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Improvement of Surfactant Flooding Performance by Application of Nanoparticles in Sandstone Reservoirs

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Chemical materials such as alkaline, surfactants, and polymers are widely used for the chemical EOR to reduce the trapped oil saturation in the reservoirs. Parameters such as surfactant adsorption and surfactant loss affect the performance of the mentioned EOR method. In this paper an attempt is made to enhance the performance of the surfactant flooding by application of nanoparticles. A series of core flooding tests were completed for sandstone core samples under reservoir conditions to study the effect of a novel application of nanoparticles to alter the properties of the surfactant in chemical flooding EOR processes. Sodium dodecyl sulfate (SDS) is widely used for the EOR approach. Silica nanoparticles were used to change the surfactant adsorption on the rock surfaces. The results showed that the addition of hydrophilic nanoparticles reduces the surfactant adsorption on the rock and improves the performance of the surfactant flooding which increases the oil recovery.

Keywords

Chemical EOR, Chemical flooding, Surfactant flooding, Surfactant adsorption, Nanoparticle

1. Introduction

The main goal of the surfactant flooding as an EOR (enhanced oil recovery) process is to lower the interfacial tension between the injected water and the reservoir oil which leads to the reduction in the residual oil. Each surfactant molecule as a surface-active substance has a hydrophilic polar head and a non-polar hydrophobic tail as shown in Fig. 1.

Therefore, a surfactant molecule contains either a water insoluble or oil soluble component and a water soluble component. Depending on the nature of the hydrophilic group, surfactants are classified into four categories as anionic, cationic, nonionic, and zwitterionic¹⁾.

Surfactants are surface active compounds; which means that they have a tendency to absorb at interfaces. In water/oil solution, surfactants molecules diffuse in the water phase and absorb at interfaces between oil and water. The insoluble hydrophobic group extends out of the bulk water phase, into the oil phase, while the water soluble head group remains in the water phase. This arrangement of surfactant molecules at the surface modifies the special surface behavior at the water/oil interface as the hydrophobic part dissolves in the oil

phase, and the hydrophilic part dissolves in the water phase. Thus IFT (interfacial tension) decreases and two immiscible fluids such as oil and water mix together and become as emulsion as shown in Fig. 2. In this process, surfactant molecules should aggregate and

Fig. 1 The Molecular Structure of the Surface-active Substance

Fig. 2 Schematic of Emulsion

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Fig. 3 Schematic of the Critical Micelle Concentration of a Surfactant Molecule at Three Concentrations: (a) the critical concentration, (b) the critical concentration range, and (c) above the critical concentration

form a new configuration which consists of 50 or more molecules called micelle²⁾. The micelle acts like a barrier between the two phases so they do not come in direct contact to each other³⁾.

Hence, formation of micelles is critical for the performance of the surfactant molecules. CMC (critical micelle concentration) is defined as the concentration of surfactants above which micelles are spontaneously formed. **Figure 3** shows the schematic of the critical micelle concentration form. The CMC can be affected by many variables like chain length of the tail, temperature, and pressure. For ionic surfactants it also depends on the nature and concentration of counterions in solution. Added salt/electrolytes decrease the CMC, and this tendency is enhanced as the chain-length of the surfactant increases⁴⁾.

Control of surfactant loss in the reservoir is one of the most important factors in determining the success or failure of a surfactant flooding project. One of the main reasons of surfactant loss is high adsorption of the surfactant molecules on the rock surface.

Surfactant adsorption depends on many factors such as surfactant concentration, surfactant type, and rock minerals. The adsorption rises sharply as the surfactant concentration increases until CMC point then is nearly constant⁵⁾. On the other hand, reservoir minerals like quartz (silica) and kaolinite show a negative charge while calcite, dolomite and clay have positive charge on their surfaces at neutral pH of the brine. The adsorption of surfactants at the solid/liquid interface comes into play by electrostatic interaction between the charged solid surface and the surfactant ions. Ion exchange, ion pairing, and hydrophobic bonding are some of mechanisms by which surfactants absorb onto mineral surfaces of rock⁶⁾.

In adsorption of ionic surfactants on the sandstone rocks ion exchange mechanism is active. When this mechanism takes place, counterions in the diffusive double layer are exchanged for surfactants with the same charge. This leads to a higher concentration of

surfactant close to the surface. This mechanism can thus induce micellization close to the interface even if the bulk concentration is below CMC. Hence, ionic surfactants might be candidates for use in sandstone formations from the adsorption point of view, because ionic interactions between surfactant ions and mineral surface cause same charges and thus low adsorption⁷⁾.

The CMC is an important parameter to design a successful injection operation. Because until CMC point the IFT between two immiscible phases decreases and reaches to the lowest value at the CMC. After this point, the IFT will not change. Thus at CMC water/oil emulsion occurs which makes CMC as the optimum concentration for the surfactant flooding.

Several methods have been reported in literature to obtain CMC^{8),9)}, but UV-absorption spectroscopy method, fluorescence spectroscopy method, and electrical conductivity method are common for laboratory measurements¹⁰⁾.

Conductivity measurement method is based on the fact that under normal conditions, an ionic surfactant (below its CMC) is completely dissociated and there is a linear relationship between the molar conductivity of the surfactant solution and its concentration as the surfactant monomers behave as normal electrolytes. Above the CMC, molar conductivity is constant and independent of surfactant concentration as micelles behave like weak electrolyte. Thus plot of molar conductivity of the surfactant *versus* the surfactant concentration shows a linear behavior with two different slopes. Hence, CMC of the surfactant obtained from the intersection of the two straight lines^{11),12)}.

Nanoparticles with special properties such as ultra-small size and high surface area to volume ratio are recently used to improve the capability of different EOR methods. For example, silica nanoparticles due to its specific properties such as being water-soluble, non-toxic, and odorless are mostly common in EOR process¹³⁾.

In general, silica nanoparticles are divided into two groups which are hydrophilic and hydrophobic types. Surface of silica nanoparticles is coated by both silanol and siloxane groups. If over 90 % of the surface is covered by silanol groups, then silica nanoparticles is considered to be hydrophilic type and conversely, if the silica particles are coated with only 10 % of silanol groups on the surface, they are hydrophobic type¹⁴⁾. Hydrophilic types can be wetted with the water as silanol groups have a tendency for attraction by hydrogen bonds, but hydrophobic types cannot be wetted by the water molecules as siloxane groups with a hydrophobic nature are neutral and reactions of the silanol groups with various organosilanes groups which cause hydrophobic properties^{15),16)}. **Figure 4** shows the schematic of silanol and siloxane groups.

Several studies have been done for surfactant adsorp-

Fig. 4 Schematic of Silanol (a) and Siloxane (b) Groups

Table 1 Properties of Distilled Water at the Room Temperature

Specification	Unit	Quantity
Conducting surveys	[$\mu\text{s}/\text{cm}$]	2.24
Viscosity	[cP]	0.926
Density	[kg/m^3]	996

Fig. 5 SDS Powder

tion on the rock surfaces. Some works studied the surfactant adsorption reduction by addition of alkali, electrolyte¹⁷⁾, sodium polyacrylate¹⁸⁾, and nanoparticles¹⁹⁾ to the solution.

In this paper silica nanoparticles are used to control the stability of the surfactant and to decrease the adsorption on the rock surfaces. Also, as the main parameter in the EOR approach, its effect on the improvement of the recovery from the sandstone core samples is also investigated.

2. Materials Used in Experiments

The distilled water was used for the surfactant preparation and the suspension of silica particles. Properties of the water at the room temperature are shown at **Table 1**.

Surfactants used in these experiments were the anionic surfactant sodium dodecyl sulfate (SDS) with 99 % purity obtained from Merck group. **Figure 5** shows the SDS powder, also physical and chemical properties of the surfactant are given in **Table 2**.

Hydrophilic silica nanoparticles (AEROSIL200) provided by Evonik Degussa GmbH company is used in this study with a surface area of less than $200 \text{ m}^2/\text{g}$ as

Table 2 Several Chemical and Physical Properties of the Anionic SDS

Property	Value
Molecular weight	228.5 g
Detergent class	ionic (anionic)
Aggregation number	62
Micelle molecular weight	18000 g
Critical micelle concentration	6 to 8 mM
Cloud point	$> 100^\circ\text{C}$
Dialyzable	no

Fig. 6 Silica Nanoparticles Powder

Table 3 Physical and Chemical Properties of AEROSIL200

Property	Value
Behavior with respect to water	hydrophilic
Appearance	fluffy white power
BET-surface area	[m^2/g] 25 ± 200
Average primary particle size	[nm] 12
Tapped density	[g/L] 50
SiO ₂	[wt%] ≤ 99.8
Al ₂ O ₃	[wt%] ≤ 0.05
Fe ₂ O ₃	[wt%] ≤ 0.003
TiO ₂	[wt%] ≤ 0.03
HCL	[wt%] ≤ 0.025

shown in **Fig. 6**. The main properties of the nanoparticles are listed in **Table 3**.

3. Experimental Procedure

In this work we categorized our experiments into two groups: static and dynamic tests. At the first stage, several static tests were done to determine the CMC value in the aqueous surfactant solution without presence of the rock at different temperature. Then CMC for aqueous surfactant solution at the presence of the rock was studied, and the effect of nanoparticles on the variation of the CMC was investigated. At the next phase, several dynamic tests for evaluation of the flooding performance were completed at the reservoir conditions of 38°C and 3000 psi.

3.1. Static Tests

As mentioned, the main purpose of this work is to

Fig. 7 Schematic of the Core Flood Experimental Setup

improve the performance of the surfactant flooding. Hence, we examined the absorption of the surfactant molecules on the crushed rock samples in presence of nanoparticles and compared it to the base case. The surfactant sample at different concentration exposed in contact with the crushed core. The change in the surfactant concentration after 24 h showed the surfactant absorption on the rock surface. We applied the electrical conductivity method and conductivity meter apparatus to measure the surfactant concentration. The surfactant adsorption in terms of mg/g is calculated by:

$$\Gamma = \frac{M_S \times (C_i - C_e)}{M_R} \times 10^{-3} \quad (1)$$

Where Γ is amount of surfactant adsorption, M_S is the mass of the surfactant solution, M_R is the total mass of the crushed rock, C_i is the initial surfactant concentrations before equilibrated with rock, and C_e is surfactant concentrations after equilibrated with rock.

3.2. Dynamic Tests

Figure 7 shows a schematic of the core flooding system used in the experiments. At the first step the core sample was loaded into the core holder and vacuumed by a pump. Water was then injected at very low $0.1 \text{ cm}^3/\text{min}$ rate to measure the porosity and the absolute permeability of the core.

Oil was then injected at $2 \text{ cm}^3/\text{min}$ for 3 pore volumes to reach to the connate water saturation. The effective permeability of the oil is calculated by Darcy's equation. After aging the core by oil, the core samples were flooded by water, surfactant and nanoparticles/surfactant at different concentrations. Each flooding was conducted for 1.8 pore volumes at $2 \text{ cm}^3/\text{min}$. The oil recovery was measured at all the steps.

4. Result

4.1. Critical Micelle Concentration (CMC)

To obtain CMC, molar conductivity amount at various initial concentrations of surfactant was measured by conductivity meter apparatus. CMC is determined

Fig. 8 Molar Conductivity vs. Initial Surfactant Concentrations

Fig. 9 CMC vs. Temperature

from the intersection of two straight lines of conductivity versus SDS concentration as shown in Fig. 8. Our measurement showed that the CMC occurred at the surfactant concentration equal to 2450 ppm. As concluded from Fig. 8, until 2450 ppm the surfactant solution behaves as normal electrolytes. Hence, molar conductivity sharply increased as a function of concentration, but after 2450 ppm surfactant solution behaves as a weak electrolyte due to micellization. Hence, molar conductivity tends to increase slowly.

Figure 9 shows the relation of the CMC value as a function of temperature. As shown, by increasing the temperature, CMC increases gradually. Up to 35°C , micellization is nearly stable because of the decrease of the hydration of hydrophilic groups. After 35°C micelles become unstable as the structured water molecules around the hydrophobic group are disturbed due to the high temperature. Hence, after 35°C , CMC increased sharply.

4.2. Static Surfactant Adsorption

Surfactant adsorption on the crushed rock was measured and reported at various concentrations of surfactant as shown in Fig. 10. The adsorption rises sharply as the concentration increases and then levels off to a constant value. The concentration at which the transition occurs from a rapidly increasing trend to a constant value is roughly equal to the CMC value which confirms the conductivity measurements in the previous section. As mentioned, the further increase of concentration above the CMC value only results in the formation of more micelles and does not affect the adsorption.

Fig. 10 Surfactant Adsorption vs. Surfactant Concentrations without the Presence of Nanoparticles

Fig. 11 Surfactant Adsorption vs. Concentrations of Silica Nanoparticles

Surfactant adsorption at various concentrations of silica nanoparticles at the CMC value was measured as shown in Fig. 11. It is clear that adding nanoparticles controls the adsorption of the surfactant molecules on the rock surface. Optimum nanoparticles concentration occurs at 1000 ppm which decreases the absorption for 13.62 %. SDS is an anionic surfactant and in water solutions generates the sulfate negative ions (SO_4^{2-}). On the other hand, applied silica nanoparticles is hydrophilic type and in water solutions generate the hydrogen positive ions (H^+) which increases the tendency of the silanol groups to establish the hydrogen bonds. Thus when nanoparticles added to the surfactant solution, surfactant negative ions and nanoparticles positive ions attached together by hydrogen bonds which prevents the ion exchange mechanism between surfactant molecules and rock and decreases the absorption.

4.3. Recovery Tests

In this section the effects of the application of surfactant solution with hydrophilic silica nanoparticles instead of normal surfactants on the oil recovery in the core scale under reservoir condition of 38 °C and 3000 psi were studied. 12.9 cm length and 3.8 cm diameter sandstone cores were prepared from the samples of an Iranian oil reservoir. The porosity range of the samples was 15-16 % and the permeability range was between 40 md and 60 md. After washing, drying the cores, and injection of the distilled water, dead oil was injected. Figure 12 shows the residual water in the

Fig. 12 Injection of Oil to Achieve Connate Water

Fig. 13 Recovery Curves for Different EOR Processes

core during the injection. Hence, the irreducible water saturation was measured to be equal to 24 %.

We injected different chemicals as the tertiary flooding after the initial waterflooding. In all the experiments, we stopped the initial waterflooding after the water breakthrough. For the chemicals, we used the optimum cases based on the experiments discussed in the previous section. Hence, we choose 2500 ppm and 1000 ppm for the concentration of surfactant and nanoparticles, respectively.

Three kinds of experiments were completed to study the effects of nanoparticles/surfactant flooding on the recovery. Figure 13 shows the recovery curves for different cases. During surfactant and surfactant/nanoparticles flooding cases, 0.6 pore volume of water was injected as the secondary recovery phase and then chemicals were injected as the tertiary recovery stage. Table 4 shows the recovery of oil for three cases. As shown, injection of nanoparticles/surfactant improves the efficiency of the chemical flooding and recovers 12.71 % more oil compared to the normal surfactant flooding which is a noticeable value. In fact, decrease of surfactant absorption on rock surface due to nanoparticles presence led to bridge of slug dilution. Hence, ability of surfactant slug for enhance oil recovery is maximum limit.

5. Conclusion

In this work, flooding performances of water, surfac-

Table 4 Experimental Results for Different EOR Processes

EOR Processes	Oil recovery [%]	SDS concentration [ppm]	Nano concentration [ppm]
Water flooding	71.40	0	0
SDS flooding	81.96	2500	0
Nano/SDS flooding	94.67	2500	1000

tant, and nanoparticles/surfactant injection as a new method were investigated.

The critical micelle concentration (CMC) of sodium dodecyl sulfate (SDS) in water increased as a function of temperature. Temperature disrupts the structured water around the hydrophobic groups and disfavors micellization which leads to the increase in CMC.

Also CMC increased when SDS solution exposed in contact with the crushed core due to the surfactant absorption on the rock surface which disfavors micellization.

The amount of surfactant adsorption raised sharply as the concentration increases then levels off due to the occurrence of the micellization. Our experiments showed that adding silica nanoparticles to the surfactant decreases the surfactant adsorption on the rock surface as more hydroxyl groups are formed and more hydrogen bonds are made with the surfactants molecules which controls the absorption.

Injection of nanoparticles/surfactant chemicals at the optimum concentration increases the oil recovery up to 94.67 % which is 12.71 % higher than the recovery achieved by the normal surfactant flooding. This occurs as the injection of nanoparticles reduces the adsorption of surfactant molecules for 13.62 % which enhances the performance of the chemical flooding.

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Nomenclatures

C_e	: surfactant concentrations after equilibrated with rock	[ppm]
C_i	: initial surfactant concentrations before equilibrated with rock	[ppm]
M_R	: total mass of the crushed rock	[g]
M_S	: mass of surfactant solution	[g]
wt%	: weight percent	[%]
<Greek>		
Γ	: amount absorbed	[mg/g]

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