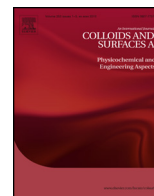




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Reducing adsorption of anionic surfactant for enhanced oil recovery: Part II. Applied aspects

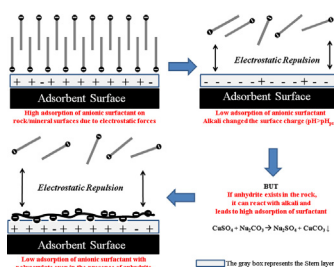
Hadi ShamsiJazeyi, Rafael Verduzco¹, George J. Hirasaki^{*}

Rice University, Chemical and Biomolecular Engineering Department, 6100 Main Street, MS-362, Houston, TX 77005, USA

HIGHLIGHTS

- In previous work, the mechanism of competitive adsorption was studied.
- Polyacrylate reduces adsorption of different anionic surfactants on different rocks.
- Effect of salinity, Ca^{2+} ion concentration, and temperature was tested.
- Dynamic and static tests were compared when anhydrite and polyacrylate are present.
- An economic model was developed and showed cost benefit of using polyacrylate.

GRAPHICAL ABSTRACT



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ABSTRACT

The surfactant loss due to adsorption has significant economic consequences for surfactant-based enhanced oil recovery (EOR) processes. Alkali, traditionally used as sacrificial agent to reduce adsorption of anionic surfactants, cannot be efficiently used in the presence of anhydrite due to the reactivity of carbonate with anhydrite. In our previous publication, the competitive adsorption mechanism of an anionic surfactant and polyacrylate has been studied. In this work, the effect of some reservoir parameters on application of polyacrylate as a sacrificial agent is investigated. Addition of polyacrylate is shown to reduce adsorption of different anionic surfactants on different outcrop minerals, including Carpool dolomite, industrial calcite, kaolinite, Berea sandstone, and Indiana limestone. The effect of salinity, concentration of Ca^{2+} ions, and temperature on effectiveness of sodium polyacrylate as sacrificial agent has been evaluated on different minerals/rocks. Results of dynamic adsorption measurements with sodium polyacrylate are also reported. Cost analysis shows that addition of a small amount of polyacrylate can significantly decrease the total material cost to as low as one-fifth of that without use of sacrificial agent. The reduction in cost depends on the values of dimensionless numbers developed in this paper. Altogether, these experiments demonstrate the advantage of using sodium polyacrylate as sacrificial adsorption agent for anionic surfactants even in the presence of anhydrite in the reservoir.

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1. Introduction

With the increasing demand of energy around the world and diminishing amount of conventional oil, enhanced oil recovery (EOR) methods have recently attracted significant attention for production of oil. Chemical EOR processes are those in which alkali, surfactants and/or polymers are used to lower interfacial

^{*} Corresponding author. Tel.: +1 713 348 5416; fax: +1 713 348 5478.

E-mail addresses: hadi.shamsi.jazeyi@rice.edu (H. ShamsiJazeyi), rafaelv@rice.edu (R. Verduzco), gjh@rice.edu (G.J. Hirasaki).

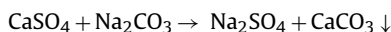
¹ Tel.: +1 713 348 6492.

tension, change the wettability, and control mobility in order to increase the amount of oil recovered often from a previously water-flooded reservoir [1–3]. In spite of significant potential that surfactant-based EOR methods offer, there are still challenges to make chemical EOR economically viable in most reservoirs.

One of the main challenges is the surfactant loss due to adsorption on formation rocks [4,5]. High adsorption of surfactant can make the chemical EOR processes economically unfeasible. One way to reduce adsorption of surfactants in a reservoir is to inject chemicals that adsorb on the rock and reduce surfactant adsorption. Such chemicals are known as sacrificial agents.

The net charge of most typical rock/mineral surfaces is strongly dependent on pH; that is, above a certain pH known as point of zero charge (pH_{pzc}), the net charge of the surface is negative and below this pH the surface charge is positive [6,7]. Fig. 1(left) 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 [8]. Once this first adsorbed patch forms on the surface, a second layer of surfactant may be adsorbed by surfactant tail–tail hydrophobic interactions at high surfactant concentrations [8,9]. Adsorption of this second layer of anionic surfactant helps to change the net surface charge to negative, thereby, repelling further anionic surfactant molecules from the surface and saturating the adsorption.

Traditionally, alkali has been used as a sacrificial agent to decrease the adsorption of anionic surfactants on rocks [2]. The addition of alkali increases the pH and thus it can make the surface charge negative ($\text{pH} > \text{pH}_{\text{pzc}}$), which causes electrostatic repulsion between the rock/mineral surface and anionic surfactant, leading to a significant decrease in adsorption of anionic surfactant (Fig. 1(middle)). However, presence of anhydrite, a slightly soluble calcium sulfate present in some types of rocks especially in dolomites, can reduce the effectiveness of alkali due to a reaction shown in following Scheme [10–13]:



As shown schematically in Fig. 1(right), a negatively-charged polyelectrolyte can also effectively change the net charge of the surface by being irreversibly adsorbed on the surface, which is through a different mechanism than alkali. The mechanisms involved in this process have been studied in our previous work [14].

In our previous publication [14], we focused on fundamental understanding and the mechanisms of reducing adsorption of anionic surfactant using polyacrylate. In this study, the effect of reservoir parameters on application of polyacrylate as a sacrificial agent is investigated. Static and dynamic adsorption studies are conducted to demonstrate the benefits of using sodium polyacrylate as sacrificial agent and its superior performance, compared with alkali, especially in the presence of anhydrite. The effect of different rock types, two different anionic surfactants, as well as range of salinities, Ca^{2+} ion concentrations, and temperatures are studied. We conclude with analyzing cost benefits of using polyacrylate as sacrificial agent for reducing adsorption of anionic surfactant.

2. Materials and methods

Indiana limestone and Berea sandstone granules are provided by Kocurek industries and are powdered using a shutter box. Then, they are sieved and mesh of 100–200 is used for adsorption tests. Industrial calcite is purchased from Franklin industrial minerals, and the mesh of 100–200 is selected after sieving. Kaolinite is purchased from Sigma-Aldrich and is used as received. Calcium carbonate (calcite) is purchased from Alfa Aesar and used as received. The rocks/minerals are not washed to ensure anhydrite would be present during measurements.

The molecular weight of polyacrylate used in this study is 4500 Da. Petro-step S13B ($\text{i-C}_{13}\text{-(PO)}_7\text{-SO}_4\text{Na}$) is supplied by TIORCO, and used as one of the surfactants in this study. Neodol-67 (N) (activity 22.88%, $\text{bC}_{16-17}\text{-(CH}_2\text{-CH(CH}_3\text{)-O)}_7\text{-SO}_4\text{Na}$) and IOS15-18 (I) (activity 21.29%, $\text{R-CH(OH)-CH}_2\text{-CH(SO}_3^-)\text{-R}$ ($\sim 75\%$) + $\text{R-CH=CH-CH(SO}_3^-)\text{-R}$ ($\sim 25\%$)) were purchased/acquired from STEPAN and used as received. The surfactant blend studied (NI blend) consists of a 4:1 molar ratio blend of N:I surfactants. 0.5 wt% (active material) solutions of NI-blend in a 3.5% NaCl brine were used as initial solution for adsorption experiments unless otherwise is stated. Table 1 shows some of the characteristics of the rocks/minerals used as adsorbents for this study. The procedures for measuring BET surface areas of rocks/minerals, anhydrite content, concentration of surfactant, and surfactant adsorption static test have been described in our previous work [14].

2.1. Effect of salinity and Ca^{2+} ions

Static adsorption tests are used to study the effect of salinity and Ca^{2+} ion concentration on application of polyacrylate as sacrificial agent. By mixing different stock solutions of NI-blend surfactant, the salinity of the initial solutions (before contacting the rock) is varied without changing the concentration of surfactant or polyacrylate (if present).

In the case of presence of anhydrite in the rock, the equilibrium concentration of Ca^{2+} may be different from the concentration of Ca^{2+} initially present in brine due to solubility equilibrium of anhydrite. However, we have presented our data in terms of initial concentration of Ca^{2+} since the concentration of Ca^{2+} in the injected brine is a parameter that can be modified for the field application.

2.2. Adsorption at different temperatures

The effect of temperature on adsorption of NI-blend in the absence or presence of polyacrylate is studied through static adsorption tests at two different salinities. The vials containing mixture of aqueous solutions and adsorbents are tightly sealed to prevent liquid evaporation. The total mass of the vials are accurately measured before and after equilibrium at different temperatures, and no significant change is observed, indicating that evaporation has not occurred during equilibrium.

2.3. Dynamic adsorption measurements

Dynamic adsorption measurements are carried out using a continuous injection (NI-blend with or without polyacrylate at 3.5% NaCl salinity) at a flow rate of $2.5 \text{ cm}^3/\text{h}$ (corresponding to 1 ft/day). This low flow rate was used to ensure that the dynamic adsorption results are near equilibrium, as is the case for static adsorption measurements. Carlpool dolomite powder, same as that used in the static tests, is packed in a glass column, which is connected to an in-line bromide electrode cell and a fraction collector. Prior to injection of surfactant solution (NI-blend) with or without polyacrylate at 3.5% NaCl salinity, a mixture of NaCl and NaBr solutions (pre-flush brine) with equivalent ionic strengths as that of 3.5% NaCl brine solution is injected. NaBr is used as a non-adsorbing tracer in both the pre-flush brine and surfactant/polyacrylate solutions. The concentrations of NaBr in the pre-flush brine and in the surfactant/polyacrylate solution are 3000 and 30,000 ppm, respectively. The concentration of bromide in the effluent is measured using a bromide ion sensitive electrode, ENVCO Br43-0001, and lab-view software is used for signal averaging (a multifunctional data acquisition module is used, National Instruments, NI USB-6210). Samples collected by a fraction collector have been manually analyzed to determine the concentration of NI-blend surfactant and/or polyacrylate. Vials in the fraction collector have been covered to

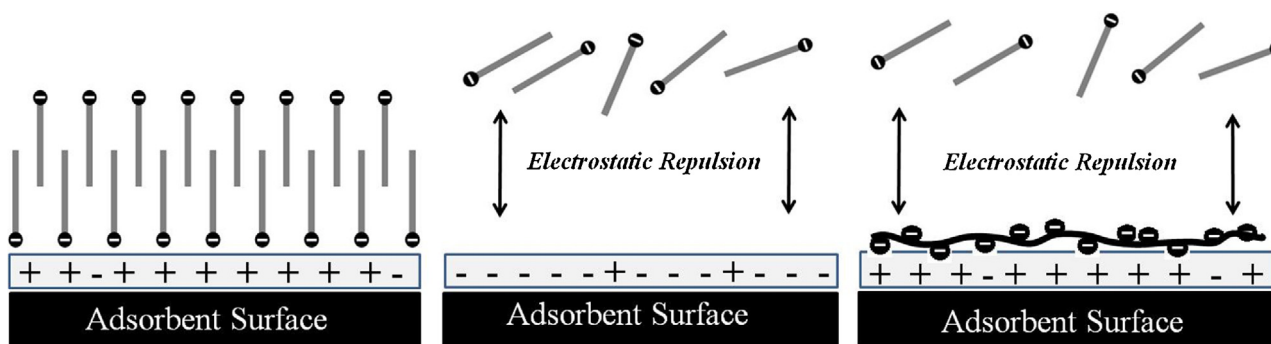


Fig. 1. (Left) Schematic illustration of adsorption of anionic surfactant on positively charged surface, (middle) schematic illustration of electrostatic repulsion between surfactant and negatively-charged surface with using alkali, and (right) Schematic illustration of adsorbed negatively-charged polyelectrolyte on a positively charged surface causing repulsion with bulk surfactant and reducing the adsorption of anionic surfactant (adapted with permission from [13]) the gray box on the surface represents the Stern layer.

Table 1

Properties of the powdered rocks and minerals used.

Adsorbent (powdered rock/mineral)	Multi-point BET surface area* (m ² /g)	T-method external surface area (m ² /g)	Anhydrite percentage (%)	Other notes
Calcite	1.32	1.22	<0.07	(99.5 wt% CaCO ₃) Alfa Aesar [Lot no. C270009]
Industrial calcite	1.61	1.30	0.11	97.00 wt% CaCO ₃ (38.80 wt% Ca) Franklin Industrial Minerals
Carlpool dolomite	0.79	0.74	1.76	(20.00 wt% Ca) (10.00 wt% Mg) Earthsafe Organics Carlpool Products
Indiana limestone	0.99	0.98	0.82	Kocurek Industries
Purified kaolinite	20.87	19.56	<0.07	Sigma-Aldrich [Lot no. 048K0046]
Powdered Berea sandstone	2.68	2.67	NA	Kocurek Industries

* 11 points were used for calculation of BET.

prevent evaporation during collection; otherwise, evaporation can lead to considerable noise in measurements.

3. Results and discussions

3.1. Sodium polyacrylate as sacrificial agent for different anionic surfactants and different minerals/rocks

To demonstrate that sodium polyacrylate can be used as an effective sacrificial agent for anionic surfactants, adsorption of two different anionic surfactants is measured for different added concentrations of sodium polyacrylate. The experimental method used to measure the adsorption is the same as that previously reported [14]. Briefly, 5 ml of a 0.5% solution of each surfactant or surfactant-blend at 3.5% NaCl salinity is contacted with Carlpool dolomite and allowed to equilibrate at room temperature unless otherwise stated. The resulting surfactant concentration in solution is then measured by titration, providing a measure of the amount of surfactant adsorbed on the rock surface. As shown in Fig. 2, the addition of sodium polyacrylate reduces the adsorption of both surfactants on Carlpool dolomite to low values. This indicates that sodium polyacrylate is an efficient sacrificial agent for both types of anionic surfactants, which possess different structures and different optimal salinities.

The effect of 2500 ppm sodium polyacrylate on the adsorption of NI-blend on variety of rocks and minerals that are common in different oil reservoirs is evaluated. As described in our previous work [14], adsorption on different surfaces can be compared by measuring the plateau region of the surfactant adsorption isotherms. It is interesting to know if sodium polyacrylate could effectively reduce adsorption of anionic surfactants on a variety of rocks and minerals that can be found in different oil reservoirs.

As shown in Fig. 2, sodium polyacrylate reduces the adsorption of NI-blend for all rocks both with and without anhydrite. This reduction is greater for carbonates and clays in comparison with sandstone. Fig. 2 also shows that 2500 ppm of sodium polyacrylate

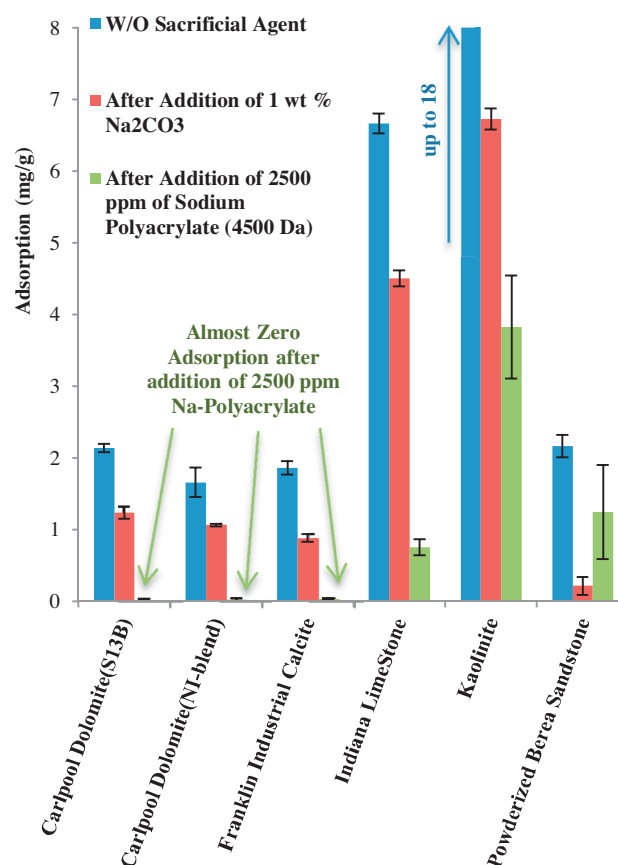


Fig. 2. Effect of sodium polyacrylate to reduce adsorption of NI-blend on different minerals/rocks.

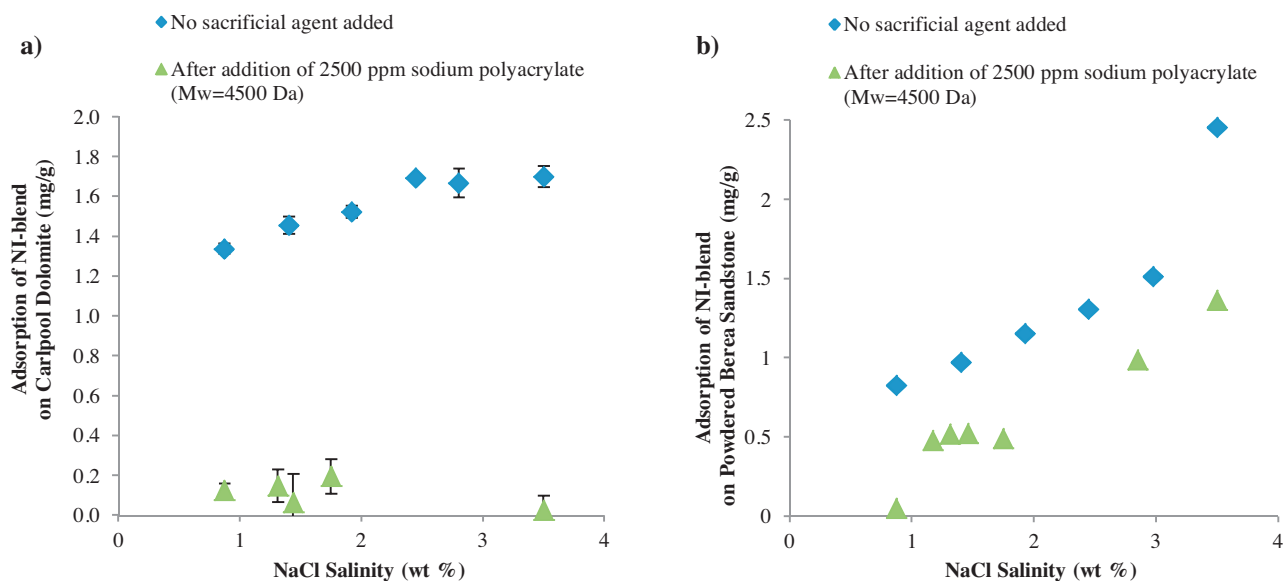


Fig. 3. Effect of salinity on adsorption of NI-blend in absence and presence of polyacrylate on (a) Carlpool dolomite, (b) powdered Berea sandstone.

decreases the adsorption of NI-blend on dolomite to much lower values than that of using 10,000 ppm of sodium carbonate.

3.2. Effect of salinity on the application of sodium polyacrylate as sacrificial agent

Salinity is an important variable in different oil reservoirs. The effect of salinity on adsorption of NI-blend on Carlpool dolomite (a rock containing anhydrite) and powdered Berea sandstone (a rock without anhydrite) with and without addition of polyacrylate is studied.

Fig. 3a shows the effect of salinity on adsorption of NI-blend on Carlpool dolomite with and without addition of 2500 ppm sodium polyacrylate. It can be seen that the adsorption increases with increasing salinity in the absence of polyacrylate, while in presence of polyacrylate, adsorption is low throughout the salinity range. This behavior is attributed to the dissolution of anhydrite, which is affected by salinity. It is well known that the dissolution of anhydrite increases with increase in NaCl salinity, which further increases adsorption of anionic surfactant due to release of Ca^{2+} and SO_4^{2-} ions. Also, the increase in the salinity generally causes the adsorption of anionic surfactants to increase. This explains the increase in adsorption of anionic surfactant on dolomite with increase in the salinity. In the presence of polyacrylate though, these changes may not be significant due to the interactions of polyacrylate and Ca^{2+} .

Fig. 3b shows the adsorption of NI-blend on powdered Berea sandstone with and without addition of 2500 ppm sodium polyacrylate. In the case of powdered Berea sandstone (with no significant anhydrite), the adsorption significantly increases with increase in salinity both in the presence and absence of sodium polyacrylate.

3.3. Effect of concentration of Ca^{2+} on sodium polyacrylate as sacrificial agent

Enhanced oil recovery usually is carried out with the injection of saline brines or sea water, which contains $\text{Ca}^{2+}/\text{Mg}^{2+}$ ions. To investigate the effect of Ca^{2+} ions on surfactant adsorption in presence or absence of polyacrylate as sacrificial agent, the adsorption of NI-blend (initial concentration = 0.5 wt%) is measured with different added concentrations of Ca^{2+} ions both with and without the

addition of 2500 ppm sodium polyacrylate on four different rocks or minerals: pure kaolinite, powdered Berea sandstone, calcite, and Carlpool dolomite.

Before measuring adsorption, a visual clarity test of surfactant solubility in the presence of Ca^{2+} ions is conducted to ensure good surfactant solubility in the presence of Ca^{2+} ions. Surfactant solutions are prepared (0.5% NI-blend, 3.5% NaCl), and the concentration of Ca^{2+} ions have been systematically varied. We found that surfactant solutions become hazy near the Ca^{2+} concentration of 3700 ppm, and all adsorption experiments are carried out with Ca^{2+} concentrations below this level.

The adsorption of NI-blend on different adsorbents, including Carlpool dolomite, powdered Berea Sandstone, calcite, and pure kaolinite is measured with and without added sodium polyacrylate (2500 ppm) while varying the concentration of added calcium chloride. Fig. 4a–d shows the effect of Ca^{2+} ions on adsorption of NI-blend (0.5% initial concentration of NI-blend, 3.5% NaCl salinity) with and without polyacrylate on powdered Berea sandstone, Carlpool dolomite, calcite, and pure kaolinite, respectively.

In case of Berea sandstone, calcite, and kaolinite (with no significant anhydrite), an increase in the adsorption of NI-blend is observed with an increase in the concentration of Ca^{2+} ions (Fig. 4a, c and d). However, in the case of Carlpool dolomite with the presence of anhydrite (Fig. 4b), adsorption does not increase dramatically. This can be interpreted by the presences of two rival mechanisms counter-balance each other in the case of an adsorbent with presence of anhydrite. With addition of CaCl_2 , the dissolution of anhydrite decreases; therefore, although more Ca^{2+} is added to the system, less Ca^{2+} comes from dissolution of anhydrite at higher added concentrations of CaCl_2 . Consequently, these two rival mechanisms can counter-balance each other that may lead to insignificant change in actual concentration of Ca^{2+} in the aqueous phase at different added concentrations of CaCl_2 .

3.4. Effect of temperature on sodium polyacrylate as sacrificial agent

The temperatures of different oil reservoirs can vary from near room temperature to upper values near 150 °C, and thus it is important to determine the role of temperature on surfactant adsorption in the presence of polyacrylate. Fig. 5 shows the effect of temperature on adsorption of NI-blend on Carlpool dolomite at two different

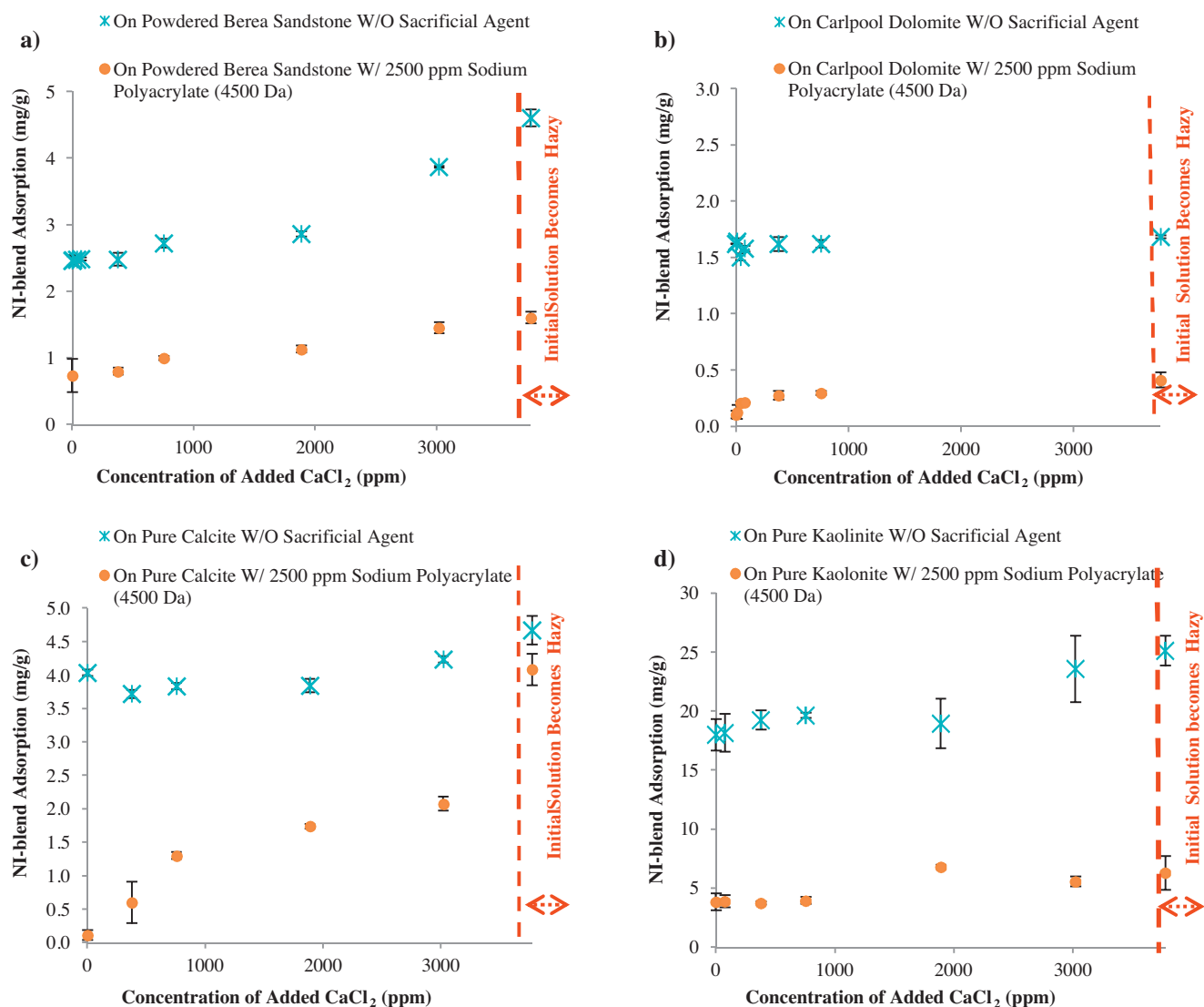


Fig. 4. Effect of Ca^{2+} ions on adsorption of NI-blend in the absence and presence of polyacrylate on (a) powdered Berea sandstone, (b) Carlpool dolomite, (c) calcite, (d) kaolinite.

salinities (0% and 3.5% NaCl) with and without addition of polyacrylate. The initial NI-blend solution in 3.5% NaCl becomes cloudy at temperatures above 48 °C. On the other hand, the NI-blend solution in 0% NaCl is completely clear at all tested temperatures. Therefore, the adsorption of NI-blend in 3.5% has not been shown at temperatures above 48 °C. It can be seen in Fig. 5 that polyacrylate can effectively decrease the adsorption of NI-blend on Carlpool dolomite at various temperatures studied here.

3.5. Dynamic adsorption

To further evaluate the potential of sodium polyacrylate in reducing adsorption of anionic surfactants, dynamic adsorption experiments are performed for different concentrations of sodium polyacrylate, co-injected with 0.5 wt% of NI-blend at 3.5% NaCl salinity in a Carlpool dolomite packed bed. Before surfactant injection, the packed bed is flushed with at least two pore volumes of a brine solution with similar ionic strength as the surfactant solution. Dynamic adsorption test for the injection of 2500 ppm polyacrylate along with NI-blend is shown in Fig. 6. All dynamic adsorption tests are shown in supplementary data (Fig. S3–S6). Sodium polyacrylate (if present) and NI-blend exhibit delayed breakthrough due to

adsorption. This retardation (the difference between breakthrough of the non-adsorbing tracer and polyacrylate or surfactant) can be used to measure adsorption in dynamic tests.

Fig. 7 demonstrates the adsorption of NI-blend from static and dynamic tests for 0, 250, 1000, and 2500 ppm of Sodium polyacrylate as sacrificial agent. The adsorption decreases with addition of Sodium polyacrylate in both dynamic and static tests. It is also evident that the adsorption is greater in case of dynamic test compared to the static adsorption measurements on Carlpool dolomite. This may be due to a larger ratio of Anhydrite to sacrificial agent in dynamic compared with static adsorption tests. In static measurements, about 5 g of rock is in contact with about 5 cm³ of solution. On the other hand, in the dynamic tests, about 350 g of rock is in contact with about 60 cm³ of aqueous solution. Therefore, the lower polyacrylate-to-anhydrite ratio in dynamic adsorption measurements decreases the effectiveness of the sacrificial agent on reducing adsorption of surfactant (electronic supplementary information, Fig. S2). The increase in adsorption of anionic surfactant and reduction in preferential adsorption of Polyacrylate with decrease in polyacrylate-to-anhydrite ratio can be interpreted by presence of the Ca^{2+} and SO_4^{2-} ions resulting from anhydrite dissolution. An extended discussion of the impacts of anhydrite on sacrificial agent

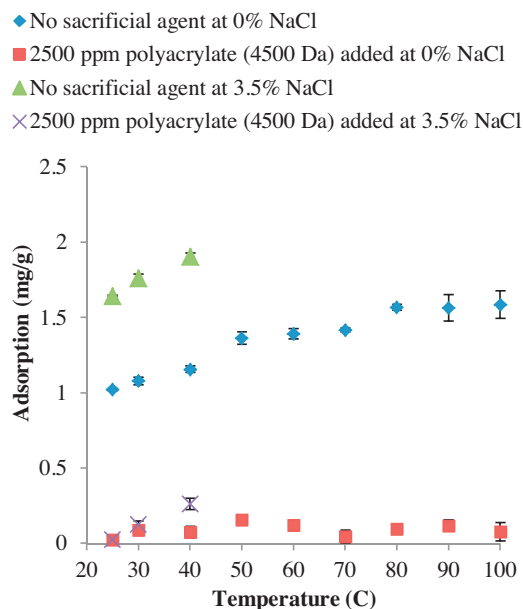


Fig. 5. Effect of Temperature on adsorption of NI-blend on Carlpool dolomite in the absence or presence of sodium polyacrylate.

effects of polyacrylate in reducing adsorption of anionic surfactants is given in our previous paper [14].

An alternative explanation about the discrepancy between the static and dynamic tests can be made by understanding the difference in the ways static and dynamic tests have to be conducted. In the case of static test, dry dolomite is contacted with fixed volume of surfactant solution to equilibrate. However, in the case of dynamic test, the dolomite inside the packed bed is flushed with at least two pore volume of a 3.5% NaCl brine in order to achieve an initial equilibrium before injection of surfactant solution. This flushing in the dynamic test could have dissolved a huge amount of anhydrite which affects the adsorption of anionic surfactant.

Fig. 7 also shows results of static adsorption of surfactant on calcite with certain amount of anhydrite added so that the molar ratio of polyacrylate to anhydrite is similar to that in the dynamic adsorption on Carlpool dolomite. It can be seen that this static

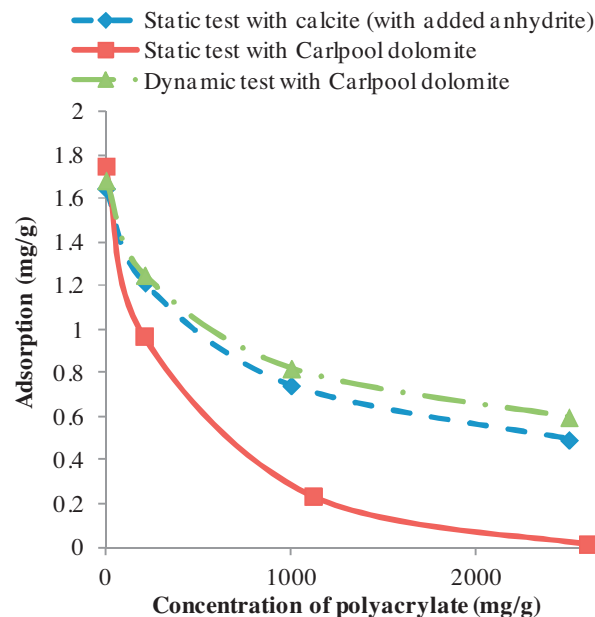


Fig. 7. Comparison between the results of static and dynamic adsorption tests; the blue dashed curve is a static test with a polyacrylate to anhydrite molar ratio similar to that of dynamic test on dolomite (lines are only for visual aid) (For interpretation of the references to color in this figure legend, the reader is referred to the web version of this article.).

adsorption measurement curve matches the dynamic adsorption curve with a reasonable difference. Therefore, we conclude that the difference between the dynamic and static tests on Carlpool dolomite is due to different ratios of sacrificial agent to anhydrite in static and dynamic tests. Therefore, for the case of applying polyacrylate as sacrificial agent for a specific reservoir with known amount of anhydrite, the static test should be designed to have a polyacrylate-to-anhydrite concentration ratio that represents the dynamic injection in the reservoir.

It can be seen in dynamic adsorption tests (electronic Supplementary information, S3–S6) that surfactant breaks through after polyacrylate although both surfactant and polyacrylate have been injected together. This is an important observation that indicates

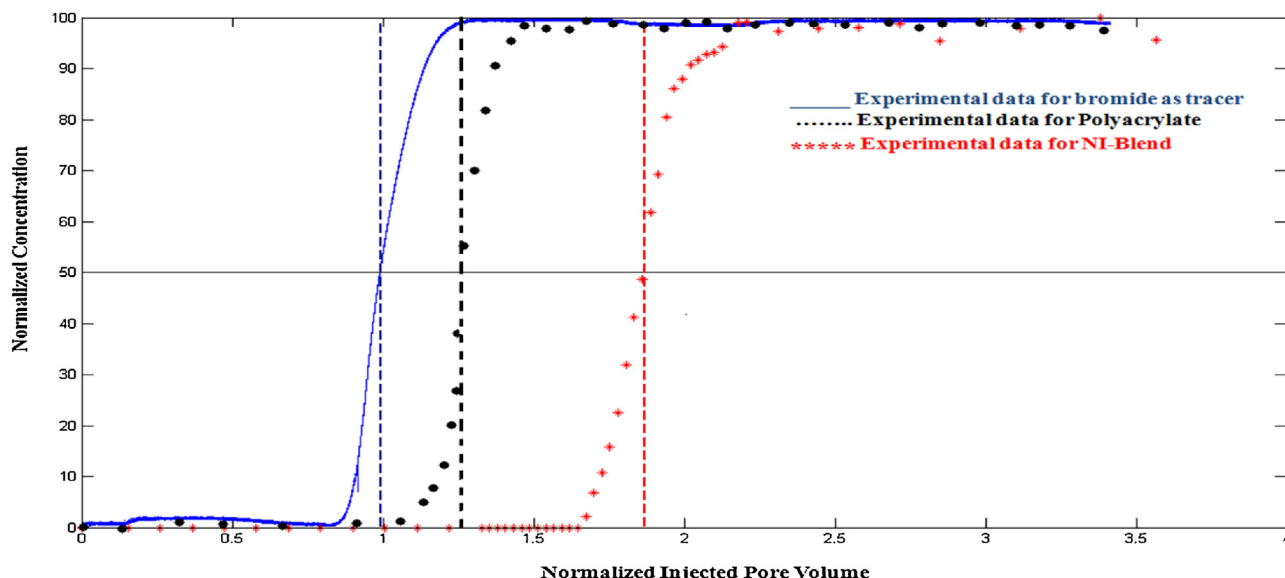


Fig. 6. Dynamic adsorption of 0.5 wt% NI-blend on Carlpool dolomite with 2500 ppm sodium polyacrylate.

that polyacrylate is always ahead of surfactant, thereby reducing adsorption throughout the sand pack.

3.6. Cost analysis for optimal concentration

A cost analysis is carried out to determine the optimum concentration of sodium polyacrylate that should be used as sacrificial agent in EOR processes. Also, the cost analysis determines the cost savings that may be achieved by using polyacrylate relative to the case where no sacrificial agent is used. The dimensionless equation that relates the total material cost to the concentration of polyacrylate is shown in Eq. (1). The total cost of materials depends on two dimensionless numbers that are described in Eqs. (2) and (3). In developing these equations, the following assumptions are met:

- (1) The amount of surfactant which is lost due to adsorption onto the rock is much more than the amount of surfactant needed for recovering oil; therefore, it has been assumed that the surfactant cost roughly equals the cost of surfactant injected just to satisfy adsorption.
- (2) The total cost of materials is the sum of cost of surfactant and cost of injected polyacrylate.
- (3) For the sake of simplicity, the cost analysis has been done based on injecting of one pore volume of surfactant and polyacrylate.
- (4) Injection and formation brines have roughly the same density.
- (5) Reservoir has been assumed to be a homogenous media (adsorption of surfactant is the same on a rock sample taken from any part of the reservoir).

$$\frac{\$_{\text{total}}}{\$_{\text{NO-SA}}} = \frac{f(C_{\text{poly}})}{f(0)} + \left(\frac{\$_{\text{PS}}}{\hat{R}} \right) \frac{C_{\text{poly}}}{f(0)} \quad (1)$$

$$\text{Cost number} = \$_{\text{PS}} = \left[\frac{\$_{\text{poly}}}{\$_{\text{surf}}} \right] \quad (2)$$

$$\text{Reservoir factor} = \hat{R} = 1000 \left[\frac{(1 - \varphi)\rho_{\text{ma}}}{\varphi\rho_w} \right] \quad (3)$$

In these equations, $\$_{\text{poly}}$ and $\$_{\text{surf}}$ are the price of polyacrylate (sacrificial agent) and surfactant per unit mass, respectively. Also, $\$_{\text{total}}$ and $\$_{\text{NO-SA}}$ are the total cost of materials and the material cost in the case no sacrificial agent is used, respectively. Cost number ($\$_{\text{PS}}$) is a dimensionless number corresponding to the relative cost of polyacrylate to that of surfactant. Reservoir factor ($\hat{R}$) is a dimensionless parameter that is a function of some reservoir characteristics, including ρ_{ma} (matrix density of the reservoir rock), ρ_w (density of the injected brine), and φ (porosity). In Eq. (1), C_{poly} is the concentration of polyacrylate, and $f(C_{\text{poly}})$ is a fitted curve to the adsorption data in Fig. 7, which is a function of concentration of polyacrylate. The derivation of these equations can be found in the electronic supplementary information.

Fig. 8 shows the plot of $\$_{\text{total}}/\$_{\text{NO-SA}}$ versus concentration of polyacrylate at two different values of dimensionless reservoir factor and cost numbers. It is notable that there is a minimum in all of these curves. This minimum corresponds to the optimal concentration of polyacrylate that should be used for EOR application.

We first examine the effect of the cost number on the optimal polyacrylate concentration. The optimal concentration of polyacrylate increases with a decrease in the value of cost number. More economic advantage can be achieved by using polyacrylate at lower cost numbers. The cost number is the ratio of cost of polyacrylate to surfactant. It is logical that in case of lower cost numbers (polyacrylate being less expensive than surfactant), the optimum condition is to use greater amount of polyacrylate.

On the other hand, it can be seen that as the reservoir factor increases, the optimum concentration of polyacrylate increases.

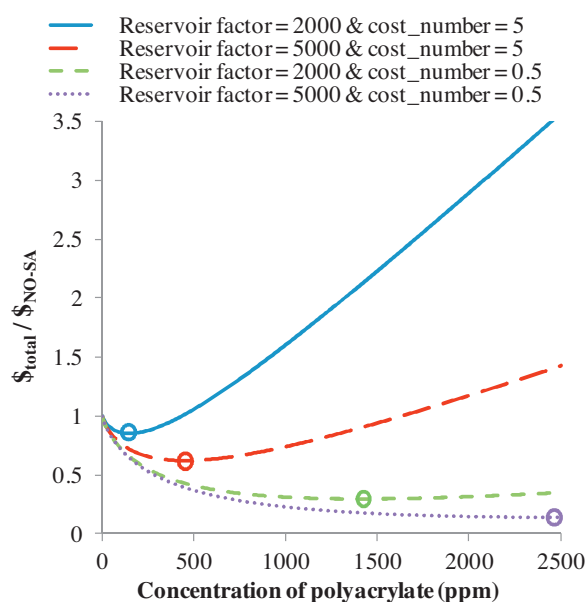


Fig. 8. Plot of $\$_{\text{total}}/\$_{\text{NO-SA}}$ versus concentration of polyacrylate; the optimum (shown with circles) can vary depending on the values of two dimensionless numbers.

The reservoir factor is the ratio of mass of the reservoir rock relative to mass of injected brine. As the reservoir factor increases, more surfactant is needed to satisfy adsorption on the rock. Therefore, it is reasonable that with increase in reservoir factor, the optimal polyacrylate concentration increases.

This cost analysis method can be applied to application of polyacrylate as sacrificial agent for any given reservoir, provided that the assumptions in this study are valid and the cost number and reservoir factor are known. The relationship between adsorption of surfactant and concentration of polyacrylate should be determined for the specific conditions of the reservoir, as is illustrated in Fig. 7 for a particular case.

4. Conclusions

The effect of sodium polyacrylate as a sacrificial agent is tested in different minerals/rocks with two different anionic surfactants. These results show that sodium polyacrylate reduces adsorption of anionic surfactant on carbonates and clays minerals as well as Berea sandstone, yet it is not as effective in the case of sandstone as it is for carbonates and clays.

Batch experiments were done to evaluate the effect of salinity and Ca^{2+} ions in the brine. The results indicate that increase in the salinity or concentration of Ca^{2+} in the brine leads to higher adsorption of anionic surfactant except when the adsorbent contains significant anhydrite (e.g. Carlpool dolomite). In the case of dolomite, the adsorption does not significantly change at different salinities or Ca^{2+} ion concentrations.

The effect of temperature on application of polyacrylate as sacrificial agent is studied and it is shown that polyacrylate can reduce adsorption of anionic surfactant at different temperatures, provided that no precipitation of surfactant, in which case that surfactant is not suitable for EOR application in the first place.

Dynamic adsorption tests also were conducted on dolomite containing anhydrite, and the results demonstrate that addition of sodium polyacrylate decreases the adsorption of anionic surfactant; however, this decrease does not match the static data. This was interpreted by lower ratio of concentration of polyacrylate-to-anhydrite in dynamic tests relative to the static tests. The static tests should be designed to represent the same

polyacrylate-to-anhydrite concentration ratio as in the dynamic injection in the reservoir.

A cost analysis is carried out, and it is demonstrated that an optimum concentration of polyacrylate should be used to minimize the total material cost. The value of this optimum concentration depends on two dimensionless variables that can be quantified for each specific reservoir. In some cases, using polyacrylate can decrease the total cost of materials for EOR to one-fifth of the case where no sacrificial agent is used.

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Appendix A. Supplementary data

Supplementary data associated with this article can be found, in the online version, at <http://dx.doi.org/10.1016/j.colsurfa.2014.02.021>.

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