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, the primary goals are studying the synergistic effects from surfactant and nanoparticles on interfacial properties and their potentials in boosting oil recovery. In addition, nanoparticles with superior salt-resistance were developed by covalently binding low molecular weight ligands.

We mainly focused on the following tasks:

1) The change in surfactant adsorption behavior when integrating with nanoparticles.
2) The interfacial tension reduction by using the developed surfactant-nanoparticle augmented systems.
3) The combined effects of surfactant and nanoparticles in altering the wettability.
4) The synergistic effects on oil recovery when surfactant-nanoparticle systems are used in contrast to brine imbibition and pure surfactant imbibition.
5) The improved salt resistance of surface modified silica nanoparticles.

Below are the detailed results of these tasks.

1. Surfactant-nanoparticle augmented system

In this part, an alkoxylated nonionic surfactant (MERPOL HCS) were mixed with hydrophilic silica nanoparticles LUDOX SM-30 and LUDOX TM-50. The average hydrodynamic diameters of LUDOX SM-30 and LUDOX TM-50 are 9.61 ± 0.39 nm and 22.35 ± 0.35 nm, respectively. Both of them have surface charge around -30 mV. Surface tension method was used to measure the critical micelle concentration of MERPOL HCS, which was around 100 mg/L as shown in Figure 1.

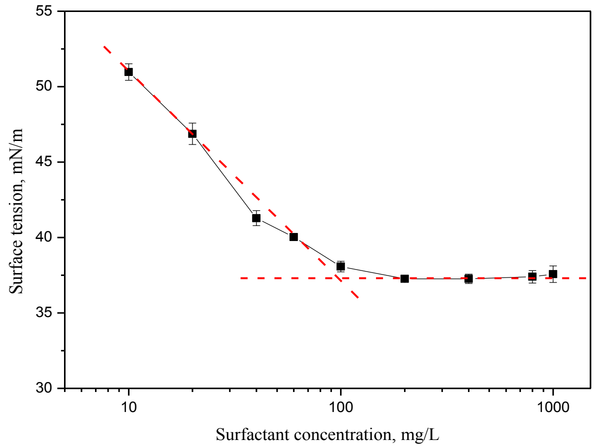


Figure 1. Critical micelle concentration of surfactant MERPOL HCS.

1.1 Effects on Surfactant Adsorption Behavior

The adsorption of surfactant MERPOL HCS on Berea sandstone and Bakken samples were measured in the absence or presence of hydrophilic silica nanoparticles.

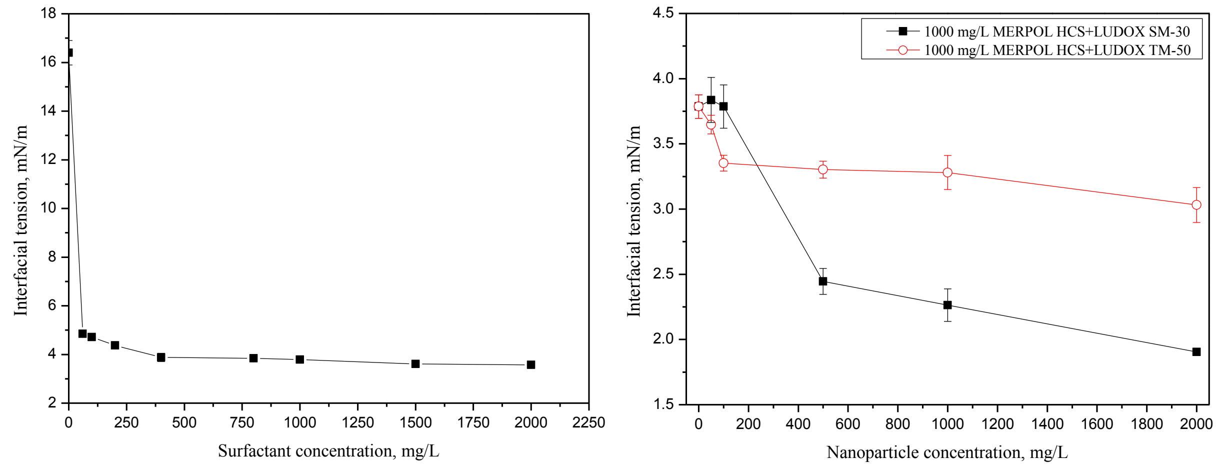
Without silica nanoparticles, the adsorption behavior of surfactant fits well with the Langmuir model, and the saturated adsorption capacity of surfactant MERPOL HCS on Bakken and Berea samples without SiNPs were 6.62 mg/g and 1.37 mg/g, respectively, both of which excessed the threshold of 1.0 mg/g for economical surfactant EOR.

However, when nanoparticles were introduced, due to the competitive adsorption of surfactant on nanoparticles and rock samples, surfactant loss on rocks was significantly restrained. Originally, about 44.1 % of surfactant was lost on Bakken rocks when 1,000 mg/L surfactant MERPOL HCS was used. With the inclusion of 2,000 mg/L LUDOX SM-30 or LUDOX TM-50 nanoparticles, surfactant adsorption loss on Bakken samples was reduced to 27.9 % and 37.3 %, respectively. While for Berea sample, the resultant adsorption densities can be even less than 1.0 mg/g, which are 0.48 mg/g and 0.91 mg/g, separately. According to the results of sensitivity analysis (Minitab 2016), surfactant adsorption was found largely depend on adsorbent, followed by nanoparticle and the interactions between adsorbent and nanoparticle.

1.2 Effects on Interfacial Properties

1.2.1 Reduction in Interfacial Tension

Surfactants, consisting of a hydrophilic head and a hydrophobic tail, usually are amphiphilic and tend to adsorb on the interfacial regions. But pure silica nanoparticles without any modification are usually of high hydrophilicity and difficult to be held at the water-oil interfaces, thus, no change in O/W interfacial tension was observed. IFT measurement may provide insightful information about the interactions between surfactant and SiNPs. As shown in Figure 2, 1,000 mg/L surfactant MERPOL HCS alone can reduce the IFT to ~ 3.8 mN/m, with the help of 2,000 mg/L LUDOX-SM and LUDOX TM-50, the magnitudes further decrease by another 50.0 % (~ 1.9 mN/m) and 13.2% (~ 0.5 mN/m), respectively.



(a) **(b)**

Figure 2. Interfacial reduction. (a) Pure surfactant solution; (b) 1,000 mg/L surfactant + nanoparticles (50-2,000 mg/L).

1.2.2 Wettability alteration

The original contact angle of rock samples after treated with paraffin was around 40.0°. Rock was rendered neutral-wet by 1,000 mg/L MERPOL HCS ($\theta \approx 81.5°$) alone and could change towards more water-wet when 2,000 mg/L LUDOX SM-30 or LUDOX TM-50 was added, showing contact angles of 98.0° and 89.5°, respectively, as presented in Figure 3.

Figure 3. Oil droplet at oil/aqueous/rock interface. (a) 2,000 mg/L KCl brine. (b) 1000 mg/L MERPOL HCS surfactant. (c) 1,000 mg/L MERPOL HCS surfactant + 2,000 mg/L LUDOX SM-

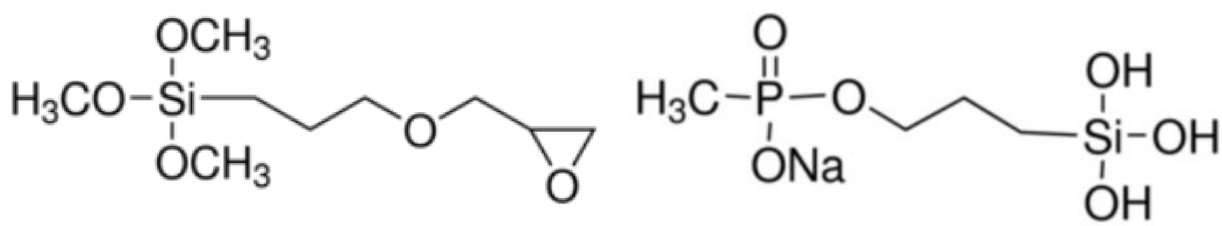
30 nanoparticle. (d) 1000 mg/L MERPOL HCS surfactant + 2,000 mg/L LUDOX TM-50 nanoparticle.

1.3 Effects on Oil Recovery

2,000 mg/L KCl brine can only recover 8.0 ~ 11.0 % of the original oil from Berea sample, and the subsequent spontaneous imbibition using 1000 mg/L MERPOL HCS surfactant solution alone in secondary mode could extract 30.6 % OOIP additional oil. 1,000 mg/L MERPOL HCS + 2000 mg/L LUDOX SM-30 nano-fluid yielded 46.19 % OOIP oil recovery, which is 37.67 % OOIP higher than KCl brine imbibition, while 1000 mg/L MERPOL HCS + 2,000 mg/L LUDOX TM-50, which wa also in secondary mode, produced additional 34.06 % OOIP oil than KCl brine imbibition.

2. Development of Surface Modified Silica Nanoparticles

Two low molecular weight ligands (GLYMO and THPMP, structures shown in Figure 4), were used to modify the commercial silica nanoparticles and improve their stability in brines with high salinity.



(a) (b)

Figure 4. (a) GLYMO; (b) THPMP.

2.1 GLYMO Modified Silica.

Generally, the mass ratio between ligand and SiNPs changes from 0.1 to 1.0 and the grafting density of GLYMO reaches an equilibrium at around 0.6. An acid-catalyzed ring opening of the GLYMO (Figure 5) epoxide at pH around 2 is necessary to obtain a highly soluble alcohol before adding into the nanoparticle dispersion. The final concentration of SiNPs in the mixture was around 10.0 wt%, and in some cases when GLYMO concentration was high (mass ratio >0.3), a small amount of methanol was added to prevent GLYMO oligomers from precipitating out. The hydrolysis condensation reaction was completed overnight at 60 ℃, alkaline condition (pH≈10.0) under stirring and methanol was removed by evaporation. Herein, LUDOX SM-30 nanoparticles supplied by Sigma Aldrich and Nexil 6 nanoparticles provided by Nyacol Nano Technologies, Inc. were used. The original diameters of which are 7.25±0.42 nm and 6.25±0.77 nm, respectively. Once the original particles meet the API Brine (8% NaCl + 2% $CaCl_2$), they would form large aggregates due to the collapse of surface electrical double layer.

When the reaction was finished, the cooled dispersion was first washed three times with deionized water to remove the ungrafted ligands using 3k MWCO centrifuge filters at 5500 rpm for 15 min. Then, 0.45 µm syringe filter was used to eliminate any large aggregates after sonication. The filtered dispersion was collected for further tests.

When particles were modified with GLYMO (mass ration=0.3), the hydrodynamic diameters of LUODOX SM and Nexil 6 were 14.07±0.08 nm and 10.68±0.61 nm, respectively, as presented in Figure 6 and 7, showing a huge improvement in salt-resistance.

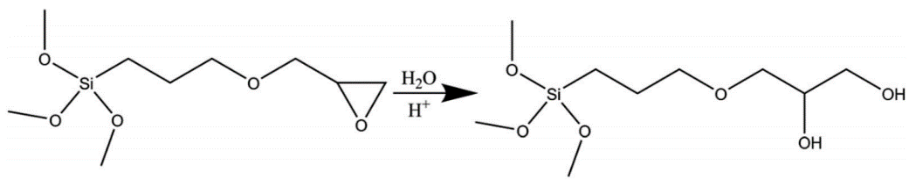


Figure 5. Ring opening of GLYMO

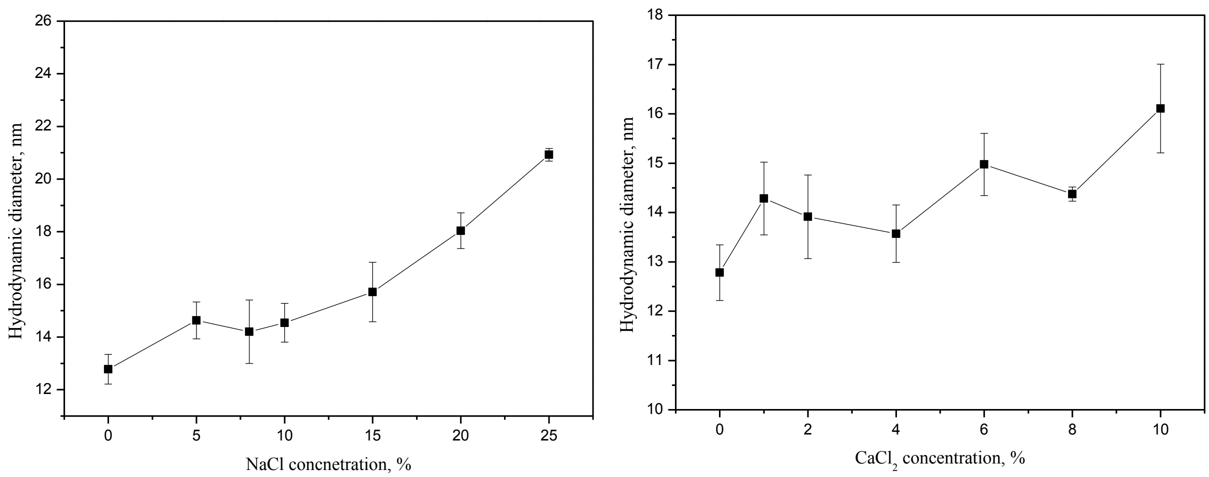


Figure 6. LUDOX SM-30 nanoparticle + GLYMO, mass ratio=1:0.3

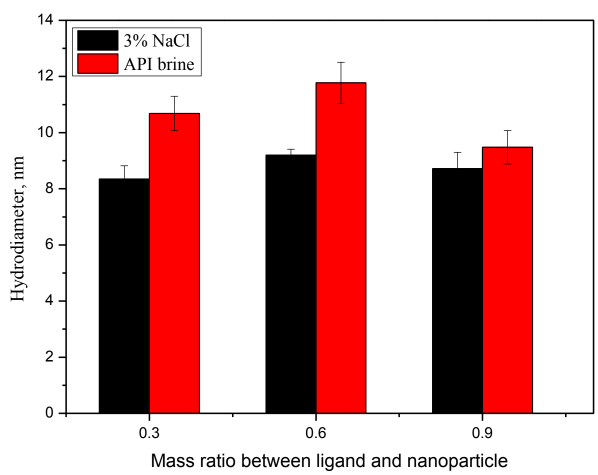


Figure 7. Nexil 6 nanoparticle + GLYMO, mass ratio=1:0.3

2.2. THPMP Modified Silica.

THPMP Modified SiNPs were synthesized in a similar manner by grafting a certain amount of MPPTS or THPMP directly to SiNPs in silica solutions. MPPTS or THPMP solution prepared by deionized water was added dropwise to nanoparticle dispersions, and the final silica concentration was approximately 10.0 wt%. Qualified dispersions were obtained after the subsequent purification process mentioned above.

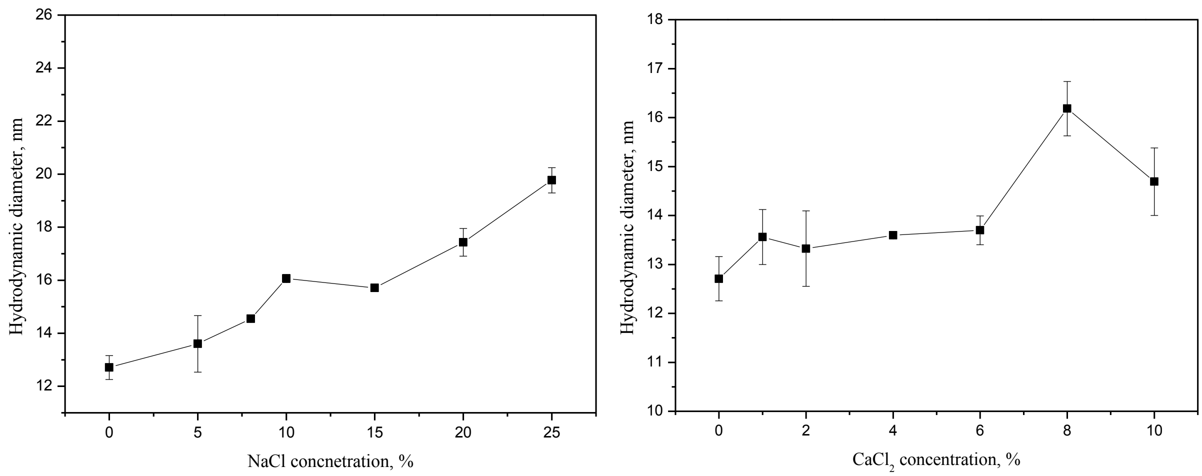


Figure 8. LUDOX SM-30 nanoparticle + THPMP, mass ratio=1:0.3

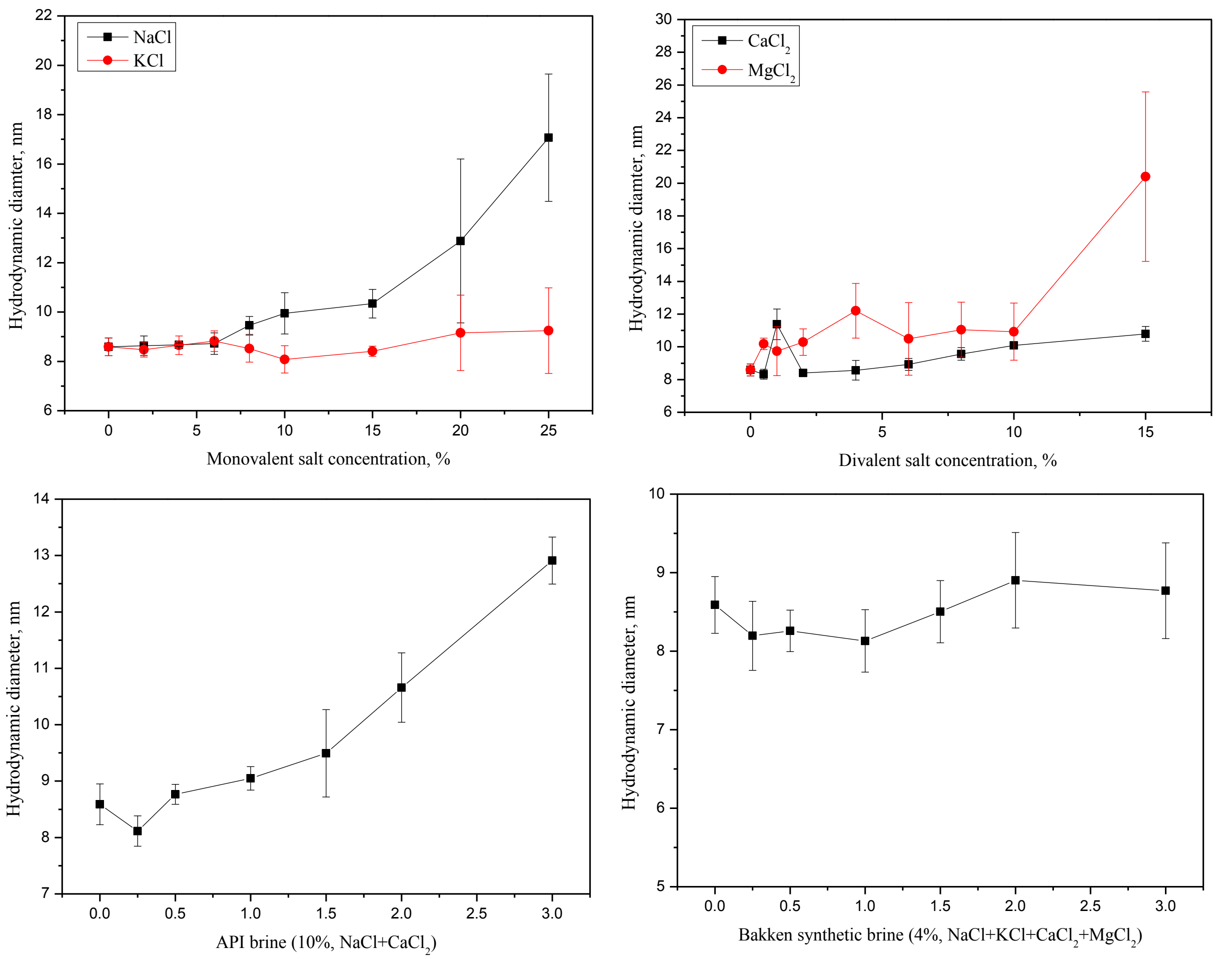


Figure 9. Nexil 6 nanoparticle + THPMP, mass ratio=1:0.6

Comparing with GLYMO (Figure 6 and 7), The THPMP saline showed similar effects, as presented in Figure 8 and 9, both ligands have excellent capability to increase the hydrophilicity of silica nanoparticles when they were covalently connected to the particle surfaces. Tough the salt resistance of the developed nanoparticle can successfully satisfy the requirement of Bakken formation water, the thermos resistance of nanoparticles is still an unavoidable problem. So our next step work will be the development of surfactant-nanoparticle augmented systems, hopefully they could better satisfy the field conditions.

Future Work

1. Development of surfactant-nanoparticle augmented systems that could satisfy Bakken conditions.
2. Development of novel nanoparticles to reduce the amount of surfactant needed and lower the cost.
3. Spontaneous imbibition test on Bakken samples.