Design and screening of synergistic blends of SiO$_2$ nanoparticles and surfactants for enhanced oil recovery in high-temperature reservoirs

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Received 7 January 2011
Accepted for publication 24 June 2011
Published 21 July 2011
Online at stacks.iop.org/ANSN/2/035013

Abstract
SiO$_2$ nanoparticles (NPs) were synthesized by the sol–gel method in an ultrasound reactor and monodispersed NPs with an average particle size of 10–12 nm were obtained. The synergy occurring in blending NPs and anionic surfactant solutions was identified by ultra-low interfacial tension (IFT) reduction measured by a spinning drop tensiometer (Temco 500). The oil displacement efficiency of the synergistic blends and surfactant solutions at Dragon South-East (DSE) reservoir temperature was evaluated using contact angle measurement (Dataphysics OCA 20). It was found that SiO$_2$/surfactant synergistic blends displace oil as well as their original surfactant solutions at the same 1000 ppm total concentration. Abundant slag appearing in the SiO$_2$/surfactant medium during oil displacement could be attributed to an adsorption of surfactants onto the NPs. The results indicate that at a concentration of 1000 ppm in total, the original surfactant SS16-47A and its blend with SiO$_2$ NPs in the ratio of 8 : 2 exhibited an IFT reduction as high as fourfold of the IFT recorded for the DSE oil–brine interface and very high speed of oil displacement. Therefore, it could potentially be applicable to enhanced oil recovery (EOR) in high-temperature reservoirs with high hardness-injection-brine, like the one at DSE. This opens up a new direction for developing effective EOR compositions, which require less surfactant and are environmentally safer.

Keywords: SiO$_2$ nanoparticles, surfactant, interfacial tension, enhanced oil recovery

Classification numbers: 2.03, 4.02

1. Introduction
The capability of SiO$_2$ nanoparticles (NPs) to alter the wettability of reservoir rock and reduce the interfacial tension (IFT) between crude oil and brine phases has recently been actively investigated to find implementation in enhanced oil recovery (EOR). It was thought by Ju *et al* [1, 2] that during NP transport in porous media, there is a mass exchange between the NPs on the pore framework and the NPs in fluids by adhering to pore walls, detaching from pore walls and blocking pore throats. In addition, the accumulation of NPs on pore walls will change the wettability of pore surfaces, as explained by Wang [3]. Di *et al* [4] have proposed the pressure drop mechanism of enhancing water injection technology with hydrophobic SiO$_2$ NPs. In 2010, Onyekonwu *et al* [5] performed the injection of blends with all SiO$_2$ NPs lipohydrophilic, hydrolipohilic and medium wet; Skauge *et al* [6] injected SiO$_2$ NPs blending with polymer solution, a blend of polymer NPs, into the sandstone core models for investigating the efficiency of oil displacement. These authors obtained quite interesting results. However, all tests were conducted in ambient temperature conditions.
The effects of NPs in spreading nanofluids, dynamically wetting and dewetting solid substrates and proposed mechanisms to interpret this behavior have been discussed by Seifane et al [7]. The observed synergistic effect of silica NPs with nonionic and/or cationic surfactants in the formation and stabilization of submicron oil-in-water dispersions was attributed to the adsorption of surfactant on solid particles, resulting in a change in particle wettability [8]. Although the effects of NPs, or in combination with surfactants, on reducing the surface forces, resulting in the alteration of the dynamic wettability of solid substrates and the oil–water IFT, have been investigated, this has predominantly been directed towards emulsion stabilization [9–12]. Recently, Hung et al [13] have announced that NPs can be used for the formation of fine fixation and in improving the performance of surfactant structure fluids during propane treatment.

Enhanced oil recovery is always an important direction for the oil and gas industry worldwide, especially now when fossil energy resources have become much more expensive for production and discovery. In addition to the results obtained from the work on the effects of NPs and surfactants in emulsion stabilization, and the transportation of nanofluids in porous media, further systematic studies are needed to fully understand the interaction of phases existing in the reservoir medium in order to find potential application in oilfields.

In South-East Asia, a large amount of crude oil is produced from offshore fractured granite-diorite basement reservoirs. This kind of reservoir is characterized by the heterogeneous porosity and permeability of the reservoir rock matrix. There are also extreme conditions often accompanied by high temperatures in reservoirs, high salinity and high levels of hardness in sea water. After the initial period of crude oil production, where oil produced by its own energy has been exhausted, water flooding is generally applied to maintain downhole pressure. This is the cheapest and most readily available technology but it is not very effective in producing highly viscous crude oil, like the Dragon South-East (DSE). Besides having the common feature of South-East Asian offshore fractured granite-diorite basement reservoirs, DSE crude oil also has high resin and asphaltene content, which causes its viscosity to be much higher compared with other paraffinic crude oil in this area. The highly viscous oil film sticks to the walls of micro channels in the matrix and produces oil-wet rock surfaces, while the difference of about five times in viscosity of crude oil and brine (1.969 mPa s versus 0.308 mPa s accordingly) under reservoir conditions makes water channeling a problem and results in poor sweep efficiency. These phenomena allow a large part of the crude oil to remain trapped and unswept from the reservoir. Continuing our series of investigating surfactant injection for EOR in the DSE basement reservoir, our aim is to investigate the effects of SiO₂ NPs and their mixtures with surfactants on the capacity of reducing the crude oil-brine IFT and altering reservoir rock surface wetting behaviors, the two most prominent factors affecting the effectiveness of oil displacement. We have found very promising results in the obvious synergy, appearing in blending SiO₂ and specific surfactants with high hydrophobic tails, causing IFT reduction to ultra-low values. Further testing showed that some of these blends were quite thermo stable and adsorbed less onto the reservoir rock surface.

Table 1. Main characteristics of DSE brine.

| Ion         | Cl⁻ | SO₄²⁻ | HCO₃⁻ | Ca²⁺ | Mg²⁺ | [Na⁺K⁺] |
|-------------|-----|-------|-------|------|------|---------|
| Content (g l⁻¹) | 19.0 | 2.6   | 0.12  | 0.4  | 1.2  | 11.1    |
| pH = 9, salinity = 3.44% |

Table 2. Main characteristics of DSE fluids.

| Parameters          | Value |
|---------------------|-------|
| Saturation pressure (MPa) | 6.87  |
| Gas content (m⁻³ T⁻¹)    | 50.6  |
| Volume coefficient     | 1.17  |
| Density of crude oil (kg m⁻³) | 851.1 |
| Separated              |       |
| In reservoir           | 769.4 |
| Viscosity (mPa s)      |       |
| Crude oil in reservoir | 1.969 |
| Brine in reservoir     | 0.308 |
| Total resin-asphaltene content (wt%) | 14.15 |

In this work, the synthesis of SiO₂ NPs by the sol–gel method was performed under ultrasound irradiation and then the particle size was determined. Evaluation on the alteration of DSE reservoir rock-crude oil contact angle and the oil displacement efficiency caused by the selected synergistic blends from the previous work and accorded surfactant solution plugging was performed using the pendant drop mode of the contact angle measurement (Dataphysics OCA 20).

2. Experimental

2.1. Materials

Double deionized water was used for the preparation of NP and encapsulation. Tetraethoxysilane (TEOS) with 99% purity, ammonium hydroxide with 25% NH₃ purchased from Merck (Germany), absolute ethanol with 99.5% EtOH obtained from Chem Cop (Vietnam), reservoir rock-diorite quartz, brine (table 1) and crude oil (table 2) from the DSE oilfield were supplied by Vietsovpetro JV, Vung Tau, Vietnam. Surfactants (table 3) were generously donated by Oil Chem, USA, except for IAMS-M2-P. A specially developed surfactant system for the DSE’ EOR project was prepared by our laboratory, IAMS.

2.2. Procedures

2.2.1. Synthesis of SiO₂NPs. SiO₂NPs were synthesized using a standard procedure [14] according to the experimental conditions shown in table 4. A quantity of 5 ml TEOS was first dissolved in 30 ml of absolute ethanol at room temperature for 10 min in an ultrasound reactor at different frequencies (30, 40 and 42 kHz). Then 1 ml of distilled water was dropped into the reaction medium with a feed rate of 0.2 ml min⁻¹ to facilitate hydrolysis of TEOS in ultrasonic radiation. After 1.5 h, 2 ml of ammonia (catalyst) was fed into the reaction mixture at a feed rate of 0.02 ml min⁻¹. Sonication was continued for 3 h. Gelation was allowed for 1 h. The gel was centrifuged and washed with ethanol and distilled water (3 × 7 min, 3500 rpm). Drying was carried out using either a conventional oven at 100 °C for 24 h or under reduced pressure at 70 °C for 24 h.
Table 3. Surfactants used in the experiments.

| No. | Structure | Abbreviation | MW | Origin   |
|-----|-----------|--------------|----|----------|
| 1   | XSA-1416D | CH₃C₁₄₋₁₆SO₃H | 738 | Oil-Chem |
| 2   | 16-47A    | CH₃(CH₂)xCH(CH₂)yCH₂O(PO)m(EO)nCH₂COOM | 1125 | Oil-Chem |
| 3   | IAMS-M2-P | AOS(C₁₄₋₁₆) | ≈390 | IAMS, VN |

Table 4. Experimental parameters for SiO₂ NP preparation.

| Parameters | Value |
|------------|-------|
| TEOS (mol l⁻¹) | 0.58  |
| NH₃ (mol l⁻¹)  | 0.6   |
| H₂O/TEOS      | 28.8  |
| Feed rate (ml min⁻¹) | 0.02 |
| Temperature (°C) | 30   |
| Reaction time (h) | 5.7  |
| Frequency (kHz)  | 30, 40 and 428 |

2.2.2. Blend of NPs and surfactant solutions. Stock solutions of 10 wt% surfactant on an active basis were prepared. The stock solutions were diluted with DSE brine to obtain surfactant solutions of 1000 ppm. The calculated amount of SiO₂ NPs to get a 1000 ppm solution was added to the brine and stirred magnetically to keep the material dispersed for 2 h. Various ratios of surfactant to NPs were prepared for further studies to determine the optimum ratios to give the best synergistic interaction.

2.2.3. Screening of the oil displacement efficiency. Slices of DSE reservoir rock (cut from a DSE core) with dimensions of 2 × 1 × 0.2 cm were polished with sandpaper of 100, 400 and 1000 mesh (particle size of 62, 35 and 18.3 μm), in turn, and then aged in DSE crude oil at 91 °C for 48 h to generate saturated crude oil, sinking down the crude oil saturated rock slice in brine at 91 °C until no more oil drops came up. We noted the oil displacement capacity in brine, then performed new tests with the blends of SiO₂ NPs/surfactant or surfactant solutions, using a high resolution electronic camera to capture the images of oil drops being displaced from the rock slice surface versus time, making a comparison of the oil displacement efficiency caused by the screened fluids.

Based on the synergy, thermo stability and adsorption capacity exhibited in our previous work, the blends in table 5 were selected and prepared in a total concentration of 1000 ppm.

Table 5. Selected blends used in oil displacement efficiency evaluation.

| No. | NPs Surfactant Ratio | IFT (dyne cm⁻¹) |
|-----|----------------------|-----------------|
| 1   | Brine                | 24              |
| 2   | SiO₂                 | 10 : 00 12      |
| 3   | SiO₂                 | 0 : 10 0.079    |
| 4   | SiO₂                 | 4 : 06 0.019    |
| 5   | SiO₂                 | 2 : 08 0.004    |
| 6   | SiO₂                 | 0 : 10 0.196    |

2.3. Characterization of obtained compounds

2.3.1. Characterization of SiO₂ NPs. The size and morphology of SiO₂ NPs were recorded by transmission electron microscopy (TEM, JEM 1010) operating at an acceleration voltage of 80 kV.

2.3.2. Interfacial characterization. IFT measurements were carried out with a spinning drop tensiometer (Temco 500) using spinning drop mode. Dynamic tracking of the drop widths as a function of spinning speed was employed until equilibrium, after which the value was recorded and IFT calculated. Crude oil–water IFT was measured at 60 °C by forming a drop of the crude oil injected into a glass tube filled with the aqueous phase (brine, or with different concentrations of surfactant and/or SiO₂ NPs). Measurements were performed at constant rpm and repeated three times for each sample. The mean values of the IFT at equilibrium are reported. The phases were pre-equilibrated before the measurements and equilibrium times were determined to be in the range 15–45 min.

2.3.3. Oil displacement characterization. The oil drops being displaced from the rock surface were observed and
Figure 1. TEM pictures of SiO₂NPs: (a) 30 kHz, (b) 40 kHz and (c) 42 kHz.

Figure 2. Oil displacement in brine.

characterized from images captured by an electronic camera of the contact angle measurement (Dataphysics OCA 20). The measurement of the contact angle alteration was performed in pendant mode on this equipment. The post wetting contact angle was measured to achieve higher accuracy.

3. Results and discussion

3.1. Synthesis of SiO₂NPs

SiO₂NPs were synthesized via the sol–gel method in an ultrasound reactor at frequencies of 30, 40 and 42 kHz. From the TEM pictures in figure 1, the size of particles was estimated to be about 35, 25 and 10–12 nm, respectively. It is noticeable that the size of the particles produced depends strongly on the ultrasound frequency. The fine NPs (10–12 nm) obtained under the ultrasound frequency of 42 kHz were used for further treatments.

3.2. Screening the oil displacement efficiency of selected synergistic blends and accorded surfactant solutions

3.2.1. In brine. We can see in figure 2 that due to the high viscosity of DSE crude oil, brine was not able to displace the oil, even after 45 min at 91°C.

3.2.2. In a blend of 1000 ppm SiO₂NPs. As seen in figure 3, in the SiO₂NPs medium, crude oil became more active; after 18 min some oil drops came up, and after 60 min there was no more detachment.

3.2.3. In a solution of 1000 ppm XSA-1416D. As seen in figure 4, initially, oil drops flowed up quickly; after 30 min, oil was continuously displaced but at a slightly lower rate, and after 1 h, oil drops still came up but at a lower rate.

3.2.4. In a blend of 600 ppm XSA 1416D and 400 ppm SiO₂NPs. As seen in figure 5, initially, oil drops flowed up much stronger compared with the solution of 1000 ppm XSA-1416D; after 30 min, oil was continuously displaced but a bit slower, and after 1 h, almost no more oil became detached. A synergy of NPs and surfactant at the optimum ratio was clearly observed. The appearance of slag was seemingly due to the absorption of surfactant onto NPs, and the high salinity of the brine was able to accelerate this situation.

3.2.5. In a solution of 1000 ppm SS16-47A. As we have learned from the previous work, SS16-47A has very high surface activity and can reduce the DSE oil–brine IFT to a very low value (10⁻² dyne cm⁻¹) so it should displace oil very well.

As observed from the images in figure 6, in the initial 5 min, oil drops flowed up very fast; after 30 min, oil was continuously displaced, and after 1 h, oil still came up but at a lower rate.
3.2.6. In a blend of 800 ppm SS16-47A and 200 ppm SiO$_2$NPs. Compared with the oil displacement in the solution of 1000 ppm surfactant, we can see in figure 7 how quickly the oil drops flowed up initially; after 30 min, oil was still continuously displaced at a slightly lower rate; after 1 h, almost no oil drops became detached. By observation,
the oil displacement by the synergistic blend was probably weaker, and the duration was not as long as that of the original surfactant solution.

3.2.7. In a medium of 1000 ppm IAMS-M2-P. As seen in figure 8, in the initial 5 min, oil drops flowed up fairly quickly; after 30 min, oil was being continuously displaced but at a lower rate, and after 1 h, almost no more oil became detached.

The oil displacement efficiency of the screened blends can be assumed to be in the order

\[
1000 \text{ ppm SS16-47A} > (800 \text{ ppm SS16-47A} + 200 \text{ ppm NPs})
\]

\[
= 1000 \text{ ppm XSA-1416D} > (600 \text{ ppm XSA-1416D} + 400 \text{ ppm NPs})
\]

\[
> 1000 \text{ ppm IAMS-M2-P} \gg 1000 \text{ ppm NPs} > \text{brine}.
\]

The oil displacement testing in this work occurred in statistical mode, so to meet the reservoir conditions these blends had to be injected into the DSE core model. This will help us in learning how blends of NPs and surfactants behave in hydrodynamic conditions in fractured granite-diorite reservoirs, and whether the slag of adsorbed surfactants onto NPs will dissolve or precipitate and disturb the oil displacement. Nevertheless, based on the obtained results of the extremely high IFT reduction and improvement of oil displacement caused by the blends of SiO$_2$NPs and surfactants, we can say that a new direction is opened up for the development of highly effective and environmentally safer compositions for EOR injection.

4. Conclusion

SiO$_2$NPs with sizes of 10–12 nm were synthesized by the sol–gel method and in an ultrasound reactor at a frequency of 42 kHz. Strong synergy appeared in the blends, with just 1000 ppm in total concentration of NPs and surfactants, and the DSE crude oil–brine IFTs were reduced to ultra-low values. The synergistic blends of SiO$_2$NPs and SS16-47A, XSA-1416D have displaced oil as well as their original surfactant solutions. The blends of SiO$_2$NPs and SS16-47A show great potential in EOR application because of their resistance to adsorption onto the rock surface and thermostability at 91 °C, extremely good in crude oil–brine IFT reduction and very high oil displacement efficiency.

References

[1] Ju B, Fan T and Ma M 2006 China Particuol. 4 41
[2] Ju B and Fan T 2009 Powder Technol. 192 195
[3] Wang H-W 2007 Diffus. Defect Data-Solid State Data B: Solid State Phenomen 121–123 1497
[4] Di Q, Gu C, Shi L and Fang H 2007 Drilling Prod. Technol. 207 91
[5] Onyekonwu M O and Ogolo N A 2010 OnePetro (SPE papers+) Oklahoma, USA, SPE paper 140744-MS
[6] Skauge T, Spildo K and Skauge A 2010 OnePetro (SPE papers+) Oklahoma, USA, SPE paper 129933-MS
[7] Seifane K, Skilling J and MacGillivray J 2008 Adv. Colloid Interface Sci. 138 101
[8] Hunter T N, Pugh R J, Frank G V and Jameson G J 2008 Adv. Colloid Interface Sci. 137 57
[9] Zhu H and Yan X 2005 Faming Zhuanli Shenqing Gongkai Shuomingshu CN 1696240 A 20051116
[10] Bink B P and Whitby C P 2005 Colloids Surf. A 253 105
[11] Zhang T, Davidson A, Bryant S L and Huh C 2010 OnePetro (SPE papers+) Oklahoma, USA, SPE paper 129885-MS
[12] Espinosa D, Caldelas F, Johnston K, Bryant S L and Huh C 2010 OnePetro (SPE papers+) Oklahoma, USA, SPE paper 129925-MS
[13] Huang T, Crews J B and Willingham J R 2008 OnePetro (SPE papers+) Oklahoma, USA, IPCT 12414-MS
[14] Khimich N N, Zvyagil’skaya Yu V, Zhukov A N and Usyarov O G 2003 Zh. Prikl. Khim. 76 875
Khimich N N, Zvyagil’skaya Yu V, Zhukov A N and Usyarov O G 2003 Russ. J. Appl. Chem. (Engl. Transl.) 76 875