Effect of Sodium Oleate Surfactant Concentration Grafted onto SiO₂ Nanoparticles in Polymer Flooding Processes

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ABSTRACT: The nanotechnology has been applied recently to increase the efficiency of enhanced oil recovery methods. The main objective of this study is to evaluate the effect of SiO₂ nanoparticle functionalization with different loadings of sodium oleate surfactant for polymer flooding processes. The sodium oleate surfactant was synthesized using oleic acid and NaCl. The SiO₂ nanoparticles were functionalized by physical adsorption using different surfactant loadings of 2.45, 4.08, and 8.31 wt % and were characterized by thermogravimetric analyses, Fourier-transform infrared spectroscopy, dynamic light scattering, and zeta potential. Adsorption and desorption experiments of partially hydrolyzed polyacrylamide (HPAM) polymer solutions over the unmodified and surface-modified nanoparticles were performed, with higher adsorption capacity as the surfactant loading increases. The adsorption isotherms have a type III behavior, and polymer desorption from the nanoparticle surface was considered null. The effect of nanoparticles in the polymer solutions was evaluated through rheological measurements, interfacial tension (IFT) tests, contact angle measurements, capillary number, and displacement tests in a micromodel. The surface-modified SiO₂ nanoparticles showed a slight effect on the viscosity of the polymer solution and high influence on the IFT reduction and wettability alteration of the porous medium leading to an increase of the capillary number. Displacement tests showed that the oil recovery could increase up to 23 and 77% regarding polymer flooding and waterflooding, respectively, by including the surface-functionalized materials.

1. INTRODUCTION

Water and gas injection processes are widely known and implemented worldwide, with about 40% of oil being produced through these methods.¹ However, the volumetric sweep efficiency of improved oil recovery processes is limited in cases where the porous medium evidences high horizontal and vertical heterogeneity, and reservoirs where the oil viscosity is high. Thus, after a waterflooding process, over 60% of the original oil in place may remain in the reservoir.² For this reason, increasing the recovery factor is required from existing fields through enhanced oil recovery (EOR) methods that are profitable under the current oil price. Particularly, the average recovery factor in Colombia is approximately 19%, of which 88% of production comes from primary recovery, 11% due to secondary recovery, and less than 1% from EOR methods.³ The use of polymer solutions to improve the volumetric sweep efficiency by lowering the mobility ratio (M) in waterflooding processes has become standard practice in the operation of various oilfields.⁴ However, this technology is sensitive to different factors such as polymer concentration, type, and size of the polymer monomer, water salinity, solution pH, and capillary properties of the rock.⁵ Polymer rheological behavior and polymer effect as a relative permeability modifier on permeability reduction are considered as determining mechanisms to improve the mobility control and obtain high recovery factors.⁶⁻⁸ Mishra et al.⁷ examined the hydrolyzed polyacrylamide (HPAM) adsorption effect on water relative permeability and original-oil-in-place. A high water permeability reduction in porous media and oil recovery increase were obtained where the higher polymer and salt concentration due to electrostatic repulsion forces with higher polymer adsorption, the thickness of polymer adsorbed layer, and resistance factors (RF and RRF), especially in acid systems. Such as is mentioned in above works, when the polymer contacts the porous medium, part of the polymer is adsorbed on the rock. High values of polymer adsorbed in the rock cause the increase of both RF and RRF. Given the hydrophilic character of the polymer, its adsorption in the rock generates a decrease in the effective permeability of the water, which corresponds to the residual RF and causes an increase in the displacement efficiency of the post-polymer water. Also, the chemical compounds employed in polymer flooding processes are commonly affected by thermal, chemical, biological, and mechanical degradation at both surface and reservoir conditions, which hinders the efficiency of the technique.⁹ The most widely used polymer in EOR
applications is partially HPAM,\textsuperscript{10} which is a copolymer of acrylamide and acrylic acid.

Recently, experimental studies of low molecular weight HPAM solutions with silica nanoparticles showed a decrease in the thermal and chemical degradation of the polymer solutions while preserving its rheological properties for an extended period at high temperatures.\textsuperscript{51} Additionally, an increase in the viscosity of the HPAM solution when adding nanoparticles was observed and was mainly attributed to the formation of a three-dimensional structure by the association of hydroxyl groups with polymer chains.\textsuperscript{15} Saito et al.\textsuperscript{13} found that when the silica nanoparticles are added at different concentrations to the polymer solutions, the viscosity decreases as the nanoparticle concentration increases until a minimum.

Further, it was concluded that the concentration effect of silica nanoparticles on the viscosity behavior is a combination of two different mechanisms, namely, polymer adsorption over the nanoparticles and polymer flocculation. Sharma and Sangwal\textsuperscript{14} investigated the effect of silica nanoparticles in polymer and polymer/surfactant systems on the wettability alteration in an EOR process, finding that by adding 10,000 mg/L of the nanoparticles, the viscosity increases at high temperatures and vice versa. Also, the addition of silica nanoparticles increases the recovery factor for the polymer/surfactant system compared to the polymer system because of the change from intermediate wettability to a strong water-wet system.

Hu et al.\textsuperscript{12} found that the addition of silica nanoparticles to HPAM solutions improves the viscoelastic properties of the polymeric solution at high temperature and salinity conditions. The results showed that after 12 days at 80 °C, the polymer stability and viscosity increase with the addition of 8000 mg/L nanoparticles. The results were linked to the cross-linking of polymer chains and an increase in the viscoelasticity by the interaction of silanol groups and carbonyl groups of HPAM through hydrogen bonds. Ahmadi et al.\textsuperscript{15} investigated the effect of hydrophobic silica nanoparticles in the interfacial tension behavior for water injection applications in carbonate systems. Results showed that the employed silica nanoparticles (up to 10,000 mg/L) could improve the oil recovery, decrease the mobility ratio, and reduce the interfacial tension (IFT).

The effect of silica nanoparticles in EOR processes can be improved by surface modification with surfactants and polymers to increase dispersion, changing its wettability nature, generate polymer nucleation centers, and enhance viscoelastic properties.\textsuperscript{12,16−18} Other studies report the silica nanoparticle effect in the aqueous phase with polymers and surfactants to improve their viscous, interfacial, and capillary performance in EOR applications.\textsuperscript{19−27} Hence, it has been reported that using surfactants for modifying the nanoparticle surface from hydrophilic to hydrophobic can improve the interaction with the polymers.\textsuperscript{17,28,29} Zheng et al.\textsuperscript{17} evaluated hexamethyldisilazane (HMDS)- and hexadecyltrimethylammonium bromide, and coupling agents.\textsuperscript{31−33} Particularly, sodium oleate could be attractive for improving the performance of polymer systems regarding viscosity and other rheological properties.\textsuperscript{16} The polymer—sodium oleate synergy lies in the polymer unraveling because of the repulsion forces between the anionic groups of both polymer and surfactant.\textsuperscript{16} Hence, the interaction between polymer and sodium oleate clusters could improve the system viscosity, decreases the IFT, and enhances the oil mobility ratio with less polymer dosage.

However, in the scientific literature, there are no studies reporting the surface modification of silica nanoparticles with sodium oleate for improving polymer flooding processes. Therefore, the primary objective of this study is to evaluate the effect of sodium oleate concentration grafted onto silica nanoparticles to low molecular weight HPAM solutions in deionized water. The sodium oleate was grafted over the nanoparticle surface by the interaction between the adsorbate/adsorbent based on the adsorption phenomena. Adsorption isotherms, rheological behavior, contact angle measurements, and IFT tests were carried out. Also, displacement tests were performed in a quarter five-spot pattern micromodel to evaluate the oil recovery after polymer flooding in the absence and presence of silica and sodium oleate-modified silica nanoparticles.

2. RESULTS AND DISCUSSION

2.1. Characterization of Sodium Oleate Surfactant.

The synthesized sodium oleate surfactant was characterized by Fourier transform infrared (FTIR) spectroscopy, critical micelle concentration (CMC), and hydrophilic–lipophilic balance (HLB). Figure 1 shows the FTIR spectrum for the synthesized sodium oleate and its comparison with the one reported by Jin et al.\textsuperscript{34}
reported by Jin et al.\textsuperscript{34} It can be observed from Figure 1 that both spectra show similar bands and intensities, which confirms that the synthesized compound is the sodium oleate surfactant. The compound shows bands at 1563 and 1444 cm\(^{-1}\), attributed to vibrations of carboxylic groups (\(-\text{COOH}\)) of the oleic acid. The characteristic bands at 3430 and 3420 cm\(^{-1}\) correspond to \(\text{C}\text{−H}\) stretching and \(-\text{NH}_2\) groups, respectively. Bands at 2881 and 2834 cm\(^{-1}\) are associated with vibrations of \(\text{C}\text{−H}\), and bands at 746 and 729 cm\(^{-1}\) are characteristic of hydroxyl groups and stretching and deformation of \(-\text{CH}_2\)\textsuperscript{34−37}.

Panels (a and b) of Figure 2 show the CMC of sodium oleate surfactant in the aqueous phase as estimated by (a) absorbance and (b) surface tension measurements, respectively. The CMC is determined by a change in the linear trend of each measurement and is estimated at 912 ± 2 mg/L.

Figure 2. CMC of synthesized sodium oleate by (a) spectrophotometry UV–vis and (b) interfacial tension at 25 °C. The CMC is determined by a change in the linear trend of each measurement and is estimated at 912 ± 2 mg/L.

2.2. Nanoparticle Characterization. The modification of the SiO\(_2\) nanoparticle surface with the sodium oleate surfactant is performed to enhance the adsorption and dispersion of the nanomaterial in the matrix of the polymer solution. Functional groups of the employed partially HPAM were characterized by FTIR analyses as reported by Giraldo et al.,\textsuperscript{11} observing OH− groups, \(\equiv\text{CH}\) bonds, \(\text{C}\equiv\text{N}\) nitrile bonds, as well as \(\text{N}−\text{O}\) bonds of nitrile groups, alkanes, and aliphatic amines. Further, interactions between hydroxyl, carboxyl, and nitro groups from sodium oleate and polymer chains can be determinant in the structure and matrix behavior of HPAM. Figure 3 shows a schematic representation of the interaction between the SiO\(_2\) nanoparticles and the sodium oleate, where hydroxyl bonds and oxygen groups from sodium oleate are linked with Si–OH groups in the nanoparticle.

The SiO\(_2\) nanoparticles have a surface area of 380 m\(^2\)/g and mean particle size of 11 nm according to the dynamic light scattering (DLS) measurements. The SiO\(_2\) support was previously characterized\textsuperscript{43} through field emission scanning electron microscopy using a JSM-6701F microscope (JEOL, Japan), observing spherical particles with a mean particle size of 9 nm, which is in agreement with the DLS results. SiO\(_2\) nanoparticles were functionalized with the sodium oleate solutions at surfactant concentrations of 9.0, 4.0, and 2.5% regarding the mass of nanoparticles. Table 1 shows the mean particle diameter (\(d_{50}\)), Brunauer–Emmett–Teller (BET) surface area, amount of grafted surfactant, and zeta potential of the selected nanoparticles. The amount of grafted surfactant was estimated through thermogravimetric analysis (TGA) under an air flow. As seen in Table 1, percentages of anchored surfactant higher than 2 wt% were obtained through the incipient wetness technique. Further, the nanomaterials were named SNP-2, SNP-4, and SNP-8 according to the amount of anchored surfactant. It is worth to mention that the grafted surfactant onto the nanoparticles does not leach to the polymer solution as confirmed through UV–vis spectroscopy. It can be observed from Table 1 that the modified nanoparticles show larger particle sizes than unmodified SiO\(_2\) nanoparticles. These results confirm that the sodium oleate surfactant adheres to the surface of the nanoparticles and hence increases the surface energy which promotes the aggregation phenomenon. Also, it was observed that the surfactant grafted on the SiO\(_2\) nanoparticles reduces the surface area (\(S_{\text{BET}}\)) as some of the micropores can be hindered.\textsuperscript{44−46}

The electrokinetic potential for all nanoparticle dispersion in water shows a strong charge surface variation. The zeta potential of the system indicates the stability of nanoparticle dispersion and their degree of electrostatic repulsion. For modified silica nanoparticles (SNP-2, SNP-4, and SNP-8), a high zeta potential value is obtained in comparison with unmodified SiO\(_2\) nanoparticles and is due to high ionic concentration or negative charges on the surface.\textsuperscript{36} Therefore, a high dispersion and interaction between polymer chains with free bonds in the nanoparticle surface can avoid nanoparticle aggregation.\textsuperscript{47,48}

Figure 3. Schematic illustration of the interaction of hydroxyl bonds and oxygen groups from sodium oleate linked with Si–OH groups on the SiO\(_2\) nanoparticles.

Table 1. Mean Particle Size (\(d_{50}\)), Anchored Surfactant, Surface Area (\(S_{\text{BET}}\)), and Zeta Potential at pH = 7 for SiO\(_2\) Nanoparticles and Sodium Oleate-Functionalized SiO\(_2\) Nanoparticles

| sample | grafted surfactant (wt %) | \(d_{50}\) (nm) | \(S_{\text{BET}}\) (m\(^2\)/g) | zeta potential @ pH = 7 (mV) |
|--------|--------------------------|----------------|--------------------------|----------------|
| SiO\(_2\) | 0 | 11 | 380 | −22.33 |
| SNP-2 | 2.45 | 63.6 | 177.6 | −31.45 |
| SNP-4 | 4.08 | 89.3 | 161.5 | −42.21 |
| SNP-8 | 8.31 | 90.7 | 146.7 | −57.91 |
between 1750 and 1700 cm$^{-1}$ corresponding to H$_2$O groups. The bands at 1040, 1100, and 1550 cm$^{-1}$ correspond to Si$^-$OH, Si-O, and H$_2$O groups, respectively. 

Also, functional groups represented by the bands 950 and 870 cm$^{-1}$ corresponding to Si$^-$H and O$^-$H can be observed, respectively. Nanoparticles with sodium oleate show characteristic bands of surfactant at 1560 and 1483 cm$^{-1}$ attributed to vibrations of COO$^-$ groups. Other bands are those for the hydrocarbon chains and carbonyl groups at 2976, 2918, and 2854 cm$^{-1}$ representative of C=O and carboxylic salt, whereas bands between 1554 and 900 cm$^{-1}$ correspond to C$^-$H and C$^-$C, respectively. However, after surfactant impregnation, the band of 3700 cm$^{-1}$ corresponding to the Si$^-$OH group is still present concerning the exposed surface of the SiO$_2$ nanoparticles. This is consistent with that reported by Hu et al., that confirmed from the FTIR analysis that the formation of hydrogen bonds contributes to a high interaction between HPAM groups as carbonyl groups (C=O, C$^-$H, and C$^-$O) and groups on surface silica such as silanol groups (Si$^-$O$^-$Si$^-$H and Si$^-$O$^-$Si$^-$O$^-$Si) bending and stretching.

2.3. Adsorption Test. To obtain the adsorption isotherms, the polymer concentration was fixed in 500 mg/L based on polymer flooding applications according to previous studies. The nanoparticle dosages were 300, 500, 1000, 3000, and 5000 mg/L. Figure 5 shows the adsorption isotherms of polymer on the silica nanoparticles (modified and the support) together with the solid–liquid equilibrium (SLE) model fitting at 25 $^\circ$C. 

The adsorption isotherms have a type III behavior, where the adsorption is inversely proportional to the concentration of nanoparticles. Modified nanoparticles with the surfactant adsorbed more HPAM polymer than the support. The trend based on the uptake of polymer for the nanoparticles was the following SNP-8 > SNP-4 > SNP-2 ≈ SiO$_2$ within the whole range of concentrations evaluated. At a polymer equilibrium concentration of 487 mg/L, the SNP-8 adsorbed 0.17 mg/m$^2$ sodium oleate, whereas the support (SiO$_2$) adsorbed 0.064 mg/m$^2$. Also, from Figure 5, it is possible to conclude that the four nanoparticles evaluated adsorb polymer because of the intermolecular forces between the most polar components of HPAM polymer and the sodium oleate grafted onto silica nanoparticles. Some functional groups of sodium oleate over silica nanoparticle surface enhance the interaction between OH$^-$ bonds and oxygen groups in the polymer. 

The results obtained in the polymer desorption process showed that the silica nanoparticles modified and unmodified with the surfactant at the different concentrations are null. The obtained SLE model parameters such as $H$, $K$, and $N_{\text{slkin}}$, are summarized in Table 2. These parameters indicate affinity and self-association ability of the polymer on the nanoparticles; the goodness-of-fit is confirmed by root-mean-square error (RSME) values lower than 1.0%. SLE parameters indicate a higher affinity ($H$), more ability to self-association ($K$), and higher polymer adsorbed ($N_{\text{slkin}}$) as the surfactant loading increases on the SiO$_2$ nanoparticle because of a synergistic effect between polymer chains and polar groups from sodium oleate. 

2.4. Rheological Behavior of Polymer Solutions in the Presence of Nanoparticles. The selection of commercial polymer concentration (500 mg/L) was based on a previous study where a viscosity of 69 cP (7.1 s$^{-1}$ at 25 $^\circ$C) with 500 mg/L polymer and 3000 mg/L silica nanoparticles (SiO$_2$) was observed, showing a better viscous and degradation behavior in oxidizing atmosphere and high temperature regarding the polymer solution in the absence of SiO$_2$ nanoparticles. Also, previous results show that the rheological behavior of the polymer dispersion does not change with the inclusion at low concentrations of nanoparticles (<3000 mg/L) and the pseudoplastic behavior remains due to the cross-linking effect between silica nanoparticles and polymer. In Figure 6, the rheological behavior of the polymer solution with (a) SNP-2, (b) SNP-4, and (c) SNP-8 nanoparticles at different dosages as a function of the shear rate at 25 $^\circ$C is showed. The results show that for the three nanoparticles evaluated at concentrations of 500 and 1000 mg/L, the viscosity is not drastically affected regarding the polymer system in the absence of nanoparticles. Nevertheless, for 2000 and 3000 mg/L and shear rate values <100 s$^{-1}$, the viscosity decreases and could be related to the high polymer uptake that inhibits the formation of the 3D network.

**Figure 4.** FTIR spectrum of SiO$_2$ nanoparticles and sodium oleate-functionalized nanoparticles with 2.45 (SNP-2), 4.08 (SNP-4), and 8.31 wt% (SNP-8) of sodium oleate.

**Figure 5.** Sorption isotherms of partially HPAM onto SiO$_2$ nanoparticles and sodium oleate-functionalized nanoparticles SNP-2, SNP-4, and SNP-8 at 25 $^\circ$C. The symbols are experimental data from adsorption experiments, and the continuous lines are from the SLE model fitting.

**Table 2.** SLE Model Parameters for the Partially HPAM adsorption on SiO$_2$ and Sodium Oleate-Functionalized Nanoparticles (SNP-8, SNP-4, and SNP-2) at 25 $^\circ$C
Table 3 summarizes the obtained parameters of the Carreau model for the rheological behavior of the polymer solution at different concentrations of the selected nanoparticles at 25 °C. It can be seen that the parameters are in agreement with the trend observed in Figure 6, where the relaxation time (λ) and the pseudoplasticity index (N) decrease with the addition of nanoparticles in the polymer network structure in comparison with the system in the absence of nanoparticles. The parameters of the Carreau model represent the viscous behavior of the polymer–nanoparticle system with the application of shear rate using four parameters as flow index (N) where values <1 that indicate a polymeric suspension with pseudoplastic behavior and the relaxation time λ that indicate the system reset after perturbation where shorter times suggest a faster system restoration.

According to Das et al.,16 zeta potential values indicate high repulsion forces in a system with the addition of functionalized nanoparticles make the polymer in solution more elongated and less susceptible to degradation. Hence, according to the results in Figure 6 and Table 3, a nanoparticle concentration of 1000 mg/L was selected for contact angle measurements and IFT tests.

2.5. Interfacial Tension Measurements. Interfacial tensions (IFTs) were measured for the HPAM solutions/crude oil systems in the presence and absence of SiO2, SNP-2, SNP-4, and SNP-8 nanoparticles at 25 °C and are summarized in Table 4. The IFT increases 22.7% with the addition of the polymer in the aqueous phase in comparison with the base system (water/crude oil) and decreases with the SiO2 nanoparticle addition of 11.8%. The effect of SiO2 nanoparticles on interfacial tension is in agreement with those reported in the specialized literature.52 Also, degradation can be inhibited because of the adsorption process as the functional groups in the polymer system that are prone to degradation are interacting with the selected nanoparticles.11

Table 3. Carreau Model Parameters for the Rheological Behavior of the Partially HPAM Solutions at 500 mg/L in Deionized Water in the Presence of Sodium Oleate-Functionalized Nanoparticles (a) SNP-2, (b) SNP-4, and (c) SNP-8 at 25 °C

| Material | Concentration (mg/L) | λ   | μ∞ (cP) | μ0,γ (cP) | N   | RSME |
|----------|----------------------|-----|---------|-----------|-----|------|
| SNP-2    | 500                  | 0.19| 4.89    | 97.73     | 0.36| 2.69 |
|          | 1000                 | 0.20| 4.74    | 96.23     | 0.37| 2.10 |
|          | 2000                 | 0.26| 3.83    | 93.86     | 0.39| 3.83 |
|          | 3000                 | 0.28| 3.58    | 92.96     | 0.41| 3.16 |
| SNP-4    | 500                  | 0.22| 4.79    | 95.88     | 0.32| 0.96 |
|          | 1000                 | 0.22| 4.70    | 95.28     | 0.39| 1.35 |
|          | 2000                 | 0.31| 3.71    | 85.51     | 0.40| 1.49 |
|          | 3000                 | 0.32| 3.11    | 70.66     | 0.44| 1.53 |
| SNP-8    | 500                  | 0.22| 4.71    | 95.81     | 0.34| 1.82 |
|          | 1000                 | 0.22| 4.68    | 94.94     | 0.39| 2.11 |
|          | 2000                 | 0.35| 2.95    | 69.78     | 0.40| 1.29 |
|          | 3000                 | 0.36| 2.86    | 69.46     | 0.47| 1.26 |

Figure 6. Rheological behavior of the partially HPAM solutions at 500 mg/L in deionized water in the presence of sodium oleate-functionalized nanoparticles (a) SNP-2, (b) SNP-4, and (c) SNP-8 at 25 °C.

Figure 7. Schematic illustration of the partially HPAM interaction with sodium oleate-functionalized SiO2 nanoparticles. High repulsion forces in a system with the addition of functionalized nanoparticles make the polymer in solution more elongated and less susceptible to degradation.
Table 4. Interfacial Tensions for HPAM Solutions/Crude Oil Systems in the Presence and Absence of SiO2 Nanoparticles and Sodium Oleate-Functionalized SiO2 Nanoparticles at 25 °C

| aqueous phase | nanoparticle | interfacial tension ±0.5 mN/m |
|---------------|--------------|-------------------------------|
| water         | none         | 19.1                          |
| polymer solution | none        | 24.7                          |
| SiO2          |              | 22.1                          |
| SNP-2         |              | 21.3                          |
| SNP-4         |              | 20.6                          |
| SNP-8         |              | 17.3                          |

*HPAM concentration was fixed at 500 mg/L, and the nanoparticle concentration was 1000 mg/L.

it can be inferred that the surface-modified SiO2 nanoparticles can act as a carrier of the sodium oleate surfactant. It is worth to mention that the sodium oleate anchored onto nanoparticles was not desorbed to the polymer solution.

2.6. Contact Angle Measurement. Figure 8 shows the contact angle of oil and water for restored samples before and after contact with HPAM solutions in the presence and absence of SiO2 nanoparticles and oleate-functionalized SiO2 nanoparticles at 25 °C. It can be observed from Figure 8 that the samples are initially oil-wet with contact angles for oil and water of 1° and 86°, respectively. After contact with the polymer solution in the absence of nanoparticles, the system changes from a strong oil-wet condition to an intermediate wettability. This could be due to the low influence of the trapped polymer without removing nonpolar fractions from the rock surface causing a slight wettability alteration. When the polymer concentration increases in the aqueous phase, the displacement phase viscosity considerably increases and maintains the mobility control and rheological performance in the porous medium. Nevertheless, an excess of the polymer in the solution increases the probability of adsorption onto the porous medium and other associated formation damage because of a high interaction between polymer molecules and rock surface as a consequence of electrostatic and repulsion forces, especially in an acid system when polymer adsorption on the sand surface is high.

After the inclusion of the nanoparticles, the preference for the water phase increases as the sodium oleate loading over the SiO2 support increases. Additionally, the contact angle of oil increases on the order SNP-8 > SNP-4 > SNP-2 ≈ SiO2 nanoparticles, indicating that the functionalized materials lead to less affinity for the oil phase. This behavior could be due to film deposition of nanoparticles and their distribution over the rock surface, nanoparticle adsorption, and change in free surface energy toward the water-wet surface.

2.7. Capillary Number Estimation. For determining the viscous/interfacial force ratio in the system, the capillary number was estimated considering the polymer viscosity, wettability alteration, interfacial tension, and an aqueous fluid velocity at 7.1 s⁻¹ and 0.0835 cm s⁻¹ representative for field applications. Figure 9 shows the behavior of the capillary number for an oil-wet surface before and after polymer contact in the absence and presence of SiO2 and SiO2-modified with surfactant (SNP-2, SNP-4, and SNP-8) at 25 °C. Capillary numbers of about 10⁻⁵ indicate an oil-wet state. Nanoparticle addition to the polymer solutions increases the capillary number regarding the system in the absence of nanoparticles. The best performance was obtained with surface-modified nanoparticles, reaching values up to 10⁻². Polymer flooding (Nc ≈ 2 × 10⁻³) contributes mainly to the viscosity of the displacing fluid and slightly to wettability alteration. However, silica nanoparticles (SiO2) contribute to fluid viscosity and wettability alteration, increasing the capillary number a 62.4%. In the case of functionalized nanoparticles, a significant contribution in the IFT reduction as a function of the surfactant loading on the nanoparticle surface leads to an increase in the capillary number in 65.7, 72.2, and 91.2%, for SNP-2, SNP-4, and SNP-8 materials, respectively. Reduction in the interfacial forces in the solid–water–oil system can be explained by Young’s law that states an interfacial force ratio between contact angle and interfacial tension of oil–water–solid in a thermodynamic equilibrium system. Accordingly, the aqueous contact angle reduction in the oil-wet surface is a consequence of the IFT reduction in the presence of nanoparticles that may lead to the high recovery of trapped
already interacting with the nanoparticle surface. The values of polymer adsorption onto rock and nanoparticle surface are 6 μg/g as reported previously and 17 mg/g, respectively, indicating that the polymer has higher selectivity for the nanomaterials because of the interactions between the adsorbate and adsorbent. This is in agreement with the retention values (adsorption and mechanical blockage) of 59.8 and 34.9 μg/g for the polymer in the absence and presence of nanoparticles, respectively, indicating a decrease in polymer retention of 41.7% with the addition of SiO2 nanoparticles. The final oil recovery with SiO2 and SNP-8 nanoparticles was 61 and 77% higher than the waterflooding, respectively. Higher recovery with the functionalized nanoparticles could be due to the IFT reduction and the wettability alteration as a consequence of the grafted sodium oleate surfactant. From the displacement tests, it can be concluded that higher recovery can be obtained with lower dosages of sodium oleate-functionalized nanoparticles in comparison to SiO2 nanoparticles.

3. CONCLUSIONS

SiO2 nanoparticles were functionalized with different loadings of sodium oleate surfactant to increase the efficiency of polymer flooding processes with partially HPAM. The surfactant–nanoparticle interaction could be ruled by hydroxyl bonds and oxygen groups from sodium oleate that are linked with Si–OH groups in the nanoparticle. TGA experiments showed that nanoparticles with surfactant loadings of 2.45, 4.08, and 8.31 wt % were obtained through physical adsorption. The functionalized nanoparticles can adsorb the HPAM from the solution, with higher adsorption for nanoparticles with higher surfactant loading. For the selected nanoparticles at concentrations of 500 and 1000 mg/L, the viscosity was not drastically affected regarding the polymer system in the absence of nanoparticles.

Nevertheless, the synthesized materials reduced the IFT and changed the wettability of the porous medium from an oil-wet state to a water-wet state, leading to an increase of the capillary number. The oil recovery in a quarter five-spot pattern micromodel was 61 and 77% higher than the waterflooding, for systems in the presence of 3000 mg/L of SiO2 nanoparticles and 1000 mg/L of SNP-8 nanoparticles, respectively. IFT reduction, wettability changes, and inhibition of polymer adsorption over the porous medium were identified as the main mechanisms for oil recovery enhancement in the presence of functionalized nanoparticles. Hence, it can be concluded that the nanoparticle functionalization improves the effect of the nanomaterial in the oil recovery with a lower dosage, which can lead to optimized EOR operations and cost savings.

4. EXPERIMENTAL SECTION

4.1. Materials. The polymer employed was a commercial partially HPAM provided by SNP Floerger (Andrézieux, France) with molecular weight and degree of hydrolysis of 6–8 MDa and 30%, respectively. Commercial SiO2 nanoparticles were purchased from Sigma-Aldrich (St. Louis, MO, USA). Oleic acid (≥99%), sodium hydroxide pellets (97%), and ethanol (99.5%) were obtained from Sigma-Aldrich (St. Louis, MO, USA) and were employed for the synthesis of the sodium oleate surfactant. Potassium bromide (PIKE Technologies, Inc., USA) was used for FTIR analysis. An extra
heavy crude oil of 7° API was used for wettability restoration of the cores to an oil-wet state. Colombian crude oil of 20° API was used for the contact angle measurements and coreflood tests. For the displacement tests, clean silica sand (Ottawa sand, US sieves 50/60 mesh) was used for the preparation of the porous medium and was purchased from Minercol S.A. (Colombia). Additionally, deionized water was used as a solvent for preparing different solutions used in this research. Toluene (99.8%), methanol (99.8%), and HCl (37%) were obtained from Panreac (Barcelona, Spain) and were employed for porous media cleaning.

4.2. Methods. 4.2.1. Synthesis and Characterization of Sodium Oleate Surfactant. For the synthesis of sodium oleate, a solution of 5 wt % NaOH in deionized water is added to a 15 v/v % solution of oleic acid in ethanol under constant stirring at 25 °C up to the solution reaches a pH value of 7, indicating that oleic acid reacted with NaOH and the sodium oleate is obtained. The hydrophobic–lipophilic balance (HLB) was determined by measuring the IFT at 25 °C of a 1000 mg/L solution of sodium oleate surfactant in deionized water (pH ≈ 7.1) as an aqueous phase and toluene as the oil phase. The linear equation for determining the HLB value from the least square of different commercial surfactants evaluated is showed in eq 1 as reported by Chun and Martin.

\[
\text{HLB} = \frac{\text{IFT} - 45.7}{-2.36}
\] (1)

4.2.2. Surface Modification of SiO₂ Nanoparticles. The surface of the SiO₂ nanoparticles was modified with the synthesized sodium oleate surfactant through the incipient wetness method considering different stock solutions with surfactant concentrations of 9.0, 4.0, and 2.5% regarding the mass of nanoparticles. After impregnation, the modified nanoparticles were washed with deionized water in excess. The absorbance of the effluent was followed by UV–vis spectrophotometry using a 60S UV–Visible Spectrophotometer (Thermo Fisher Scientific, MA, USA) until the absorbance was the same as before washing. The nanoparticles were separated by centrifugation using a Hermle Universal Centrifuge Z360 (Hermle Labortechnik GmbH, Wehingen, DEU). Surface-modified SiO₂ nanoparticles (SNP-2) will be named according to the amount Y of surfactant grafted on the surface. For instance, the SNP-2 material is composed of SiO₂ nanoparticles with 2.4 wt % sodium oleate on the surface.

4.2.3. Characterization of Surface-Modified SiO₂ Nanoparticles. The amount of surfactant remaining on the nanoparticle surface was determined using a Q50 thermogravimetric analyzer (TA Instruments, Inc., New Castle, DE) under air injection with a heating rate of 5 °C/min up to 800 °C. The surface area (Sₐ) of nanoparticles was estimated by nitrogen physisorption at −149 °C using a Gemini VII 2390 Surface Area Analyzer (Micromeritics, GA, United States). The Sₐ values were determined following the BET method.

The hydrodynamic diameter of the nanoparticles was obtained by DLS measurements using a NanoPlus-3 (Micromeritics, USA) after sonication for 6 h at 25 °C. The zeta potential was determined by electrophoretic light scattering to determine the dispersion of nanoparticles in the aqueous phase using the NanoPlus-3 (Micromeritics, USA).

Functional groups over the surface of the nanomaterials were characterized by FTIR spectroscopy with an IRAffinity spectrophotometer (Shimadzu, Japan). Each sample was diluted with KBr at a 1:3 mass ratio. For sample detection, a KCl cell with a 0.25 mm spacing was used and placed in the FTIR at 25 °C with 20 sweeps per minute for each sample in a range of 4000 to 500 cm⁻¹ at a resolution of 2 cm⁻¹.

4.2.4. Preparation of Polymer Solutions. Eight Polymer solutions at a fixed concentration of 500 mg/L were prepared according to the API-RP-63 method by dilution from a 2000 mg/L polymer stock solution based on the results obtained in a previous study.

4.2.5. Adsorption Tests. Adsorption tests of polymer onto the evaluated nanoparticles were performed in batch mode experiments at 25 °C by fixing the amount of the polymer (500 mg/L) and varying the dosage of the nanoparticles with and without surface modification in 300, 500, 1000, 3000, and 5000 mg/L. Solutions were kept under constant stirring at 50 rpm for 48 h. Further, the nanoparticles containing the adsorbed polymer are recovered by centrifugation using a Hermle Universal Centrifuge Z360 (Hermle Labortechnik GmbH, Wehingen, DEU). The amount adsorbed (N_ads) in mg/m² is estimated by mass balance using the Q50 thermogravimetric analyzer (TA Instruments, Inc., New Castle, DE) under a dry air flow at 100 mL/min and a constant heating rate of 20 °C/min from 25 to 800 °C. TGA are conducted for nanomaterials with and without adsorbed polymer. For desorption tests, the nanoparticles containing the adsorbed polymer are washed with deionized water and the absorbance of the effluent is followed until reaching the same value that than of the deionized water before washing. Further, samples are placed in clean deionized water under the same ratios of solution volume to the mass of nanoparticles employed in the adsorption experiments and kept under low stirring for 48 h. The samples are then centrifuged, and the desorbed polymer was determined by TGA.

4.2.6. Rheological Tests. Rheological measurements for polymer solutions in the absence and presence of nanoparticles were performed using a rotating rheometer Kinexus Pro+ (Malvern Instruments, Worcestershire—UK) with the concentric cylinder geometry, equipped with a Peltier cylinder cartridge for temperature control. Each measurement was performed at 25 °C in a range of shear rate of 5 and 250 s⁻¹.

4.2.7. Interfacial Tension Measurements. Interfacial tension (IFT) measurements were carried out with a GmbH K20 digital tensiometer (KRÜSS, Germany) using a Du Noisy ring composed of platinum-iridium that is suspended from a force sensor. The instrument is first calibrated with a patron (water ~72 mN/m ± 2). The oil/polymer solution system is equilibrated for 24 h before measurement.

4.2.8. Wettability Tests. Contact angle measurements were performed to observe wettability alterations after contact with polymer solutions in the absence and presence of nanoparticles. The rock samples were with a diameter of 3.8 cm and a length of 4.83 cm were obtained from an outcrop sandstone and cleaned with toluene and methanol to remove impurities. After cleaning, the samples were dried at 70 °C for 48 h. The rock samples were originally oil-wet and were restored to an oil-wet state by aging with a crude oil based on the method reported in previous studies. The restored samples (oil-wet) were used in the contact angle measurements as a baseline. The treatment with polymer solutions in the absence and presence of nanoparticles consists in soaking the oil-wet
rock in each solution under constant stirring at 500 rpm for 48 h at 70 °C. Further, the treated samples are removed from the solution and dried for 24 h at 70 °C. The contact angle is measured in liquid (water and crude oil)/air/rock systems at 25 °C by placing a drop of each fluid on the rock surface. A photograph of each drop is taken using a digital camera at a distance of 50 mm from the sample. The contact angle was estimated using the LayOut software (Trimble Inc., Sunnyvale, CA) and fitting the drop profile using sphere- or ellipse-like shapes.

4.2.9. Capillary Number Estimation. The capillary number ($N_c$) is calculated according to eq 2 for evaluating the relation between viscous and interfacial forces in the system for having a better insight into the recovery efficiency for the different scenarios evaluated.

$$N_c = \frac{\nu \mu}{\sigma \cos \theta}$$  \hspace{1cm} (2)

where $\nu$ (cm/s) and $\mu$ (poise) are the velocity and viscosity of the displacement fluid, respectively. $\sigma$ (mN/m) is the interfacial tension, and $\theta$ is the measured contact angle over the rock surface.

4.2.10. Displacement Tests in a Quarter Five-Spot Pattern Micromodel. The potential for enhancing the oil recovery with polymeric solutions in the presence and absence of nanoparticles was evaluated in a radial flow cell packed with Ottawa sand emulating a quarter five-spot pattern. For this, three recovery technologies were considered, namely: (i) a 500 mg/L polymer solution in the absence of nanoparticles, (ii) a 500 mg/L polymer solution with SiO$_2$ nanoparticles at 3000 mg/L according to previous studies, and (iii) a 500 mg/L polymer solution with surface-modified SiO$_2$ nanoparticles. The surface-modified SiO$_2$ nanoparticle concentration is selected based on the adsorption tests, rheological measurements, interfacial tension, contact angle, and capillary number results. The working fluids are a light crude oil of 20 °API and a 5 wt % KCl brine. An Ottawa sand US sieves 50/60 mesh was employed for porous medium preparation. Petrophysical properties such as porosity, as well as water and oil effective permeabilities, were estimated in 26%, and 530 and 225 mD, respectively. HCl, toluene, and methanol were employed for cleaning the sand and further dried at 120 °C according to the procedure described in previous studies.

First, the cell is saturated with brine at an injection rate of 2 mL/min. Then, oil is injected to the micromodel at 2 mL/min until the residual water saturation ($S_{wr}$) conditions are reached. At this point, waterflooding is carried out by injecting brine until no more oil is recovered at about 1.5 PVI. The next step is the injection of given PV of the chemical treatment, that is, a 500 mg/L polymer solution, a nanofluid containing 500 mg/L polymer and 3000 mg/L SiO$_2$ nanoparticles, and a nanofluid containing 500 mg/L polymer and 1000 mg/L surface-modified SiO$_2$ nanoparticles at an injection rate of 0.15 mL/min. The SiO$_2$ nanoparticle and surface-modified SiO$_2$ nanoparticle dosages were selected according to previous studies and according to the capillary number results, respectively. Finally, brine is injected again to guarantee that no more oil is recovered. In all tests, the produced volumes of oil are monitored. All of the dynamic tests were performed in a radial flow cell that emulates an array of producer—injector wells (Figure 11).

5. MODELING

5.1. Adsorption Isotherms: the SLE Model. The SLE model is based on the theory of adsorption of self-associative molecules such as polymers over the nanoparticles surface and is expressed as follows.

$$C_E = \frac{\psi H}{1 + K\psi} \exp \left( \frac{\psi}{N_{ads,m}} \right)$$  \hspace{1cm} (3)

where,

$$\xi = \frac{N_{ads,m} \cdot N_{ads}}{N_{ads,m} - N_{ads}}$$  \hspace{1cm} (4)

$$\psi = -1 + \sqrt{1 + 4KSA \cdot \xi}$$  \hspace{1cm} (5)

$N_{ads}$ (mg/m$^2$) is the amount of polymer adsorbed onto the nanoparticle surface, $N_{ads,m}$ (mg/m$^2$) is the maximum adsorption capacity of the nanoparticles under the range of concentration evaluated, and $C_E$ (mg/g) is the equilibrium concentration of polymer in the liquid phase. The SLE parameters $K$ (g/g) and $H$ (mg/g) are the adsorption constants related to the polymer self-association coefficient, and the affinity of the polymer get adsorbed on the nanoparticles surface, respectively.

5.2. Rheological Behavior. The Carreau model introduces rheological parameters such as relaxation time $\lambda_\eta$, related to the time for the polymer system return to...
equilibrium in response to a disturbance, and viscosity parameters ($\mu_{0,\gamma}$ and $\mu_{\infty,\gamma}$) that indicate the fluid behavior at zero and infinite stress. The Carreau model is expressed as follows:

$$\mu = \mu_{\infty,\gamma} + \frac{\mu_{0,\gamma} - \mu_{\infty,\gamma}}{1 + (\dot{\gamma}/\lambda)^{\gamma}}$$

(6)

where $\mu$ (cP) and $\dot{\gamma}$ (s$^{-1}$) are the viscosity and shear rate, respectively.

The root-mean-square error (RSME %) was used to estimate the goodness of fit of the employed models.$^{1,31}$

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**Notes**

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## NOMENCLATURE

- $d_{NP}$: mean nanoparticle diameter (nm)
- $S_{REP}$: nanoparticle surface area (m$^2$/g)
- $C_i$: initial polymer concentration (mg/L)
- $C_{eq}$: equilibrium polymer concentration (mg/L)
- $H_i$: Henry’s constant related to adsorption affinity (mg/g)
- $K_i$: constant related to the degree of association of the adsorbate on the surface of the nanoparticle (g/g)
- $N_{ads}$: amount of polymer adsorbed (mg/m$^2$)
- $N_{ads,m}$: maximum adsorption capacity (mg/m$^2$)
- $\lambda$: relaxation time index
- $\mu_{0,\gamma}$: fluid behavior at zero stress
- $\mu_{\infty,\gamma}$: fluid behavior at infinite stress
- $N_{P}$: pseudoplasticity index
- RSME %, root-mean-square error (%)
- $N_{CO}_2$: capillary number (dimensionless)
- $P_V$: pore volume
- SNP-2: silica nanoparticles functionalized with 2.45% of sodium oleate surfactant
- SNP-4: silica nanoparticles functionalized with 4.08% of sodium oleate surfactant
- SNP-8: silica nanoparticles functionalized with 8.31% of sodium oleate surfactant

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