curves corresponding to higher molecular weights than 4,500 (Da) lie on each other, meaning that increase in the molecular weight of polyacrylate above 4,500 (Da) does not play an important role in reducing adsorption of surfactant. It can be deduced that molecular weight of sodium polyacrylate has an important role in reducing adsorption of surfactant; that is, increase in the molecular weight of sodium polyacrylate up to 4500 Da significantly decreases the adsorption of the selected surfactant (NI-Blend) at experimental conditions used (3.5 % NaCl). However, increase in the molecular weight of polymer beyond 4,500 Da does not further reduce the adsorption of surfactant.

Consequently, 4,500 Da has been considered an optimum molecular weight, at least at the experimental conditions explored in this study. Also, 4,500 (Da) is a very suitable molecular weight, in that it is very resistant to the presence of divalent ions, and it does not usually precipitate in brines used in enhanced oil recovery. In fact, its addition may also help surfactant to tolerate the presence of divalent ions as a scale inhibitor. A complete study on the effect of divalent ions on efficiency of polyacrylate as sacrificial adsorption agent follows in this study.
Sodium Polyacrylate as Sacrificial Agent for different anionic surfactant on Carlpool dolomite

To further demonstrate that sodium polyacrylate can be used as an effective sacrificial agent for anionic surfactants, adsorption of two different anionic surfactants has been measured in different added concentrations of sodium polyacrylate. The experimental method used to measure the adsorption is the same as explained in the materials section; that is, 5 ml of 0.5 % solution of each surfactant/surfactant blend at 3.5 % NaCl salinity was used as initial solution, and the adsorption was measured on Carlpool dolomite at room temperature. Figure 6 demonstrates the result of these measurements. It can be seen that adsorption of these two different anionic surfactant/surfactant blends is different in the absence of sodium polyacrylate, but addition of sodium polyacrylate is reducing the adsorption very similarly. This indicates that sodium polyacrylate is an efficient sacrificial agent for these different types of anionic surfactants with different structures and different optimal salinities.

**Figure 6**) Effect of sodium polyacrylate on different anionic surfactants
Adsorption of Sodium Polyacrylate in the absence/presence of anionic surfactant in comparison with adsorption of Surfactant

In using any sacrificial adsorption agent, the adsorption of sacrificial agent on the rock is as important as its effect on reducing adsorption of surfactant. In this report, we are answering the following question:

- Is adsorption of polyacrylate lower than adsorption of the anionic surfactants on rocks?
- And if it is, how much lower?

If the adsorption of polyacrylate on the rock mineral is much lower than adsorption of anionic surfactant, it becomes advantageous to use sodium polyacrylate as sacrificial adsorption agent. On the other hand, if the adsorption of polyacrylate is not significantly lower than adsorption of surfactant; its application as sacrificial agent may not be beneficial.

It is important to measure adsorption of polyacrylate in the presence or absence of surfactant in order to see if the presence of surfactant may affect adsorption of polyacrylate (We have shown that addition of polyacrylate on surfactant has a great effect in reducing surfactant adsorption).

If the presence of surfactant has no effect on adsorption of polyacrylate, it may be possible to co-inject them without any concern about the effect of surfactant on adsorption of polyacrylate. An experimental method was developed and tested to measure the concentration of polyacrylate in the presence of anionic surfactants in the same experimental conditions used as polyacrylate adsorption experiments.

Figure 7 shows the adsorption of sodium polyacrylate (M_w=4500 Da) on Carlpool dolomite with and without presence of an anionic surfactant (NI-Blend) at 3.5 % NaCl salinity, comparing to the adsorption of NI-Blend at the same experimental condition (3.5 % NaCl salinity, room temperature). The blue bars are related to the adsorption of sodium polyacrylate on Carlpool dolomite, while the green bar is that of selected anionic surfactant (NI-Blend) in the absence of polyacrylate.

Figure 7 also shows that adsorption of sodium polyacrylate is about fifth of adsorption of surfactant on Carlpool dolomite at same experimental conditions (initial concentration = 0.5 wt% (plateau region), salinity = 3.5 % NaCl, Room Temperature, 24 h Equilibrium time).

It is clear that no significant change in adsorption of polyacrylate has been measured with change in concentration of surfactant. In other words, the presence of anionic surfactant does not have a significant effect on adsorption of polyacrylate; that is, adsorption of polyacrylate is independent of the presence and concentration of surfactant.

![Figure 7) Adsorption of sodium polyacrylate in the presence and absence of surfactant](image)

**Sodium Polyacrylate as Sacrificial Agent for anionic surfactant on Different Minerals/Rocks**

Effect of addition of 2500 ppm sodium polyacrylate (M_w=4500 Da) on adsorption of NI-Blend on different outcrop minerals and rocks have been investigated. Also, the reduction in adsorption of NI-Blend suing 2500 ppm sodium polyacrylate has been compared with that of 1 % sodium carbonate, and no sacrificial agent.
The motivation for investigating effect of addition of sodium polyacrylate as sacrificial agent on different rocks is to answer these two questions:

- Does sodium polyacrylate effectively reduce adsorption of anionic surfactants on a variety of rocks and minerals that are common in different oil reservoirs?
- Does sodium polyacrylate act as sacrificial adsorption agent only by chelating the divalent (calcium and magnesium) cations?

The first question can be answered by comparing plateau region of adsorption isotherms at different minerals and rocks, and comparing the results with that of traditionally-used sacrificial agent (1 % sodium carbonate) and that of no sacrificial agent.

The second question can be answered by evaluating the effect of addition of sodium polyacrylate on a pure mineral (Pure kaolinite) in soft brine (no hardness) brine.

Figure 8 illustrates the experimental results for the effect of addition of sodium polyacrylate on adsorption of a selected anionic surfactant (NI-Blend) on different rocks and minerals. As it can be seen, sodium polyacrylate reduces the adsorption of NI-Blend in all the samples with or without anhydrite. Even in the case of pure kaolinite, the adsorption reduces by adding sodium polyacrylate; which imply that the mechanism by which sodium polyacrylate decreases adsorption of anionic surfactants is not merely by chelating divalent ions. Figure 8 also shows that 2500 ppm of sodium polyacrylate decreases the adsorption of NI-Blend much more than using 10,000 ppm of sodium carbonate.

**Effect of Salinity on the Application of Sodium Polyacrylate as Sacrificial Agent**

Salinity is an important factor which should be determined on the application of sodium polyacrylate as sacrificial agent. The effect of salinity on reducing adsorption of a selected anionic surfactant (NI-Blend) on Carpool dolomite (a rock containing anhydrite impurity) and powdered Berea sandstone (a rock without anhydrite impurity) when sodium polyacrylate is added as sacrificial agent has been studied.

Figure 9-a shows the effect of salinity on adsorption of NI-Blend on Carpool Dolomite with and without addition of 2500 ppm sodium polyacrylate (M_w=4500 Da). It can be seen that the adsorption is slightly increasing with increase of salinity in the case of absence of polyacrylate. Also, it can be seen that adsorption of NI-Blend in presence of polyacrylate is equally low over the whole range of salinity. This behavior is interpreted by the presence of anhydrite in the dolomite. At low salinities, anhydrite dissolves more, which may contribute to higher adsorption. Regardless of anhydrite, increase in the salinity generally causes the adsorption of anionic surfactants to increase. It seems that these two rival mechanisms can keep the adsorption nearly constant, or at least diminish the changes.
Figure 9-a) Effect of salinity (Carlpool Dolomite) shows the adsorption of NI-Blend on powdered Berea sandstone with and without addition of 2500 ppm sodium polyacrylate (M_w=4500 Da). In the case of powdered Berea sandstone, the adsorption significantly increases with increase in salinity. This effect of salinity on adsorption of anionic surfactants is well known.

Effect of Concentration of Divalent ions on the Application of Sodium Polyacrylate as Sacrificial Agent

By this point, all the tests on sacrificial agents are tested in 3.5 % wt NaCl brine without presence of any hardness in the brine. Although some divalent ions may be present when brine being contacted with adsorbent (especially in the case of presence of anhydrite in the rock), no initial divalent ions were present in the brine.

However, Enhanced Oil Recovery usually is performed using injection of brines or sea water, containing hard ions. In fact, zero concentration of divalent ions in a real EOR application is very rare. Therefore, it is essential to investigate the effect of divalent ions on adsorption of surfactant before and after addition of sodium polyacrylate as sacrificial adsorption agent.

In this part, adsorption of NI-Blend (initial concentration = 0.5 wt %) is measured with different added concentrations of divalent ions before and after addition of 2500 ppm sodium polyacrylate (M_w = 4500 Da) on four different rocks or minerals, including pure calcite, pure kaolinite, powdered Berea sandstone, and Carlpool dolomite. This may result in a better understanding of the effect of divalent brine on efficiency of sodium polyacrylate as sacrificial agent.

Before measuring adsorption, it is essential to make sure that surfactant is soluble in the experimental condition; otherwise, precipitation may wrongly be deduced as high values of adsorption (This is commonly known as abstraction). Different surfactants start precipitating at some concentrations of divalent ions depending on the type of the surfactant, concentration of surfactant, and total salinity. To investigate the solubility of the surfactant at each different hardness, a visual test is done by preparing the surfactant solution at desired experimental condition (0.5 wt% NI-Blend, 3.5 wt% NaCl) varying the concentration of divalent ions. Clarity of such solutions is then visually judged. Table 4 represents the result of this test at the above-mentioned experimental conditions. It can be seen that solution becomes hazy near the CaCl_2 concentration of 3700 ppm. This should be the upper limit for the adsorption experiment since at higher concentrations of calcium chloride, NI-Blend precipitates.

Adsorption of NI-Blend on different adsorbents, including Carlpool Dolomite, powdered Berea Sandstone, pure calcite, and pure kaolinite has been measured in the case of absence and presence of 2500 ppm sodium polyacrylate (M_w = 4500 Da) varying the concentration of calcium chloride. These curves show how the presence of divalent ions in the brine can affect sodium polyacrylate sacrificial adsorption properties.

Figures 10-a,b,c,d show the effect of divalent ions on adsorption of NI-Blend (0.5 % initial concentration of NI-Blend, 3.5 % NaCl salinity) with and without the presence of polyacrylate on powdered Berea sandstone, Carlpool Dolomite pure calcite, and pure kaolinite, respectively.
Table 4) Clarity of a 0.5 wt% NI-Blend solution in different concentrations of CaCl₂ and 3.5 wt% NaCl

<table>
<thead>
<tr>
<th>Weight (g) of 2% NI-Blend (3.5% NaCl)</th>
<th>Weight (g) of 1% CaCl₂·2H₂O (3.5% NaCl)</th>
<th>Weight (g) of 3.5% Brine</th>
<th>Clarity</th>
<th>Concentration Of NI-Blend (wt%)</th>
<th>Concentration of Added CaCl₂ (ppm)</th>
</tr>
</thead>
<tbody>
<tr>
<td>4.9397</td>
<td>0.5125</td>
<td>14.330</td>
<td>Clear</td>
<td>0.499</td>
<td>196</td>
</tr>
<tr>
<td>4.9517</td>
<td>1.0452</td>
<td>13.831</td>
<td>Clear</td>
<td>0.499</td>
<td>398</td>
</tr>
<tr>
<td>4.9326</td>
<td>1.9908</td>
<td>12.848</td>
<td>Clear</td>
<td>0.499</td>
<td>761</td>
</tr>
<tr>
<td>4.9418</td>
<td>3.9685</td>
<td>10.871</td>
<td>Clear</td>
<td>0.500</td>
<td>1515</td>
</tr>
<tr>
<td>4.9415</td>
<td>4.9727</td>
<td>9.9007</td>
<td>Clear</td>
<td>0.499</td>
<td>1894</td>
</tr>
<tr>
<td>4.9423</td>
<td>6.9263</td>
<td>7.905</td>
<td>Clear</td>
<td>0.500</td>
<td>2644</td>
</tr>
<tr>
<td>4.9500</td>
<td>7.9121</td>
<td>6.918</td>
<td>Clear</td>
<td>0.500</td>
<td>3020</td>
</tr>
<tr>
<td>4.9551</td>
<td>8.8984</td>
<td>5.929</td>
<td>Clear</td>
<td>0.501</td>
<td>3395</td>
</tr>
<tr>
<td>4.9492</td>
<td>9.8780</td>
<td>4.9547</td>
<td>Hazy</td>
<td>0.500</td>
<td>3769</td>
</tr>
<tr>
<td>4.9341</td>
<td>11.8611</td>
<td>2.9668</td>
<td>Cloudy</td>
<td>0.499</td>
<td>4531</td>
</tr>
<tr>
<td>4.9336</td>
<td>12.8770</td>
<td>1.9778</td>
<td>Cloudy</td>
<td>0.499</td>
<td>4912</td>
</tr>
<tr>
<td>4.9397</td>
<td>14.8142</td>
<td>0.0000</td>
<td>Cloudy</td>
<td>0.500</td>
<td>5661</td>
</tr>
<tr>
<td>4.9426</td>
<td>13.8624</td>
<td>1.0154</td>
<td>Cloudy</td>
<td>0.499</td>
<td>5280</td>
</tr>
</tbody>
</table>

Figure 10-a) Effect of Divalent ions (Berea Sandstone)

Figure 10-b) Effect of divalent ions (Dolomite)

Figure 10-c) Effect of divalent ions (pure calcite)

Figure 10-d) Effect of divalent ions (pure kaolinite)
Generally, it can be seen (Figures 10-a,c,d) that in all three adsorbents that do not possess anhydrite, there is a monotonic increase in the adsorption of surfactant with increase in the added concentration of calcium chloride, both in the absence or presence of sodium polyacrylate. This is due to the concentration of divalent ions (Ca\(^{+2}\)) inside the solution increasing with increase in the added amount of calcium chloride. Increase in the adsorption of surfactant with increase in the equilibrium concentration of hard ions is a well-known fact.

However, in the case of Carlpool dolomite (Figure 10-b), with the presence of anhydrite, adsorption does not increase dramatically. This might be due to presence of anhydrite, which acts like a hard-ion buffer. In one hand, at low concentrations of calcium chloride, anhydrite dissolves, resulting in the presence of calcium in equilibrium condition. On the other hand, at high concentrations of added calcium chloride, anhydrite does not dissolve much. Thus, the equilibrium concentration of divalent ions may not change much with addition of calcium chloride.

In order to understand the data from this section, it is noteworthy to refer to the effect of sodium polyacrylate on adsorption of NI-Bend on purified kaolinite where no divalent ions are added, neither from brine, nor the adsorbent. In such case, addition of sodium polyacrylate still led to a significant decrease in the adsorption of NI-Bend. This can be interpreted that reducing adsorption of surfactant by addition of sodium polyacrylate is not only due to the divalent ions being screened by the presence of sodium polyacrylate.

**Dynamic Adsorption**

To further demonstrate the effect of sodium polyacrylate in reducing adsorption of anionic surfactants, dynamic adsorptions were performed at different concentrations of sodium polyacrylate (0, 1000, and 2500 ppm) co-injected with 0.5 wt% of NI-Blend at 3.5 % NaCl salinity on Carlpool dolomite sand pack. Before the surfactant injection takes place, the packing is flooded with at least 2 pore volume of the same brine (3.5 wt% NaCl brine). Sodium bromide was used as a non-adsorbing tracer, which is supposed to breakthrough at 1 pore volume. However, sodium polyacrylate (if present) and NI-Blend demonstrates different breakthroughs due to adsorption. This retardation (the difference between breakthrough of the non-adsorbing tracer and surfactant/polyacrylate) is related to the adsorption.

Figure 11-a, 11-b, and 11-c demonstrate the result of dynamic adsorption for 0, 1000, and 2500 ppm of sodium polyacrylate as sacrificial agent, respectively. The adsorption from the dynamic test is 1.55, 0.83, and 0.78 mg/g for 0, 1000, and 2500 ppm of sodium polyacrylate, respectively. It is noticeable that the adsorption decreases with addition of sodium polyacrylate. However, the reduced amount of adsorption is not comparable with the static tests; that is the adsorption of surfactant in the dynamic test is reduced less than the adsorption in the static test (Figure 12). This phenomenon can be related to presence of anhydrite in the dolomite, which makes the ratio of divalent ions to polyacrylate in static and dynamic tests to be different.

![Figure 11-a) Dynamic adsorption of 0.5 wt% NI-Blend on Carlpool Dolomite with no sacrificial agent](image)
Figure 11-b) Dynamic adsorption of 0.5 wt% NI-Blend on Carlpool Dolomite with 1000 ppm sodium polyacrylate

Figure 11-c) Dynamic adsorption of 0.5 wt% NI-Blend on Carlpool Dolomite with 2500 ppm sodium polyacrylate

Figure 12) Comparison between the results of static and dynamic adsorption
Conclusions

The application of sodium polyacrylate as sacrificial agent for reducing adsorption of anionic surfactant is investigated in this paper. Sodium polyacrylate was shown to be a better candidate as sacrificial agent in comparison to some other candidates including sodium carbonate, glycolic acid, glycric acid, disodium EDTA, as monomers as well as pectin from citrus peel and sodium algin ate as polymers. The candidates were selected to be bio-compatible and have carboxylic functionality (due to a better chemical affinity for carbonates). Also, sodium polyacrylate was compared with other sacrificial agents introduced in the literature (polyethylene glycol, sodium carbonate, and sodium metaborate) to evaluate the effectiveness of polyacrylate for reducing adsorption of anionic surfactants. The results showed that sodium polyacrylate is significantly more effective sacrificial agent compared to the previously introduced ones, at least in the experimental conditions used here.

The effect of molecular weight of sodium polyacrylate on sacrificial properties was investigated. The results showed that increase in the molecular weight has an important effect on reducing adsorption of anionic surfactant until a point (MW=4500 Da) that increase in the molecular weight does not add any further advantage. The fact that a molecular weight of about 4500 Da is optimum condition also eliminates any concerns about precipitation of polyacrylate in the excess of divalent ions, which is the case if a very high molecular weight of polyacrylate were to be used.

The adsorption of sodium polyacrylate on a selected carbonate (Carpool Dolomite) was measured to be 1/5 of the adsorption of a selected anionic surfactant on the same experimental conditions. Also, it was shown that the adsorption of polyacrylate does not significantly change in the absence or presence of surfactant. This makes the design of a dynamic injection much simpler because of independency of the polyacrylate wave to that of surfactant wave from a fractional flow point of view.

Also, the effect of sodium polyacrylate as a sacrificial agent was tested in different minerals/rocks as well as different anionic surfactants to further show the effectiveness of polyacrylate as sacrificial agent if the right molecular weight and concentration is chosen. These results revealed that sodium polyacrylate is an effective sacrificial agent on carbonates, sandstones, and clays. The results also suggests that the mechanism through which polyacrylate reduces adsorption of anionic surfactant is not merely by sequestering divalent ions in the aqueous phase due to the fact that the adsorption of anionic surfactant on pure kaolinite (no divalent ions in the adsorbent) decreases significantly by using sodium polyacrylate in a soft brine (no divalent ions in the brine). In addition, sodium polyacrylate decreases the adsorption of two different anionic surfactants.

Batch experiments were done to evaluate the effect of salinity and divalent ions in the brine. The results indicate that increase in the salinity or concentration of divalent ions in the brine result in higher adsorptions except when the adsorbent is dolomite.

Dynamic adsorption tests also were carried out and the results demonstrate that addition of sodium polyacrylate decreases the adsorption; however, this decrease does not match the static data. The explanation is that the ratio of divalent ions concentration/polyacrylate in dynamic test is much higher than in static test.

References


