Study on the Influence of Silica Nanofluids on Surfactant Adsorption on Rock

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Abstract

Among the Enhanced Oil Recovery (EOR) techniques, methods employing surfactants stand out for their high efficiency. Surfactant injection is a particularly advantageous option, as it can reduce oil-water interfacial tension and alter the wettability of the rock/reservoir, leading to higher oil recovery. However, the high adsorption of surfactants on reservoir rock reduces the efficiency of this process. This study aimed to investigate the influence of silica nanoparticles (SiNP) on the adsorption of anionic and cationic surfactants on quartz samples. In static adsorption tests, the surface properties of SiNP, adsorption time, and surfactant concentrations were evaluated. Based on the type of surfactant and the zeta potential of quartz, two different mechanisms were proposed to explain the behavior of surfactant adsorption on the quartz surface. Hydrophobic interaction plays a fundamental role in SDS adsorption. The results showed that the addition of SiNP reduces surfactant adsorption on rock, with up to a 54.1% reduction when functionalized with hydrophobic groups. This can be attributed to the decrease in adsorption area due to the occupation of silica nanoparticles on the quartz surface and the formation of surfactant-SiNP complexes. The study suggests that applying SiNP in EOR methods that use surfactants could be a cost-effective way to increase oil recovery efficiency

Keywords: Silica nanoparticles; EOR; Surfactant; Nanofluid.

1. Introduction

Despite significant efforts toward other renewable energy sources, such as biofuels, solar energy, and wind energy, fossil fuels will remain the world's largest energy source for many years, a fact highlighted by the current global dependence on fossil fuel energy, which currently accounts for around 80 to 90% [1]. In light of this, it is unquestionable that the future of the oil and gas industry largely depends on the development of new technologies that can meet the growing demand for energy.

Enhanced Oil Recovery (EOR) involves the injection of special fluids, such as chemicals, gases, and thermal fluids, among others. These EOR techniques aim to improve the overall efficiency of oil displacement, which can be achieved by reducing

oil viscosity, altering rock wettability, and lowering interfacial tension [2]. Among these techniques, surfactant injection is widely used in the oil industry due to its ability to affect the water/oil interface, the surface properties of rocks, and the generation and stability of emulsions and foams [2, 3].

Although several chemical recovery methods have been considered effective and successfully applied in oil fields, their applications are limited under conditions of high salinity and hardness, and surfactant losses due to adsorption on reservoir rock surfaces as the surfactant is injected through porous media [2, 4]. Adsorption is an important parameter affecting surfactant efficiency and, therefore, the economic viability of EOR projects. Acceptable surfactant adsorption levels range from 3 to 8 mg/g of rock [5]. Studies have focused on improving methods to control surfactant adsorption by adjusting the ionic composition of injection water

[4], adding alkalis [6], and incorporating nanoparticles [7]. In addition to reducing surfactant adsorption, certain types of nanoparticles enhance the rheological properties of surfactant solutions, foams, and emulsions, thereby increasing recovery [2]. It is noteworthy that nanoparticles significantly benefit oil recovery by altering the wettability of porous media, changing fluid properties, improving the mobility of trapped oil, and reducing interfacial tension [8].

2. Materials and Methods

Quartz samples provided by the company Brasil Minas were used, with the primary mineral composition being SiO_2, and particle sizes below 0.425 mm. The SiNPs with 99.8% purity were obtained from Sigma-Aldrich, with an average diameter of 12 nm and a surface area of 175 to 225 m²/g. SiNPs were also functionalized with oleic acid (cis-9-octadecenoic acid) according to the methodology of Lobato, Mansur, and Ferreira (2017) [9], allowing for an esterification reaction between the carboxyl group (COOH) present in the acid molecule. These nanoparticles were designated as SiNP-OA.

The quartz sample and the nanoparticles (SiNP and SiNP-AO) were characterized by zeta potential measurements using 0.001 mol L^{-1} KCl as the electrolyte at pH 6.0 (Litesizer, Anton Paar).

The nanofluids were prepared at a concentration of 0.05% (mass/volume) by dispersing the nanoparticles via ultrasonication (Ultronique) for 2 minutes at a power of 750 Watts. Subsequently, surfactant solutions were prepared at concentrations of 0.5, 1.0, 1.5, 2.0, and 2.5 g/L, both with and without the presence of nanofluids.

For the adsorption test, 0.5 g of quartz and 7.5 mL of nanofluid with surfactant at concentrations of 0.5, 1.0, 1.5, 2.0, and 2.5 g/L were brought into contact and kept under agitation for 24 hours. The surfactant molecules adsorbed on the quartz particles were then separated from the solution by centrifugation, and the quantification was performed according to Equation 1:

$$y = \frac{v_{solution} \, x \, (C_0 - C)}{m_{quartz} \, x \, 1000} \qquad (1)$$

Where $v_{solution}$ is the volume of solution used (7.5 mL), C_0 is the initial surfactant concentration, C is the surfactant concentration in the supernatant (at equilibrium), and m_{quartz} is the mass of quartz (g). Each experiment was conducted three times to eliminate sources of uncertainty and verify the repeatability of the adsorption measurement results, conducted at a temperature of 23°C.

For surfactant quantification, a calibration curve was prepared by measuring the conductivity of surfactant solutions at concentrations of 1000 to 8000 mg/L for SDS.

3. Results and discussion

Table 1 presents the zeta potential results. These results will allow us to predict the adsorption behavior of SDS on the quartz surface. As observed, the quartz has a negative zeta potential at the analyzed pH. This is due to the deprotonation of silanol groups (-SiOH) on the surface, forming $\equiv SiO^-$ groups, which are responsible for the negative surface charge and the increase in the zeta potential in magnitude [10].

Table 1. Zeta potential results.

Sample	Zeta potential (mV)
Quartz	-25,00 ± 0,44
SiNP	-19,60 ± 0,53
SiNP-AO	-34,12 ± 0,45

The same effect is observed for NPSi, as illustrated in Figure 1. For SiNP-AO nanoparticles, a decrease in zeta potential is observed. With surface modification, COOH groups from oleic acid are introduced onto the surface, as shown in Figure 1. These groups deprotonate at the analyzed pH, giving a negative charge to the SiNP.

Figure 2 shows the calibration curve for SDS solutions. The increase in conductivity in the solution occurs due to the presence of surfactant ions, as a result of the charges on the hydrophilic heads; therefore, this increase leads to a rise in conductivity. Consequently, once the surfactant reaches the value of the critical micelle concentration (CMC), the slope of the conductivity graph as a function of concentration decreases,

indicating that beyond this concentration, surfactants begin to aggregate into micelles [11].

Fig. 1. Schematic representation of the NPSi surface before and after functionalization with oleic acid.
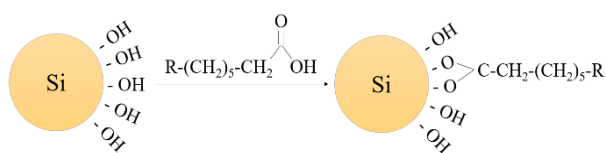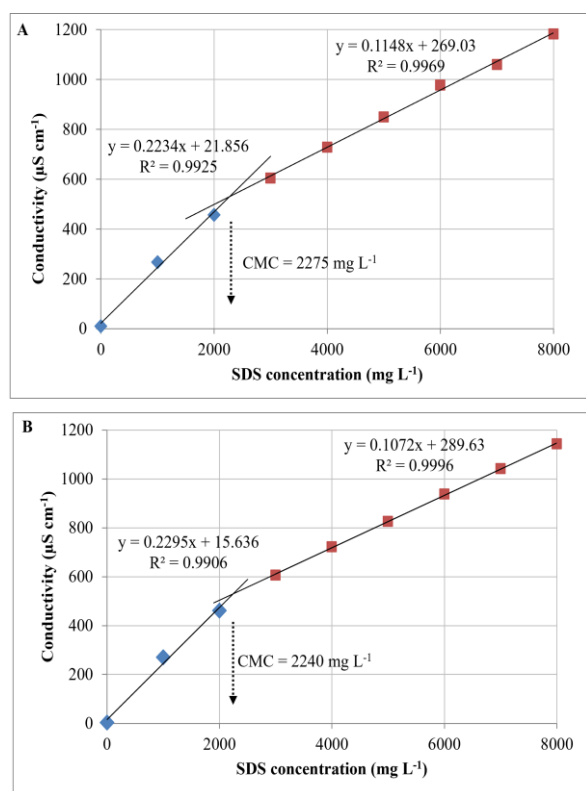

Fig. 2. Calibration curve of the SDS solutions: (A) SDS and (B) SDS in nanofluid 0.1% SiNP.


The CMC indicates that any further increase in surfactant concentration beyond this point does not increase surfactant adsorption at the interface; instead, the added surfactant only increases micellization in the solution [12]. For SDS without the presence of SiNP, a CMC of 2275 ± 4.57 mg L^{-1} was obtained, a value very close to that found in the literature, such as 2310 mg L^{-1} [13] and 2264.3 mg L^{-1} [14]. Variations can occur due to the use of different methods for determining the CMC, such as

the conductivity method used in this work, the interfacial tension method, the density method, among others. In the presence of NPSi, the CMC of SDS is reduced for 2240 ± 3.45 mg L^{-1}. The NPSi are negatively charged, as shown by zeta potential results, and an electrostatic repulsion between the negatively charged nanoparticles and the anionic surfactant is expected, improving SDS adsorption at the air/water interface [15]. With a higher concentration of SDS molecules at the interface compared to the bulk solution, the CMC is reduced.

Figure 3 presents the adsorption isotherm results as a function of SDS concentration. The adsorption equilibrium for SDS without the presence of SiNP is reached at around 2.09 mg/g. As the surfactant concentration increases, lateral (hydrophobic) interactions become significant for further surfactant adsorption, forming ad-micelles [10, 16]. Comparing with the literature, similar results can be observed for the amounts of SDS adsorbed on quartz samples: 2.61 mg/g for SDS [16], 2.84 mg/g for SDS [15]. In the presence of the nanofluid with 0.05% NPSi, the adsorbed amount of SDS reduced to 1.43 mg/g, around a 31% reduction. For NPSi-AO, the adsorption reached about 0.96 mg/g, a 54% reduction.

Fig. 3. Effect of nanoparticles on SDS adsorption on quartz.
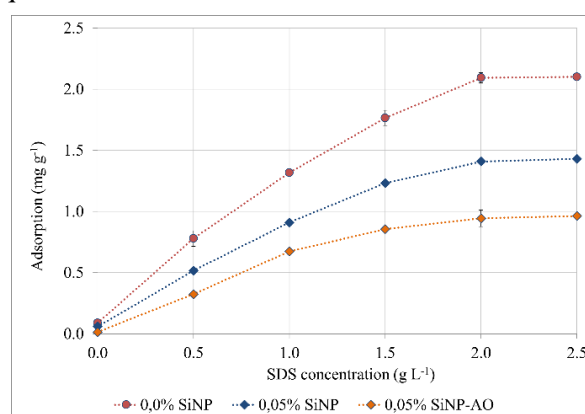
Two possible mechanisms can explain this reduction: (1) a reduction in the available quartz surface area for surfactant adsorption and (2) adsorption of the surfactant onto SiNP. Both SiNP and quartz are negatively charged and hydrophilic at the analyzed pH. For SiNP nanofluids with SDS, it is suggested that the effect of surface area reduction

prevails. The SiNPs in the solution reduce the adsorption area on the quartz surface due to their affinity for the mineral surface. As a result, the probability of contact between SDS and the rock surface is reduced, leaving more surfactant in the bulk solution [17]. Interactions between SDS molecules and SiNP may occur, but the mentioned effect likely prevails. For SiNP-AO, which have a hydrophobic surface, surfactant adsorption on the nanoparticle surface likely prevails. Hydrophobic interactions occur between the hydrophobic groups of SiNP-AO and the hydrophobic tails of SDS, resulting in more surfactant adsorption on the nanoparticle surface and less on the quartz surface. This is clearly reflected in the results. Figure 4 schematically represents these effects.
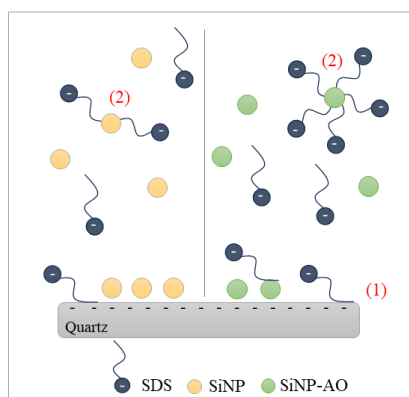

Fig. 4. Schematic representation of SDS adsorption mechanisms in the presence of NPSi: in (1), the adsorption of NPSi on the quartz surface reduces the available surface area for surfactant adsorption. In (2), there is the formation of nanoparticle-surfactant complexes.

4. Conclusion

In this study, the adsorption of SDS with and without the presence of SiNP on quartz samples was investigated. The presence of SiNP reduces SDS adsorption due to the effects of reducing the available quartz surface area for surfactant adsorption and the adsorption of the surfactant onto the nanoparticles. This effect is more pronounced for SiNP-AO, due to the hydrophobic interactions between SDS and the nanoparticles, resulting in a reduction of approximately 54.1%. Thus, the study indicates that the application of silica nanofluids in methods employing surfactants could be a way to minimize adsorption in EOR, potentially leading to significant economic impacts.

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