Functional Nanoparticle-Augmented Surfactant Fluid for Enhanced Oil Recovery in Williston Basin

Quarterly Status Report
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Summary of Current Progress

During the past quarter, our primary goals were to synthesize, evaluate and characterize modified silica nanoparticles. Specifically, we tested the performance of the synthesized silica nanoparticles at high salinity brine, and carried out spontaneous imbibition experiments. The adsorption of commercial nanoparticle-surfactant hybrid was also evaluated.

We mainly focused on the following tasks:

1) Synthesis of silica nanoparticles modified with amino groups
2) Characterizations of the synthesized silica nanoparticles using
   a.) SEM for morphology
   b.) DLS for size and zeta potential distribution in distilled water
3) Performances of silica nanofluid at high salinity brine
   a.) Interfacial tension
   b.) Contact angle
4) Spontaneous imbibition test
   a.) In 15wt% NaCl brine
   b.) In silica nanofluid
5) Evaluation and optimization of the nanoparticle-surfactant hybrid for EOR
   a.) emulsification tendency
   b.) adsorption isotherms

Below are the detailed results on the tasks.

1. Synthesis of silica nanoparticles modified with amino groups

1.1 Introduction

The silica nanoparticles were synthesized using the reverse microemulsion method with APTES (3-minopropyltriethoxysilane) modification.

1.2 Summary

The silica nanoparticles modified with amino groups were synthesized in our lab. Figure 1 showed the structures of main chemical agents used in the synthesis procedures. Three chemicals, 7.5 ml of cyclohexane, 1.8 ml of 1-hexanol and 1.77 ml of Triton™X-100, were placed in a 30 ml bottle under magnetic stirring at 990 rpm (the following experiments used the same speed). After 20 min stirring, 480 μl of H_2O was added into the bottle and stirred for 20 min. Then, 100 μl of TEOS (Tetraethyl Orthosilicate, regent grade,98%) was added and stirred for 20 min. Finally, 100 μl of $NH_3.H_2O$ was added as a catalyst for hydrolysis of TEOS. The silica nanoparticles were formed after 24 h stirring.

The modification of the nanoparticles were carried out in following steps. 100 μl of TEOS was added in the bottle. After 30 min stirring, 20μl of APTES was added. The amino groups from APTES will coat the meshed Si-O of silica nanoparticles. After 4 h stirring, the reaction was stopped by adding 15 ml of acetone. After 10 min washing, the solution was centrifuged at 8,000 rpm for 15 min. Then, 3 times washing with 15 ml ethanol and 15 ml deionized water were performed respectively.
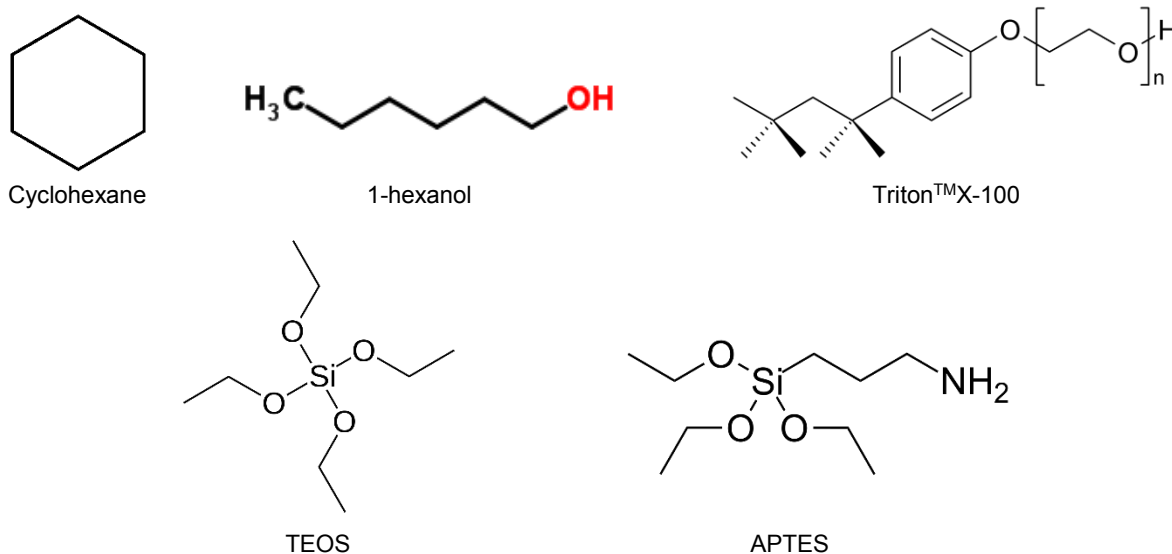

Figure 1 Structures of main chemicals used in the synthesis of silica nanoparticles

2. Characterizations of the synthesized silica nanoparticles

2.1 Introduction

The morphology of the synthesized modified silica nanoparticles was characterized using SEM (Scanning electron microscope, Hitachi). DLS (dynamic light scattering) for size and zeta potential distribution in distilled water were conducted using Zetasizer Nano Series, Malvern, U.K.

2.2 Summary

Figure 2 showed the SEM image of the synthesized silica nanoparticles modified with amino groups. The nanoparticles were generally spherical shape, and their size was approximately 50±2.1 nm.
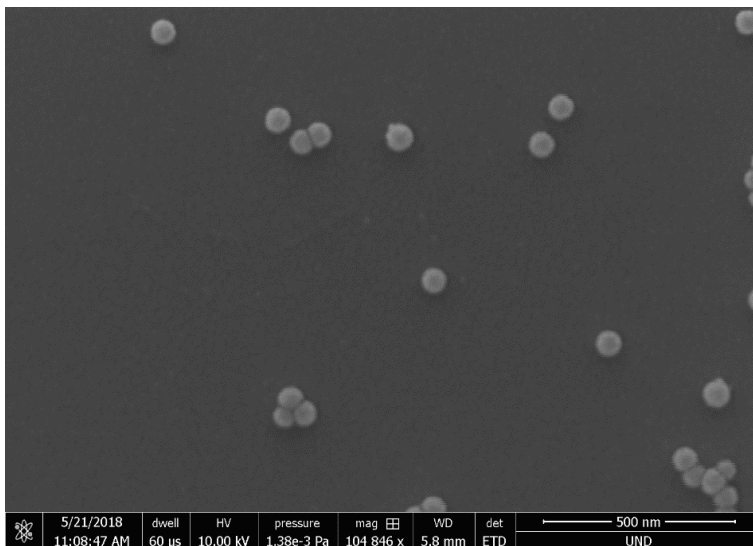
Figure 2 SEM image of the silica nanoparticles modified with amino groups
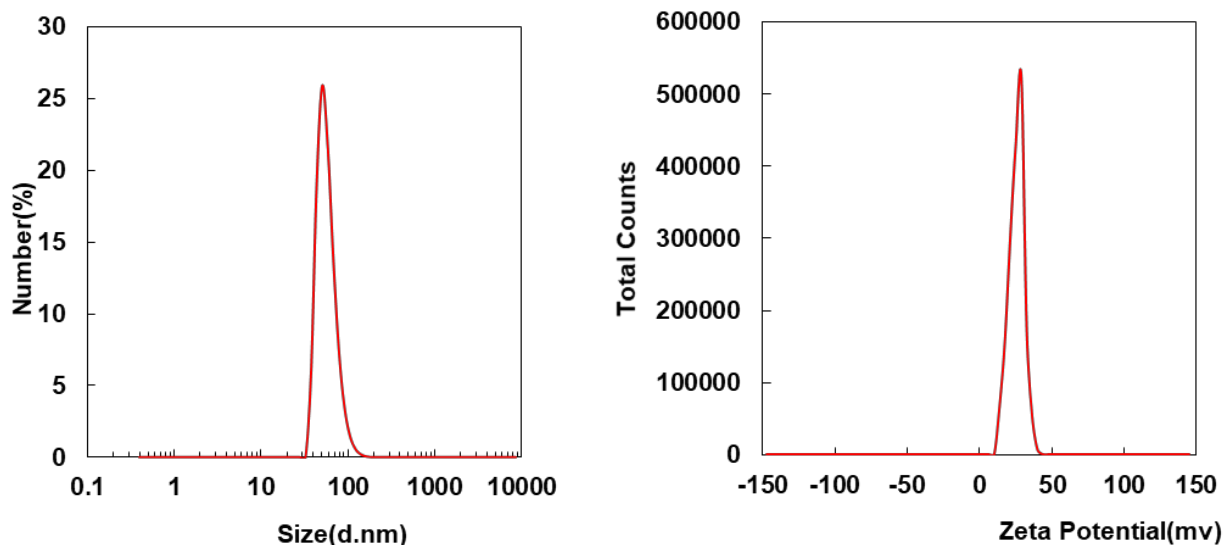

Figure 3. DLS for size (left) and zeta potential (right) distribution of silica nanoparticles modified with amino groups

Figure 3 showed the DLS (dynamic light scattering) for size and zeta potential distribution of the silica nanoparticles modified with amino groups in distilled water. The hydrodynamic diameter

distribution of particle size was narrow between 40-60 nm. The zeta potential was between 28-32 mV which indicated the surface of silica nanoparticles was positive charge. This proved the amino groups have been linked on silica nanoparticle surface.

3. Performances of silica nanofluid at high salinity brine

3.1 Introduction

The performance of modified silica nanoparticles dispersed in 15 wt% NaCl brine (called silica nanofluid) were tested, including interfacial tension and contact angle. The experiments were carried out using Pendent Drop Interfacial Tension and Contact Angle Cell MODEL (ramé-hart instrument co., 19 Route 10 East, Suite 11 Succasunna, NJ, USA).

3.2 Summary and Discussion

Low oil-water interfacial tension is conductive to enhance oil recovery (EOR). The oil–water interfacial tension of silica nanofluid with different molar concentrations of silica nanoparticle at 65℃ were measured (Table 1). The oil-water interfacial tension decreased with increasing molar concentration of nanoparticles. The nanofluid could reduce the oil-water interfacial tension to 0.36 mN/m. Comparing to 15 wt% NaCl brine (the molar concentration being 0 mol), the modified silica nanoparticles had a strong ability to reduce the oil –water interfacial tension.

Table 1. Oil-water Interfacial Tension of Different Concentration of Nanolfuid at 65℃

Concentration of modified silica nanoparticles (μmol/L)	0	1	2	3	4	5	6	7	8	9	10
Oil-water interfacial tension of silica nanofluid (mN/m)	13.78	7.30	3.88	2.06	1.21	0.81	0.66	0.57	0.49	0.42	0.36

Wettability is an important parameter in EOR process. There are many methods to evaluate the wettability. Contact angle is a very common quantitative method for this purpose. As we know, water-wet is beneficial for EOR. It is necessary to test contact angle among rock samples, oil and nanofluid. The Berea sample slices were prepared with a diameter of ∼0.5 cm and length of ∼0.1 cm for testing contact angle. Before contact angle testing, these sample slices were immersed in Baken oil at 80℃ for 10 days to make sure the rock surface was oil-wet. The oil droplets were captured on the oil-wet surface of Berea sample slices at 65℃. Then the contact angle can be measured. Figure 4 and Figure 5 showed the contact angle images and values in 15 wt% NaCl brine and different molar concentrations of silicon nanofluid (1 μmol/L, to 10 μmol/L). Figure 5 showed the contact angle of Berea core sample originally was 43.4º, indicating the core sample was oil-wet. With the increasing of nanofluid concentration, the contact angle increased. At the beginning, the contact angle of oil on the surface increased rapidly. After adding 6 μmol/L silica nanoparticles, the dropping range of contact angle slowed down and the wettability changed into 93.1º. At this moment, the core sample was almost mediate wettability. After adding 8 μmol/L

4

silica nanoparticles, the contact angle was over 100 º, and the wettability of nanofluid changed to water-wet. Thus, the optimized molar concentration of modified silica nanoparticles was 8 µmol/L. Finally, the contact angle of silica nanofluid on the oil-wet surface was changed to 103.2º. Compared with the pure brine, the contact angle of silica nanoparticle solution increased greatly and transferred from oil-wet to water-wet.
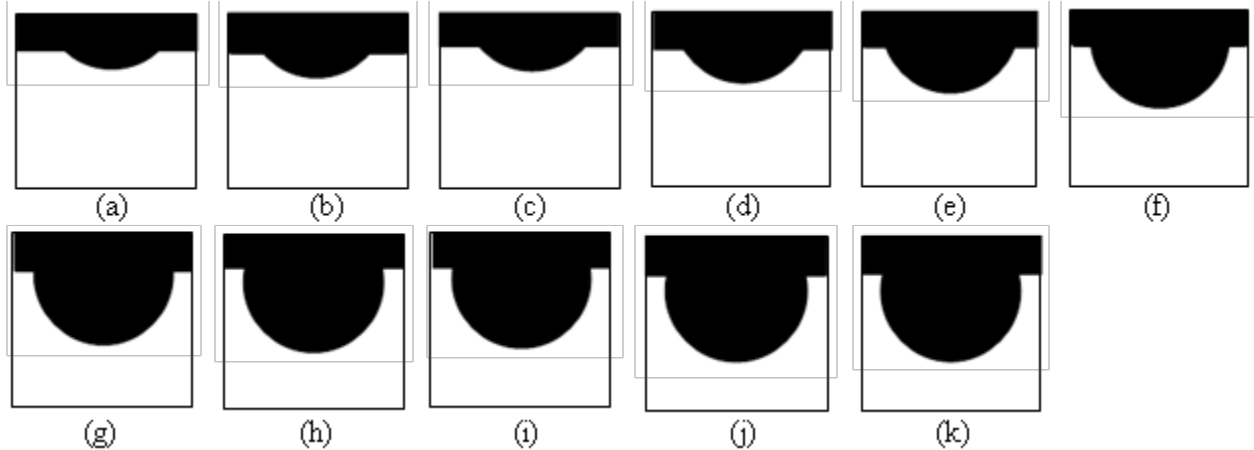

Figure 4 Contact angle photos of the oil-wet surface in different concentrations of nanoparticles (upper rectangle stood for Berea core sample, spherical stood for oil droplet, white area stood for nanofluid or brine): (a) 0 µmol/L, (b) 1 µmol/L, (c) 2 µmol/L, (d) 3 µmol/L, (e) 4 µmol/L, (f) 5 µmol/L, (g) 6 µmol/L, (h) 7 µmol/L, (i) 8 µmol/L, (j) 9 µmol/L, (k) 10 µmol/L
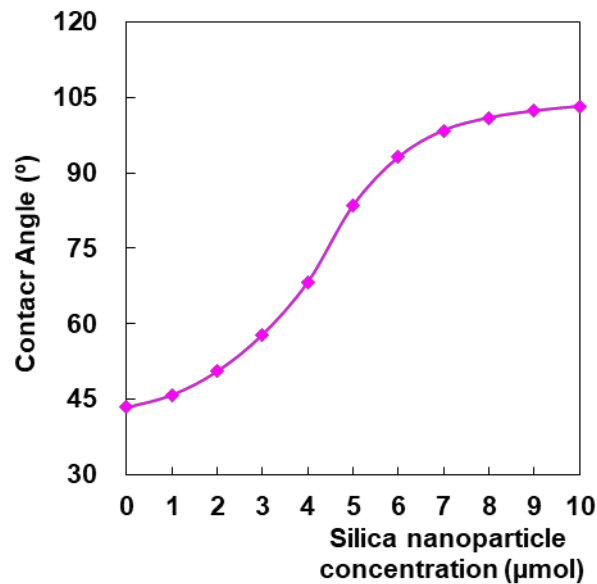

Figure 5 Contact angles at the oil-wet surface in brine and Nanofluids

4. Spontaneous imbibition test

4.1 Introduction

The spontaneous imbibition experiments for Berea core samples were conducted in 15 wt% NaCl brine and nanofluid (8 μmol/L silica nanoparticles dispersed in 15 wt% NaCl) at 65℃.

4.2 Summary and Discussion

Berea outcrop sandstones were purchased from Cleveland Quarries (850 West River Rd, Vermilion, OH 44089). The Berea samples were drilled out into cylindrical cores with a diameter of ~2.54 cm and length of ~5.0 cm. Then, their porosity and permeability were tested using a porosimeter (Brand: Coretest Systems, Inc., California, USA, Model: TPI-219) and a gas permeameter (Brand: Coretest Systems, Inc., California, USA, Model: TKA-209) respectively. The property of the two Berea sandstone core samples were shown in Table 2.

Table 2. Physical property of Berea core samples

sample	imbibition liquid	length, cm	diameter, cm	porosity, %	permeability, 10^{-3} μm^2	oil saturation, %
B1	15wt%NaCl brine	2.883	2.546	19.06	90.72	95.19
B2	Nanofluid	3.256	2.551	18.68	89.27	93.77

Figure 6 showed the results of spontaneous imbibition tests in different liquids. Berea core samples were immersed in different imbibition liquid in an imbibition cell. These imbibition cells were placed in an oven at a constant temperature of 65℃ to verify the oil recovery ability of nanofluid. The volumes of oil distracted from these cores were recorded.
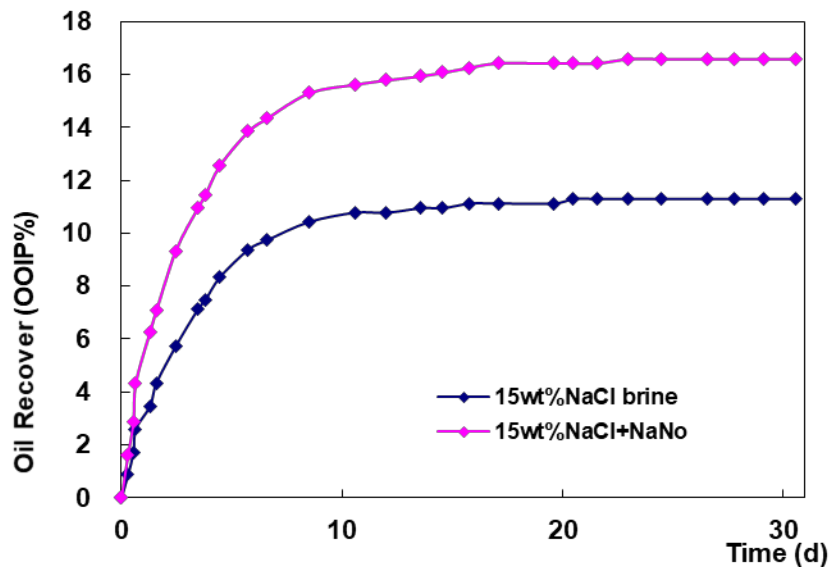

Figure 6 EOR of spontaneous imbibition experiments

Figure 6 showed that the imbibition liquid of nanofluid has a higher EOR comparing with 15 wt% NaCl brine. The reason was that the nanoparticles can absorb on the surface of core sample

which can improve the wettability. Wettability alternation is an extremely important factor for oil recovery. Meanwhile its lower interfacial tension assisted in oil to strip out from the rock surface.

5. Evaluation and Optimization of the Nanoparticle-surfactant Hybrid for EOR

5.1 Introduction

Surfactant favorable adsorption would improve solution wettability while unfavorable adsorption may impair the effectiveness of injected solution and turn the surfactant EOR process into economic unfeasible. The emulsification tendency and adsorption isotherms of the three surfactants (HCS, 964 and Betaine) were studied.

5.2 Summary or Results and Discussions

Under ambient pressure at 80℃, the emulsification tendency of the three surfactants (HCS, 964 and Betaine) were studied at water/oil ratio equals to 1:1, with 1,000 mg/L surfactant concentration and a wide salinity range (0, 1%, 3%, 6%, 7.5%, 15%, 30%). In order to detect the existence of emulsion, photos of above solutions were taken (Figure 7, Left) and under UV light (Figure 7, Right). The results were in accordance with the interfacial tension measurement, which were in the range of 0.5-1.5 mN/m. Compared with HCS and 964, the darker color appeared in Betaine systems implied higher emulsification tendency because more oil compositions have been dissolved into the aqueous phase.

(a) HCS

(b) 964

(c) Betaine
Figure 7 Emulsification tendency test

The adsorption isotherms of HCS, 964 and Betaine (50-1000 mg/L) were studied at the salinity of 289,817 mg/L at 80℃. In this study, spectrometric method using KI+ I_2 solution as a color developing agent was applied. In addition, two series of adsorption test in DI water and 20 ℃ were included for comparison. The adsorbents used were crushed Bakken rocks, which was characterized as clay-rich dolomitic quartzes sandstone, with negative charge for the whole system in DI environment. FTIR was used to verify the adsorption of different surfactants and the results indicated that Langmuir adsorption model fits well with the three surfactants. HCS has the largest adsorption (9.50 mg/g), followed by Betaine (8.04 mg/g) and 964 (6.87 mg/g). Increasing temperature and surface area of adsorbents would promote the adsorption. The driving for HCS adsorption is the hydrogen bonding formed between EO groups in surfactant structure and hydroxyl groups on mineral surfaces. For the zwitterionic surfactant Betaine, electrostatic interactions played the dominant force. While for 964, both the electrostatic interactions and chemical interactions (hydrogen bonding) are not negligible, but the effects of electrostatic interactions may be stronger. At Bakken salinity, the charge on mineral surfaces would be shielded. According to the normal case, the adsorption of ionic or zwitterionic surfactants would be lower. The high adsorption of Betaine may be explained by the change in adsorption pattern or the weakened repulsion interactions. The adsorption mechanism of Betaine is rather complex due to the coexistence of cationic and ionic parts in surfactant structure and the presence of positively charged calcite and dolomite and negatively charged quartz and clays.

Crushed Berea sandstone was used to better clarify the adsorption mechanism. Its composition is simple, with quartz occupies over 70 % of the whole weight. Moreover, the contents of clay, dolomite or calcite are negligible. In our pilot test, the adsorption of HCS is slightly lower on Berea sandstone surfaces compared with Bakken rock surfaces, which was about 9.46 mg/g at Bakken conditions and 5.62 mg/g in DI water. The higher adsorption at high salinity may be explained by the more compact adsorption layer, formation of surfactant aggregates and reduced solubility. Overall, the adsorption was still high even in DI water.

Future Work

1. Performance of surfactant solution and surfactant/nanoparticle suspension at high salinity brine.
2. Spontaneous imbibition experiments of surfactant solution and surfactant/nanoparticle suspension at high temperature.
3. Synthesis of different nanoparticles.
4. Filtering commercial nanoparticles to reduce surfactant adsorption.