Evaluation of Clay and Fumed Silica Nanoparticles on Adsorption of Surfactant Polymer during Enhanced Oil Recovery

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Static and dynamic adsorption have key role in chemical flooding process and they are important parameters in surfactant polymer degradation and decrease oil recovery. The effects of nano concentration on static adsorption of surfactant were investigated at variable condition polymer and surfactant concentration and nanoparticles are critical parameters influence the adsorption behavior at a flooding process. Surfactant polymer solutions and newly developed nanoparticles solutions were tested. The crude oil had a viscosity of 1320 mPa s at test conditions. In this paper, the role of nanoparticles in the adsorption of surfactant polymers onto solid surfaces of reservoir core is studied. The results which obtained by means of static adsorption tests, show that the adsorption is dominated by the clay and silica nanoparticles between the polymer molecules and the solid surface. Higher nanoparticles concentration leads to less adsorption, where the adsorption may decrease to 20 % of the adsorption level of surfactant polymer. The clay and Aerosil A300 nanoparticles in surfactant polymer solutions improved oil recovery by about the same amount. The clay, however, showed improved performance in comparison to Aerosil A300.

Keywords
Adsorption, EOR, Surfactant polymer flooding, Nanoparticle

1. Introduction

Surfactant-polymer (SP) flooding processes involve the injection of a surfactant-polymer slug followed by a polymer buffer and chase water injection. If designed correctly, the surfactant increases the capillary number, which is crucial for the mobilization and recovery of tertiary oil. Polymer increases the sweep efficiency by lowering the mobility ratio. If the reservoir crude oil has sufficient saponifiable components, soap (surfactant) is generated in-situ by the reaction of these components with the injected alkali, thus adding more surfactant to the flood. Surfactant-polymer interactions in solution are important with regard to the flow behavior in the porous media and the potential to displace the oil. Furthermore, the surfactant-polymer interaction at the solid/liquid interface is extremely important with respect to the loss of chemicals by adsorption onto the minerals of the rock material. The loss of surfactant by adsorption is one of the main factors prohibiting, on economic grounds, the use of surfactants in field applications. In recent years, much attention, both experimental and theoretical, have been focused on surfactant-polymer interactions in solution, and several reviews have been published. Alkali free SP flooding avoids the drawbacks associated with alkali. Surfactants with concentrations higher than the critical micelle concentration (CMC) can achieve ultra-low IFT. However, such surfactants are expensive. The use of a hydrophilic surfactant mixed with a relatively lipophilic surfactant or a new surfactant was also investigated. However, studies on SP flooding only focused on the screening and evaluation of the polymer and surfactant and their interaction. Reduction in mobility ratio and IFT is influenced by reservoir brine salinity, reservoir temperature, concentration of chemical ingredients an oil components, and others.

Surface modification of clay minerals has been studied extensively since the produced clay minerals exhibit appropriate properties for many material science applications, such as clay polymer nanocomposites. Recently, clay polymer nanocomposites have received a widespread attention by scientists. Among all nanostructured materials, natural or synthetic layered silicates have been focused by several researchers to produce clay polymer nanocomposites. In general, the interface structure affects the properties of clay polymer nanocomposites.

Surfactant adsorption during flow of the surfactant solutions in porous systems is typically conveyed through a range of complex phenomena. Some
research works related to the adsorption of commercial surfactants have been published but reasonable comparison of reported data is pretty difficult since surfactants with various purities have been employed\(^{[71-23]}\). The adsorption of surfactant may happen in the form of monomers at low concentrations of aqueous surfactant, if soil or sediment is present in the porous medium, while if the surfactant concentration increases, the adsorbed surfactant monomers tend to aggregate and form micelle-like structures. Depending on the number of layers for aggregated surfactant, the micelles are called admicelles for one layer and hemimicelles for two layers\(^{[19-22]}\). Adsorption of ionic surfactants on solid surfaces has been investigated extensively. At sufficiently high liquid phase concentrations, the surface coverage becomes high and lateral hydrophobic interaction may begin to cause association of adsorbed surfactants into aggregates\(^{[24-32]}\). Surfactant adsorption is a phenomenon on solid-liquid interfaces where transport of surfactant molecules from the bulk phase to the interface occurs. This process can be explained as the interface is energetically favored by the surfactant compared to the bulk phase\(^{[21,22]}\).

However, the current widely used polymers, polyacrylamide (PAM) and partially hydrolyzed polyacrylamide (HPAM), cannot completely meet the requirements due to the hydrolysis, degradation, and others under high temperature or high salinity\(^{[35,36]}\). Furthermore, PAM and HPAM have poor shear resistance\(^{[34-37]}\). Polymer molecular chains will be cut off when polymer solution passes through the pump, pipeline, perforation, and porous medium at high speed, so the viscosity of polymer solution will be greatly reduced\(^{[34,37,38]}\). Polymer viscosity was seriously affected by salinity. The effect of shearing on polymer viscosity and oil recovery was significant. Thus, high concentration of polymer was utilized to maintain high viscosity\(^{[39]}\).

Polymer adsorption on rock surfaces has been an important issue in EOR applications. EOR applications that use polymer flooding, polymer adsorption or retention in porous media should be avoided. Not all polymer retention is caused by adsorption because some polymer molecules, depending on their size and rheological characteristics, get trapped inside formation pores. It is generally believed that sandstone formations are negatively charged and carbonate formations are positively charged. Clay particles in a formation contain neutral, anionic, and cationic sites. One of the most important properties which made polymers interesting for EOR processes as mentioned earlier was their viscosifying property. Another important parameter which may affect the feasibility study plan of a polymer flooding project is the retention and adsorption of polymer in porous media. Adsorption and retention may be defined as the interaction between the polymer molecules and the porous medium which leads polymer to be retained or adsorbed\(^{[40,41]}\).

The amount of polymer adsorbed depends on the natures of the polymer and the rock surface. However, three phenomena have been observed regarding polymer adsorption: (1) Laboratory tests often indicate higher adsorption than field performance; (2) adsorption is significantly less in consolidated rock than in sand pack, and (3) adsorption increases with increasing water salinity\(^{[42]}\). Abadli and Sadikhzadeh reported that laboratory results often cannot be extrapolated to predict polymer adsorption in oil reservoirs because of polymer retention in porous media\(^{[43,44]}\). Mishra \textit{et al.}\(^{[45]}\) investigated the effect of polymer adsorption and mobility control on additional oil recovery with different polymer concentrations. The result showed that with the increase in polymer concentrations, oil recovery increased.

Adsorption mechanism which is the major part of retention will be discussed more afterward, but mechanical entrapment happens when the polymer molecules are trapped in narrow pore throat\(^{[36,47]}\). Polymer adsorption measurement, the mineral sample is soaked in the polymer solution. The difference of polymer concentration before and after mixing with rock sample is measured. The static adsorption onto the mineral surfaces is measured by the depletion method. Adsorption is the only mechanism which removes polymer from the solution and results in a significant viscosity reduction at a high level of adsorption. Typically, the adsorption by the bulk static method is much greater than that by dynamic flow conditions\(^{[48]}\).

Nanoparticles have wide range of applications which demonstrated briefly in next. Hamedi Shokrlu and Babadagli, investigated the effects on nano metals on viscosity reduction of heavy oil and bitumen for thermal oil recovery applications. Based on their obtained results, various parameters such as nanoparticle types, size and concentration could effect on the mechanism of the viscosity reduction of heavy oil/bitumen. Moreover, they figured out the optimum values of the addressed parameters in their studies\(^{[49]}\). In addition to previous applications of nanotechnology in petroleum upstreams, enormous researches have been made on the title of implementing of nanoparticles on the enhanced oil recovery (EOR) from petroleum reservoirs\(^{[50,51]}\). Hence, in some studies the applications of nanoparticles in oil industry have been reported and classified based on priority. Researchers have concluded that nanotechnology has the greatest usage in chemical EOR methods\(^{[52]}\). Therefore, in some studies, the role of nanoparticles in EOR operations has been reported\(^{[53,54]}\). The nanofluids are created by the addition of nanoparticles to fluids for intensification and improvement of some properties at low volume concentration of the dispersing medium. Then, the main feature of nanofluids is that their properties greatly depend on the
dimensions of nanoparticles added to them\textsuperscript{55}).

The objective of this paper is to investigate the potential of SP flooding for heavy oil. In this work, the adsorption phenomenon and its effect on SP is studied. Polymer, surfactant and nanoparticles concentration have been varied and their impact on the process has been studied experimentally. The adsorption of a dual nanoparticles system of the type clay and Aerosil A300 nanoparticles has been studied by: (a) static adsorption, (b) dynamic adsorption, on a reservoir core. Adsorption data for SP samples in different concentration are determined by static adsorption and dynamic adsorption methods. A series of lab flooding experiments have been carried out to find the additional recovery using nano surfactant-polymer.

2. Materials and Experimental Methods

2.1. Materials

2.1.1. Preparation of Brine

A synthetic brine with the concentration of 20,000 volppm was prepared by dissolving NaCl, Na\textsubscript{2}SO\textsubscript{3}, CaCl\textsubscript{2}, MgCl\textsubscript{2}·6H\textsubscript{2}O and Na\textsubscript{2}HCO\textsubscript{3} into distilled water. The formulation of the artificial brine is listed in Table 1.

2.1.2. Surfactants and Polymer

Sodium dodecyl sulfate (SDS) (approximately 99 % purity) was used as surfactant. SDS (C\textsubscript{12}H\textsubscript{24}SO\textsubscript{4}Na, MW = 288.38) was purchased from Central Drug House (P) Ltd. The polymer used were all commercially available, completely water soluble and differed mainly in their concentration (see Table 2). In particular, we tested polyacrylamide that was chemically similar to acrylamide from Beijing Hengju Co. (China), with an average molecular weight (MW) of 12.0 \times 10\textsuperscript{6} and a degree of hydrolysis of about 26 %. The maximum in the surfactant concentration is about 0.3 wt%, which is below the CMC (= 0.31 wt%). A wide range of concentrations around the critical micellization concentration of SDS (0.1-0.3 wt%) and HPAM concentrations (1200-4200 volppm) were chosen for the present study.

2.1.3. Nanoparticles

Local sodium bentonite with a mesh size of 200 and a particles size less than 50 nm was used in this study. The bentonite was produced in Iran and amended with the chemicals shown in Table 4. Oxford-ED2000 XRF and GC-2550TG (Teif Gostar Faraz Co., Iran) were used for all chemical analyses. Fumed nanosilica (Aerosil A300) was purchased from Degussa. Specific surface area of Aerosil A300 is 300 m\textsuperscript{2}/g with average primary particle size 7 nm, pH 3.7-4.7 and SiO\textsubscript{2} content 99.8 wt%. The silica fume used with a specific surface area of 21 m\textsuperscript{2}/g was supplied by Azna Ferroatloy Co. and complied with requirements of ASTM C1240.

The commercial clay mineral, Cloisite\textsuperscript{Na}\textsuperscript{+} (Mt) (Southern Clay Products Inc., Texas, USA), is a natural Mt used in this study were reagent grades. Following preparation and analysis of the raw materials, the clay was purified using a 2-inch hydrocyclone apparatus. To do so, a suspension of 3 wt% clay in distilled water was prepared and then passed through the cyclone at a

| Table 1 | Preparation of Brine |
|---------|----------------------|
| Composition | [wt%] |
| NaCl | 1.71 |
| Na\textsubscript{2}SO\textsubscript{3} | 0.01 |
| CaCl\textsubscript{2} | 0.32 |
| MgCl\textsubscript{2}·6H\textsubscript{2}O | 0.09 |
| Na\textsubscript{2}HCO\textsubscript{3} | 0.02 |

| Table 2 | Properties of Examined Samples |
|---------|------------------------------|
| Sample ID | Polymer con. [ppm] | Surfactant con. [wt%] |
| A | 0 | 0.0 |
| B | 1200 | 0.0 |
| C | 2200 | 0.0 |
| D | 3100 | 0.0 |
| E | 3150 | 0.0 |
| F | 3200 | 0.0 |
| G | 4200 | 0.0 |
| H | 2800 | 0.1 |
| I | 2800 | 0.2 |
| J | 2800 | 0.3 |
| K | 3000 | 0.1 |
| L | 3000 | 0.2 |
| M | 3000 | 0.3 |
| N | 3200 | 0.1 |
| O | 3200 | 0.2 |
| P | 3200 | 0.3 |

| Table 3 | Chemical Composition of Bentonite |
|---------|----------------------|
| Formula | [wt%] |
| L.O.I | 13.2 |
| Na\textsubscript{2}O | 2.04 |
| MgO | 2.22 |
| Al\textsubscript{2}O\textsubscript{3} | 14.59 |
| SiO\textsubscript{2} | 61.03 |
| SO\textsubscript{2} | 0.37 |
| Cl | 0.46 |
| K\textsubscript{2}O | 0.76 |
| CaO | 0.77 |
| TiO\textsubscript{2} | 0.22 |
| Fe\textsubscript{2}O\textsubscript{3} | 2.09 |
| BaO | 0.11 |

| Table 4 | Core Properties |
|---------|-----------------|
| Diameter | [mm] | 34.50-34.55 |
| Length | [mm] | 32.4-32.6 |
| Weight | [g] | 88-89 |
| Porosity | [%] | 18.1-18.8 |
| Water permeability | [md] | 282-287 |
pressure of 0.15 MPa. This resulted removal of impurities and large particles. Montmorillonite particles with a diameter of less than 6 μm were then dried and used in the compatibility process. To ensure compatibility following the dispersion of clay in distilled water, a suspension comprised of clay was prepared and amended with 10, 20, 30, 40 or 50 (wt%) percent of the modifier materials “silane.” The mixtures were then heated at 80 °C for 6 h, after which the products were washed with distilled water and dried. The distribution of clay particle sizes was measured before and after purification using a Laser Particle Size Analyzer. The distribution of clay particle sizes was measured before and analyzed by scanning electron microscope (SEM). The intercalation of the samples was evaluated using an X-ray diffraction (XRD). The results of the XRD analysis revealed that most of the impurities, which included quartz, cristobalite, calcite, gibbsite and feldspar were removed from the clay by the purification process. In addition, analysis of the particle size distribution revealed that most of the particles were less than 5 μm in diameter and that more than 80 % of the particles were less than 2 μm in diameter following purification. Finally, the thickness of the layers in the crystal structure of montmorillonite and the patterns generated by XRD indicate that following purification, the clay was comprised of crystal layers on the top of each other. The polymer molecular structure was performed using AFM-type electron microscope (ARA-AFM, Ara Research Co., Iran). The produced nanoparticles are shown in Fig. 1.

2. 1. 4. Core Material

A medium-permeability reservoir sandstone core was used. The core was cleaned with a mixture of ethanol and chloroform to remove oil, and with ethanol to remove water. The core was then dried in an oven at 60 °C for 24 h. Table 4 shows the properties of the core sample.

2. 1. 5. Oil Sample

The oil sample was dead oil which was supplied from one of the Iranian heavy oil fields located in the south of Iran with 17°API at 25 °C. The density and viscosity of crude oil were 973 kg/m³ and 1320 mPa s, respectively.

2. 2. Experimental Methods

2. 2. 1. Critical Micelle Concentration

Determination of critical micelle concentration (CMC) measurement of surface tension is very much useful supplementary test method for determination of CMC of surfactant. The CMC of the surfactants in free- and complex-state was determined in soft brine following the conventional surface tension method at 25 ± 1 °C using a TensiCaD tensiometer manufactured by CAD Instruments. In all cases, the standard deviation did not exceed ± 0.1 mN/m.

2. 2. 2. Scanning Electron Microscopy Analysis

Leo 440i SEM was used to study the morphology of surfaces of nanoparticles on core samples at uniform magnifications. The scanning electron micrograms of different cross-sections with uniform magnification of the samples of polymer surfactant filled with Aerosil A300 and clay nanoparticles are studied.

2. 2. 3. Experimental Procedure

(1) Surfactant-polymer flooding

The experimental procedures of SP flooding in core samples are described briefly as follows:

First, after the conventional treatment and physical-property test were finished (including washing oil and salt and porosity and permeability measurement), the core was evacuated and saturated with brine; then the initial permeability to brine (this may represent the absolute permeability of the rock) was measured by use of the brine flooding.

The SP solution was then pumped at a designed constant flow rate through the core sample (Fig. 2), and the differential-pressure data and flow-rate data were measured and recorded when the flow was stabilized. During the displacements, the pressure drop about (0-600 psi) was changed after the flow rate was about 1.5 cm³/min stabilized. Therefore, the rheological characteristics of the SP solution could be obtained through the rheometers during the single-phase flow of the SP solution, could be measured and calculated.

(2) Static adsorption

Static surfactant polymer adsorption experiments were performed to evaluate the adsorption of the different surfactant polymer concentrations. These tests were conducted at room temperature by adding sand to the SP solution and stirring until adsorption was complete. At the end of the test, the samples were reviewed. The amount of SP retained by the sand was then calculated by difference, after correcting for any sample. After adsorption, the SP solutions were isolated by centrifugation with Hettich centrifuge instrument (Model No. Rotanta 460).

Adsorption (q) measured by using this method can be calculated as the following:
\[ \Gamma = \frac{(C_0 - C_e)V}{m} \]  \hfill (1)

Where, \( C_0 \) and \( C_e \) are the initial and equilibrium concentrations of surfactants (mg/g), respectively, \( V \) is the volume of the surfactant solution (L), and \( m \) is the weight of the sand particles (g) (adsorbent) used.

Samples of SP solution were taken from the container in seven time steps; after 1, 2, 3, 6, 12, 24, and 48 h. Batch adsorption experiments were carried out by allowing a precisely weighted amount of nano fumed silica and different states of clay to reach equilibrium with crushed sandstone solutions of various initial concentrations ranging from 0.5 to 3.5 wt% for clay nanoparticles and Aerosil A300. The solid to liquid weight ratio was 1:5. Known weights of crushed sandstone samples (4 g) were added to a 30 mL solution of the SP at different concentrations. All the adsorption experiments on crushed rocks were performed at 28°C and atmospheric pressure. A volume of 30 mL of each nano SP solution was added to a centrifuge tube containing a 4 g mass of crushed rock. The samples were centrifuged for 20 min at 2000 rpm. Supernatants were separated and analyzed for residual SP concentrations. The supernatant liquid was filtered and analyzed. The amount of surfactant adsorbed was determined by measuring different concentrations in the solution before and after contact with sandstone. The pH value of each solution was also determined.  

(3) Dynamic adsorption

The dynamic adsorption experiments were performed at a constant temperature of 28°C by injecting chemical solution at various surfactant concentration through core until produce surfactant concentration reaches an equilibrium state. The core was made by mixing well treated sand. Measure the length and the diameter of the core, and weight it before and after test so as to calculate the mass of the sand mixture. Subsequently, the core was saturated by 15 g/L NaCl solution. 10 g/L NaCl solution was used to flood the core. The conductivity data of outlet were measured regular times and the pore volume of core was obtained by the method discussed as follows.

3. Results and Discussion

3.1. Viscosity Experiment

Viscosity values for polymer solutions and nanopolymer fluids in the ranges of 0.001-330 s\(^{-1}\) were measured. In shear rates higher than 330 s\(^{-1}\) due to probable degradation of polymer chains measured data were not reliable, and therefore to analyze data, shear rates higher than 330 s\(^{-1}\) were not considered. Rheological investigation of data was done in two steps.

The effect of the polymer content: One of the crucial factors in recovery of polymer flooding is the concentration of polymer. Suitable polymer concentration should be determined by considering economical aspects. Common polymer concentration is between 1200 to 4200 vol ppm, but in this study a high concentration was preferred for injection due to the high viscosity of the oil and commercial aspects. Some samples were performed to quantify the effects of polymer concentration in the coreflood oil recovery experiments. After that the two samples were prepared the effects of polymer concentration increment in saline system were investigated. It is seen from the graph, increase in polymer concentration has positive impacts on solution and leads to viscosity increasing. In this case, simply one should express that having low concentration of polymer, sample A variation graph for its viscosity regarding to shear rate is different, so that in high levels of this rate an increase to shear viscosity leads to solution increase (Fig. 3).

The typical flow curves of rheology solutions of HPAM polymer at different concentrations are shown in
The viscosity of solutions increased with increasing polymer concentration as expected. It can be seen from the figure, the viscosities of all samples decreased with the increasing shear rate. The zero shear viscosity can be measured by extrapolating the viscosity curve as shear rate approaches to zero. This is the maximum viscosity of the solutions. The behaviors of such fluids which display a decreasing apparent viscosity with increasing shear rate can be characterized as pseudoplastic fluid.

Three different concentrations of 3100, 3150 and 3200 volppm of polymer were prepared and used in polymer injection processes. According to the diagrams obtained, oil recovery values after polymer injection showed an increasing trend by increase in polymer concentration, but after a certain increase value, oil recovery is steady state. So the 3150 volppm concentration was selected for main experiment (for adding clay nanoparticles and SDS). The results of injection with various concentrations are shown in Fig. 4.

The CMC, one of the main parameters for surfactants, is the concentration at which surfactant solutions begin to form micelles in large amount. The experimental adsorption data measured at the concentration range the CMC are shown in Fig. 5. The concentration at the turning point of the curve is CMC. The surface tension versus surfactant concentration plots in presence of polymer shows three distinct zones. Above the critical aggregation concentration (CAC), the interaction between the water-soluble polymer and surfactants is started. Dynamic equilibrium between surfactant-saturated polymer and the regular aqueous micelles coexist just above the polymer saturation point (PSP). With further increase in surfactant concentration, surface tension remains constant and normal surfactant micelles start to form.

A comparative picture of the flooding performances by SP flooding is shown in Fig. 6. Considering this figure, surfactant flooding at different concentrations was conducted. The polymer (2800 volppm and 3200 volppm) and the surfactant (0.1-0.3 wt%) were mixed with formation water to form the SP system. Increasing the concentration of SDS to 0.1 wt% and 0.3 wt%, leads to higher oil recovery. Also, increasing the concentration of polymer to 2800 volppm and 3200 volppm, due to more reduction of IFT, leads to higher oil recovery. However, as can be seen, there is no significant difference between the curves of 0.2 wt% and 0.3 wt%. This is due to the CMC number of SDS which is 0.21 wt% and it means that higher concentrations of CMC have a slight effect (or even sometimes a negative effect) on enhanced oil recovery.
3.2 Adsorption Measurements

Figures 7 and 8 present the adsorption static of sodium dodecyl sulfate surfactant onto the sample using a wide range of surfactant concentration below the CMC. To evaluate the effects of nanoparticles concentration increment on a reservoir core system samples I, L, and O were compared (Fig. 7). By increasing concentration of nano in aqueous solution, more reduction in adsorption of surfactant on sandstone observed.63) It can be seen that the amount of SP adsorption has been reduced for a wide range of surfactant concentrations from low concentrations up to a specific concentration around CMC. As can see from Fig. 8, the SP rate is less in core samples. The samples of the same stone with nano-fumed silica have less adsorption than solutions containing nano-clay. Based on contact area of stone, the adsorption shows the least level of SP related to nanoparticle in Fig. 8 and for this test related to nano-fumed silica. In this test, the concentration of SP solutions is considered the same.

Figure 10 shows the dynamic adsorption curves clay and Aerosil A300 nanoparticles in three concentration SP solution. From Fig. 9, the adsorption of sample I is lower than that of sample O at the same conditions, and nano-Aerosil A300 has better effect than clay nanoparticles on decreasing the adsorption on the surface. The dynamic trends of results correspond to those obtained from the static method for 90% of samples. In this figure, the adsorption of sample L with clay nanoparticles has the lowest decreasing the adsorption on the surface at the same conditions. In field applications, the concentration of surfactant used is generally several times lower than the CMC. Therefore, in this study, surfactant concentration (100 volppm and 300 volppm) lower than the CMC of the respective sur-
factants was used.

3.3. Dispersion of Nanoparticles

Figure 11 shows the dynamic light scattering distribution for two type nanoparticles in SP solution. Size analysis was performed to understand whether the dispersed particles may block the pore sizes in core samples, which may affect the rate of recovery due to unsuccessful penetration of SP. It was observed that the clay forms larger than the nanoparticles, which may lead to the increased retention in the core leading to higher permeability reduction. The volume percentage distribution shows size with mean particle diameters of less than 10 nm and 50 nm for NPs fumed silica and clay, respectively.

3.4. Coreflood Experiment

To investigate the effect of these nanoparticles on oil recovery, three flooding tests by surfactant polymer solution and nano SP fluid were done in a coreflood for each sample and the results are shown in Fig. 12. As can be seen in Fig. 12, approximately 10, 9 and 2 % increase in oil recovery after injection of nano SP was observed in comparison with injection of SP solution, respectively. The figure shows that increasing the concentration of each nanoparticles causes an increase in the ultimate recovery. Considering Fig. 12(a), oil recovery by SP flooding without any nanoparticles was 54 %. After this step, surfactant polymer flooding at different nanoparticles concentrations was conducted. According to the diagrams obtained, the injection of sample L at a concentration 2 wt% clay nanoparticles showed an increase of about 10.8 % compared to the base test (sample L). Also, the injection of sample L at a concentration 1.9 wt% nano-Aerosil A300 showed an increase of about 9.18 % compared to the base test (sample L).

Figure 12(b) plots the curves of cumulative oil recovery versus injection pore volumes for core flood. SP flood oil recoveries of the two tests (with clay and Aerosil A300 nanoparticles) were nearly the same. About 47 % oil recovery was obtained at 1.6 PV water injection polymer solution into the sandpack. Although the ultimate oil recovery will be different, it was decided to select the oil recovery after injecting 1.6 pore volume of polymer solution for comparison purposes. As shown in Fig. 12(b), oil recovery in sample I with clay and Aerosil A300 (58.8 % and 61.4 % OOIP) are more than sample O with clay and Aerosil A300 (54.3 % and 53.3 % OOIP). Higher oil recovery in the SP flooding sample L with clay and Aerosil A300 are due to the lowest rates of adsorption rate with nanostructures.

Oil recovery at different injected pore volumes for all three samples of O is given in Fig. 12(c) for clay nanoparticles, nano-fumed silica and base SP sample of O, respectively. However, as can be seen, there is no significant difference between the curves of sample O with nano-clay and nano-Aerosil A300. This is due to the CMC number of SDS which is 2.1 wt% and it means that higher concentrations of CMC have a slight effect (or even sometimes a negative effect) on enhanced oil recovery. In the core flooding Fig. 12(c), by increas-
ing the nano-concentration, fewer SP molecules are retained in the core; this is the same trend as found in the static adsorption experiments. The adsorption amounts are very low for sample I with nano, and itself still has the highest adsorption, so, recovery in nano-samples enhanced about 15% from base SP model.

The SEM scan (Fig. 13) was performed on the samples to determine the morphology of each layer. Figure 13 shows larger and smaller surfactant with chains of polymer on sand background. The obtained results showed that SP solutions contained a mixture of grains of a large size. The clay and fumed silica particles in solutions were dispersed completely, so this subject can increase recovery performance. The results showed that the polyacrylamide has good dispersion and the particle size distribution was uniform when using clay as optimizer, its average size was about 1 nm. To investigate the relationship between the incremental oil recovery and the effective concentration of nano in solutions, a series of core flood tests were carried out for each oil sample by injecting SP solutions of different viscosities. The general trend is that the enhanced oil recovery increases with increasing the concentration of nanoparticles due to improved adsorption ratio.

4. Conclusions

In this study, the SP flooding experiments were conducted to heavy oil, and the effect of nano on adsorption and oil recovery were examined. The adsorption of the three types of surfactants concentration onto sand cores from aqueous solutions was studied. Experimental investigations were carried out to examine the adsorption isotherm and dynamics of adsorption of these nano-surfactants. The following conclusions were drawn:

According to the results obtained in the present study, as we move from low concentration surfactant, adsorption of surfactants on sand particles changes. With increasing nanoparticles of the solution adsorption of SDS decrease on sand surface. In order for surfactant polymer flooding of heavy oil to be effective, the concentration of the polymer solution must be beyond a threshold value. In experiments presented in this paper, the threshold concentration seems to be about 2.1 wt% and 3000 volppm, surfactant and polymer respectively. When the viscosity of polymer solution is outside of this range, the increase in viscosity of polymer solution was found to have only a small incremental in oil recovery.

The results show that the adsorption for these nano SP are reduced with increasing nano-concentrations, however, all nano-surfactant polymers have considerably lower adsorption than SP. Polymer solutions containing Aerosil A300 nanoparticles have less adsorption based on the weight percent than similar samples containing clay and also this behavior is the same regarding adsorption based on the area of contact for stone.

Further, it was found that the sample O had significantly higher adsorbed phase concentration in all cases. Nevertheless, the isotherms of the two samples of O could be described with the nano additives clay and Aerosil A300. Ultimate oil recovery by clay nanoparticles surfactant polymer at optimized range (sample L) flooding enhances by a factor of 10.8% in comparison to SP flooding. Clay nanoparticles SP solution is recommended as a more efficient nano SP solution type compared to SP solution.

The results of this study reveal the effect of nanoparticles on oil recovery efficiency in SP flooding, and may be helpful for successful design of nano SP during flooding processes.

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Nomenclatures

| Symbol | Definition                  |
|--------|----------------------------|
| IFT    | interfacial tension        |
| OOIP   | original oil in place      |
| EOR    | enhanced oil recovery      |
| SP     | surfactant-polymer         |
| SDS    | sodium dodecyl sulfate     |
| HPM    | partially hydrolyzed polyacrylamide |
| PV     | injection pore volume     |
| CMC    | critical micelle concentration |
| Γ      | surfactant adsorption on rock surface |
