Effects of Silica Nanoparticle after Modification with (3-Aminopropyl) Triethoxysilane and Its Combination with Surfactant for Enhanced Oil Recovery

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Abstract. Silica nanoparticle (SNP) shows exceptional characteristics and therefore attracts much attention in enhancing the oil recovery factor. However, it tends to agglomerate in the water phase due to the presence of tremendous surface free energy, which limits greatly application in oil fields. To this end, it is essential to perform the modification of the SNP surface to increase its dispersibility. In this work, (3-aminopropyl) triethoxysilane (KH550) was used to modify the SNP surface, and the structural characterization of the KH550-SNP was carried out using FT-IR and TGA. Then, a composite system (KH550-SNP/SDBS) was prepared by integrating negatively charged sodium dodecylbenzene sulfonate (SDBS) and positively charged KH550-SNP under the action of the electrostatic attraction force, and its interface properties and imbibition efficiency were further evaluated. The characterization results indicated that the modification process of the SNP surface by KH550 was successful. Besides, the interfacial tension (IFT) of the composite system (KH550-SNP: SDBS = 0.05%: 0.05%) was 0.6 mN/m and the water contact angle (CA) of the core slice treated with the composite system (KH550-SNP: SDBS = 0.05%: 0.01%) was 36.5° compared to the KH550-SNP of 15.1 mN/m and 42.6°, which stated that the composite system had better interface properties than the KH550-SNP. Finally, the imbibition recovery factors were 24.7% and 30.8% when the KH550-SNP and composite system (KH550-SNP: SDBS = 0.05%: 0.01%) was used.

1. Introduction

Although the continuous development of renewable energies, including solar energy, wind energy, and biomass energy, oil is still the most significant source of energy [1]. However, the conventional oil resource has been declining during the long-term exploration and development, and finding new oil fields is difficult at present [2, 3]. Therefore, many petroleum engineers pay attention to the unconventional oil resource, which refers to the oil resource that cannot be developed effectively using traditional technologies under current economic and technological conditions. It is preliminarily evaluated that the unconventional recoverable oil in the world accounts for 80% of the conventional oil.
[3]. A low permeability reservoir, an important component in the unconventional oil reserves, becomes a new exploration and development target. However, due to low porosity and poor permeability, multi-stage volume fracturing is an important technology to achieve economic production [4]. During water injection development after fracturing, the injected water not only effectively displaces the oil near the fracture of the water-wet reservoir, but also imbibes into the pores of the matrix system thanks to the strong capillary force, thus realizing an exchange of oil and water between the matrix and the fracture, which helps to reduce residual oil saturation of the matrix [5]. Nevertheless, most reservoirs have oil-wet or partial oil-wet characteristics as the result of the adsorption of acidic substances in the oil. Thus, the injected water cannot enter this reservoir under the action of the capillary resistance force, which difficultly exerts imbibition.

In recent years, silica nanoparticle (SNP) as a high-efficient chemical agent gradually becomes a research hotspot in the field of oil and gas field development, this is due to its outstanding characteristics of the small size, large specific surface area, high active surface, and special chemical reaction that can enter in the nanoscale pores and peel off the remaining oil in these pores, therefore playing an important role in enhanced oil recovery [6]. However, due to the presence of huge surface free energy and a large number of hydroxyl groups, SNP produces strong van der Waals force and chemical bond force with each other, making it tend to aggregate in the water phase and further form clusters with a larger size than the original SNP, which is easy to block the small and nanopores of rocks and thus unfavorable for the migration of SNP in reservoirs. Some researchers believe that the modification of the SNP surface is a better choice to solve these problems.

The SNP surface is usually modified using the chemical method, which refers to that the hydroxyl groups or unsaturated chemical bonds on the SNP surface undergo the condensation reaction with the functional groups (carboxylic acids, amines, maleimides, and alkynes) in the structure of modifier molecules, therefore achieving the purpose of functional modification of the SNP surface. The organofunctional trialkoxysilane molecules are widely used to modify the SNP surface [7]. The reaction mechanism of surface modification involves the hydrolysis of the alkoxy groups of silane to form silanol groups, followed by the condensation reaction between the silanol groups and SNP [8].

The literature has reported that the SNP combined with the surfactant has outstanding characteristics of improving interface activity and oil recovery factor [9]. Zhu et al. [10] performed an experimental study on the combination of SNP and nonionic surfactant (TX-100) to promote imbibition, they found that the combined system had better performances in altering wettability and increasing oil production than TX-100. However, there are few investigations on the combination of positively charged modified SNP and negatively charged sodium dodecylbenzene sulfonate (SDBS) to enhance the imbibition efficiency.

In this work, (3-aminopropyl) triethoxysilane (KH550) was used to modify the SNP surface. The structure characterization of KH550-SNP was performed using FT-IR and TGA. Then, the KH550-SNP was combined with SDBS under the action of the electrostatic attraction force to form a composite system, and its interface properties and imbibition efficiency were evaluated.

2. Experimental section

2.1. Materials
SNP (98.2%) in the form of white powder was provided by Shanghai Chemical reagent Co., Ltd. SDBS (99.8%), KH550 (98.5%), toluene (99.8 %), distilled water, and absolute alcohol (99.8%) were offered from Beijing science and technology development Co., Ltd. Aviation kerosene was purchased from Dalian Qingyi Petrochemical Co., Ltd.

| Ionic  | Concentration (mg/L) |
|--------|----------------------|
| K⁺⁺Na⁺ | 3064                 |
| Ca²⁺   | 77                   |
| Mg²⁺   | 50                   |
| Cl⁻    | 1602                 |
| SO₄²⁻  | 173                  |
| CO₃²⁻  | 900                  |
| HCO₃⁻  | 2134                 |

Table 1. The main ions of the formation water utilized in the test.
The formation water was collected from Chang 6 section in Yanchang Oilfield and its main ions were summarized in Table 1. The oil sample was prepared through the mixture of the oil of Yanchang Oilfield and aviation kerosene in a volume ratio of 1:1, and its viscosity and density were 3.25 cP and 0.89 g cm\(^{-3}\) at ambient temperature. The core plugs were offered from Chang 6 section in Yanchang Oilfield and its basic parameters were listed in Table 2.

Table 2. The basic parameters of core plugs used in the test.

| Core plug | Length (cm) | Diameter (cm) | Permeability (mD) | Porosity (%) |
|-----------|-------------|---------------|-------------------|--------------|
| B-1       | 7.35        | 2.58          | 15.45             | 18.14        |
| B-2       | 7.38        | 2.51          | 15.72             | 18.25        |
| B-3       | 7.29        | 2.54          | 15.38             | 18.32        |
| B-4       | 7.42        | 2.52          | 15.25             | 18.45        |
| B-5       | 7.37        | 2.51          | 18.32             | 18.37        |

2.2. Experimental methods

2.2.1. Surface modification of SNP. 4 mL of KH550 was placed in a glass beaker containing 100 mL of distilled water and 2mL of absolute alcohol. To ensure complete dissolution, the mixture was stirred using a glass rod and then stirred using a magnetic stirrer for 5 min at 30°C. The desired amount of SNP was added to the solution and the stirring was continued to perform for almost 30 min at 25°C. After that, the dispersed solution was sonicated using an ultrasonic homogenizer for 3 h to further hinder the aggregation of adjacent SNP. When the ultrasonic treatment was completed, the dispersed solution was cooled to 25°C and centrifuged at 3000 pm for 25 min to collect KH550-SNP following by washing with an excess of absolute alcohol. The mechanism proposed for the modification process of the SNP surface is given in Figure 1.

Figure 1. The mechanism for the modification of the SNP surface with KH550.

2.2.2. Fourier-transform infrared (FTIR) analysis. Fourier transforms infrared (FTIR) analysis was carried out to confirm the presence of KH550 on the SNP surface. FTIR analyses were performed using a Fourier transform infrared spectrometer with a resolution of around 0.9 cm\(^{-1}\) and a scanning range of
The spectra of KH550-SNP was recorded after making a piece by mixing it with potassium bromide.

2.2.3. Thermogravimetric analysis (TGA). Thermogravimetric analysis (TGA) of KH550-SNP was performed using a TA instrument. The test conditions were consistent with those reported by Khurana et al [7].

2.2.4. Interface tension (IFT) measurement. The test tube was filled with prepared KH550-SNP solution, and a drop of the oil sample was injected into the middle of the test tube. At ambient temperature, the IFT of KH550-SNP was measured using a rotating drop ultra-low interfacial tension meter at a rotating speed of 6000 r/min.

2.2.5. Wettability test. Before the test, the core slice was obtained by cutting the core plug and then washed with the mixture of toluene and absolute alcohol at a volume ratio of 1:2 in a self-made instrument. To achieve wettability alteration toward an oil-wet condition, the washed core slice was aged in the oil sample for almost 7 days at 40°C. After that, the oil-wet core slice and core support were placed into a glass container and then filled the space around the core slice inside the glass container with the required volume of KH550-SNP solution. Following that, a drop of the oil sample was injected by using a curved needle and stuck to the bottom of the core slice, and then the contact angle (CA) was measured by the sessile drop method [11].

2.2.6. Imbibition test. To saturate the core plug with the oil sample using the vacuum saturation method. First, the core plug was placed in a suction filter bottle connected with a vacuum pump to remove the gas in the core plug. The suction filter bottle was then filled with the oil sample and continued to vacuum [12]. After that, the obtained oil-saturated core plug and KH550-SNP solution were placed into an Amott bottle, which stands in a thermostat water bath at ambient temperature for 15 days. Finally, the volume of the oil discharged from the oil-saturated core plug was read at regular intervals.

3. Results and discussion

3.1. Characterization studies

FTIR technique is used to study the new functional groups caused by the reaction of KH550 with SNP. It can be seen from Figure 2 (A) that the wide absorption peak at around 3428 cm\(^{-1}\) is the stretching vibration of hydroxyl groups on the SNP surface. Furthermore, the significant absorption peak at 1106 cm\(^{-1}\) presents the Si-O stretching vibration. However, in the spectra of KH550-SNP, the absorption peak of hydroxyl groups is found to become weak, indicating that hydroxyl groups on the SNP surface undergo the condensation reaction with KH550 and thus be consumed. Besides, it is observed the newborn absorption peaks at 2934, 2838, 1657, 1438, 1181, and 1062 cm\(^{-1}\), which are attributed to the stretching vibration of C-H bonding in methylene and methyl-functional groups, the bending vibration of N-H bonding in the amino-functional group, the bending vibration of the methylene-functional group, and the stretching vibration of C-N bonding. Thus, it is confirmed that KH550 molecules were grafted on the SNP surface.
In Figure 2 (B), it is found that the SNP has one thermogravimetric stage, while the KH550-SNP has two thermogravimetric stages. The weight loss between 30°C to 200°C is caused by the physical adsorption of water molecules on the SNP surface. The weight of SNP losses 4.2%, and that of KH550-SNP losses 3.1%, this is because the hydroxyl groups on the SNP surface are replaced by the organic groups, which makes the amount of adsorbed water molecules reduce. When the temperature up to 780°C, the SNP undergoes the dehydroxylation of silanol groups, and thus the final weight loss is 2.7%. However, the weight loss of KH550-SNP up to 5.4% thanks to both the dehydroxylation of silanol groups and the decomposition of organic groups in the KH550 molecules, indicating that the modification process of the SNP surface is successful.

3.2. IFT investigation

The IFT is an important parameter to investigate the imbibition performance of the fluid. In this work, the KH550-SNP are compounded with different concentrations of SDBS to establish the KH550-SNP/SDBS systems. Through the comparative analysis method, the concentration of KH550-SNP in the composite system is fixed at 0.05%, the performances of reducing IFT of KH550-SNP and KH550-SNP/SDBS are systematically evaluated.

Fig. 3 illustrated the dynamic IFTs of KH550-SNP and KH550-SNP/SDBS. For KH550-SNP, the IFT is hardly changed with time, and the equilibrium IFT is measured to be 15.1 mN/m. This is due to the presence of a large number of hydrophilic groups that enable KH550-SNP to disperse in the formation water rather than adsorb on the oil-water interface, therefore hardly reducing IFT [13]. When KH550-SNP/SDBS is used, the variation trend for the IFT curve of KH550-SNP/SDBS is similar to that of KH550-SNP. However, the equilibrium IFT of the KH550-SNP/SDBS is lower than that of KH550-SNP. The reason is that the adsorption of negatively charged SDBS on the surface of positively charged KH550-SNP under the action of electrostatic attraction in the formation water provides a partially hydrophobic character to KH550-SNP surface, which can adsorb effectively on the oil-water interface and finally reduce the IFT. Furthermore, it is noticed that the increase of SDBS concentration leads to the IFT reduction, this is attributed to the fact that the charge density of KH550-SNP decreases with the increase of SDBS concentration so that KH550-SNP adsorbed on the interface can be arranged tightly, thus forming a high-strength interface film. As a result, the IFT is found to significantly reduce. However, if the concentration of SDBS is increased further, the formation of the double adsorption layer makes KH550-SNP hydrophilic again, which is unfavorable to the IFT reduction [14].
3.3. Wettability analysis

The influence of KH550-SNP and KH550-SNP/SDBS on the wettability of the oleophilic rock surface is investigated by measuring contact angle (CA) at ambient conditions. It is well known that when the water CA is measured to be lower than 75°, the rock has a water-wet surface. If the water CA is in the range of 75° and 105°, the rock has an intermediate-wet surface. The water CA for the oil-wet rock is greater than 105°.

The water CAs of the oleophilic core slices treated with the solution of KH550-SNP and KH550-SNP/SDBS with time are shown in Figure 4. It can be seen from this figure that the five curves display a similar behavior: the CAs reduce at the initial stage and slowly lower at the intermediate stage and finally reach equilibrium values at the end of the test. Besides, it is observed that there are significant differences among the equilibrium CAs of KH550-SNP and KH550-SNP/SDBS. For KH550-SNP, the equilibrium CA is 42.6°, indicating that the oil-wet surface of the core slice is reversed to the water-wet surface. This is because the acidic components adsorbed on the surface of the core slice are negatively charged and KH550-SNP are positively charged. Therefore, KH550-SNP can firmly adsorb on the core slice surface, and its hydrophilic groups turn the core slice surface to water-wet.

However, when SDBS concentration in the composite system is lower than 0.05%, SDBS cannot absorb completely on the KH550-SNP surface, leading to the KH550-SNP surface exist original hydrophilic groups with positively charged whose produce the strong electrostatic adsorption action with the negatively charged core slice surface. Accordingly, the water CA is still low. With the increase of SDBS concentration, the increase of hydrophobic groups for KH550-SNP can rapidly adsorb the organic active components on the core slice surface, meanwhile, the decrease of hydrophilic groups for KH550-SNP turns the core slice surface to the weak water wetness or oil wetness. When SDBS
concentration is further increased, the double adsorption layer forms and thus makes KH550-SNP hydrophilic again, finally reducing the water CA.

### 3.4. Imbibition performance

Figure 5 shows the imbibition oil recovery factor of KH550-SNP and KH550-SNP/SDBS at ambient temperature. It can be seen from this figure that the five curves display a similar behavior: the oil recovery factor increases rapidly at the initial stage then increases slightly at the middle stage and reaches an equilibrium value at the end of the test. Furthermore, by comparing the equilibrium oil recovery factors of KH550-SNP and KH550-SNP/SDBS, it is found that the oil recovery factor obtains a maximum value of 30.8% when the concentration of SDBS in the complex system is 0.01%, this is attributed to the fact that the water CA is 36.5°, indicating that the wettability of the core slice is changed toward strong water wetness and therefore promote the imbibition. Besides, a low IFT of 4.8 mN/m can reduce the adhesion work between the oil and core slice surface, which makes the oil film more effortless to remove from the surface of the core slice and thus achieves more water-wetness, eventually improving the oil recovery factor.

![Figure 5. The oil recovery factor of KH550-SNP and KH550-SNP/SDBS with time.](image)

### 4. Conclusions

In this work, the SNP surface was surface modified with a certain amount of KH550, and the structural characterization of KH550-SNP was performed using relative techniques. The characterization result indicated the presence of new chemical functional groups on the KH550-SNP surface. Then, KH550-SNP/SDBS was prepared by integrating negatively charged SDBS and positively charged KH550-SNP under the action of the electrostatic attraction force, and their interface properties and imbibition efficiency were evaluated. The obtained results stated that KH550-SNP/SDBS had a better performance in reducing IFT than KH550-SNP. The equilibrium water CA of the oleophilic core slice treated with the composite system (KH550-SNP: SDBS = 0.05%: 0.01%) was 36.5°, which was lower than that treated with the KH550-SNP. The imbibition recovery factor of KH550-SNP was 24.7%, while that of the composite system (KH550-SNP: SDBS = 0.05%: 0.01%) was 30.8%.

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