

Contract No. G-041-081

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

Submitted by: University of North Dakota - Department of Petroleum Engineering, Department of Chemistry, and Institute of Energy Studies

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PARTICIPANTS

Sponsor	Cost Share
Hess Corporation	\$ 0*
InPetro Technologies, Inc.	\$ 236,250 (in-kind)
University of North Dakota	\$ 524,628 (in-kind)
North Dakota Industrial Commission/OGRC Funding	\$ 678,932 (cash)
Total Project Cost	\$1,439,810

*Hess will be providing crude oil samples - value undetermined

Project Schedule – 3 years

Contract Date – March 4, 2017

Start Date – May 1, 2017

Final Report: April 30, 2020

Project Deliverables:

Status Report: August 1, 2017 ✓

Status Report: November 1, 2017 ✓

Status Report: February 1, 2018 ✓

Status Report: May 1, 2018 ✓

Status Report: August 1, 2018 ✓

Status Report: November 1, 2018 ✓

Status Report: February 1, 2019 ✓

Status Report: May 1, 2019 ✓

Status Report: August 1, 2019 ✓

Status Report: November 1, 2019

Status Report: February 1, 2020

Final Report: April 30, 2020

OBJECTIVE/STATEMENT OF WORK:

The objective of this project is to develop a novel nanoparticle enriched surfactant fluid for enhanced oil recovery (EOR) in Williston Basin. In this fluid, the nanoparticles will carry surfactant to deeply penetrate rock matrix, then effectively displace oil locked in micro- and nano-pores of tight rocks, and finally carry the oil out of the rocks. The features of the designed nanoparticles will be: 1) controllable delivery of surfactant and alter the wettability of interfaces of oil with the fluid; 2) high mobility, water solubility, stability, and uniform dispersion in the reservoir fluids; 3) tunable chemical composition, shape, size, porosity and functionality; 4) environmentally friendly; and 5) low cost. The commercialization of this technology will lead to higher oil recovery, prolonged reservoir life, reduced operation cost and further minimizing the environmental complications.

The results will provide conceptual validation of nanoparticle loaded surfactant fluid for EOR in Bakken tight formation. Vital data will be collected based on the fluid performance regarding their wettability, mobility and the effects of EOR in the Bakken play from macro-to nanoscale levels. Positive recovery rates are expected. Accumulated data, mechanisms and optimization outcomes will lay a solid foundation to the technology’s commercialization in the near future.

STATUS

The Contract has been executed by the Commission and the University of North Dakota.

Quarterly Report for the period of May 1 - July 31, 2017 received. It has been posted on the Oil and Gas Research Program website. The report notes the following:

NDIC project is a three-year project with the goal of developing a novel nanoparticle enriched surfactant fluid for enhanced oil recovery (EOR) in Williston Field. In order to fulfil this project, we are supposed to have good knowledge of the reservoir conditions of the Williston Basin, to design different types of nanoparticle enriched surfactant fluids, and to find the optimum types of fluids that is cost-effective and environmental-friendly under the Williston Basin reservoir conditions.

During the first quarter of this project, our primary goals are to screen nanomaterials and Bakken core samples. We mainly focused on the following five tasks:

- 1) Systematically reviewed literature for deep understanding of Bakken reservoir conditions in Williston Basin;
- 2) Obtained various Bakken core samples from North Dakota Geological Survey Wilson M. Laird Core and Sample Library and conducted preliminary screening of these samples;
- 3) Conducted preliminary IFT experiments in order to prepare future IFT measurements;
- 4) Selected targeting nanomaterials and studied their properties;
- 5) Prepared experimental plan for next quarter.

Detailed results of these tasks are included in the quarterly report.

Quarterly Report for the period of August 1 - November 1, 2017 received. It has been posted on the Oil and Gas Research Program website. The report notes the following:

During the past quarter our primary goals are to start synthesizing and testing of different types of nanoparticles. Our focus is the characterization of nanoparticles and the stability test for those nanoparticles. We mainly focused on the following tasks:

- 1) Preparation and Characterization of PEG-coated Silica Nanoparticles for Oil Recovery;
- 2) Evaluation and Optimization of the nanoparticles and Nanoparticle-surfactant Hybrid for EOR;
 - a) Stability test of graphene oxide nanosheet (GON);
 - b) Stability test of partially reduced graphene oxide nanosheet (PrGON)
 - c) Stability test of Silica-Triton X-100 system
 - d) Stability test of Silica Nanoparticles

Detailed information on this work is included in the quarterly report. It was stated that Future Work will include:

1. Prepare polymer nanoparticles, carbon nanoparticles, and porous silica nanoparticles as outlined in the proposal for investigation.
2. Reduce the size of the silica nanoparticles to less than 20 nm for fitting the requirement in the Bakken formation.
3. Modify silica nanoparticles with different types of surfactants to test the stability and oil recovery efficiency.
4. More stability test will be done based on nanoparticles, since the changes in type, size, wettability and electrical property will all have effects on the final results.
5. Measure the interfacial tension and conduct the adsorption test.

Quarterly Report for the period of November 1, 2017 - February 1, 2018 received. It has been posted on the Oil and Gas Research Program website. The report notes the following:

During the past quarter, our primary goals were to select the interested area to acquire core samples and characterized the core samples with the scanning electron microscope (SEM). Meanwhile, we tested the stability of silica nanoparticles. Furthermore, we are trying to develop polymer nanoparticles and measure their physicochemical properties.

We mainly focused on the following tasks:

- 1) Selected areas for core samples and their SEM measurement;
- 2) Pore space characterization;
- 3) Stability experiment of silica nanoparticle
 - a.) Salinity effect;
 - b.) Concentration of silica nanoparticles (wt%)
 - c.) Composition of synthetic brine water
 - d.) Lower concentrations of silica nanoparticles (wt%)
 - e.) Brines with different cation valence
- 4) Evaluation and optimization of the nanoparticle-surfactant for EOR
 - a.) Description of newly purchased nanoparticles;
 - b.) Stability test;
 - c.) Effects of pH and zeta potential test;
 - d.) Emulsion test.
- 5) Preparation and characterization of silica nanoparticles for oil recovery;
- 6) Preparation and characterization of polymer nanoparticles for oil recovery.

Detailed information on this work is included in the quarterly report. It was stated that Future Work will include:

1. Nanoscale simulation of fluid properties in tight formations.
2. Interfacial tension between oil and water made up of different nanoparticles.
3. The synergistic effect of surfactant and nanoparticles.
4. Recovery by different kinds of surfactant and nanoparticles.
5. Adsorption of different kinds of surfactant and nanoparticles.
6. How to modify the properties of nanoparticles and surfactants to make them applicable in high salinity brine.

Quarterly Report for the period of February 1, 2018 - May 1, 2018 received. It has been posted on the Oil and Gas Research Program website and includes detailed results of the tasks completed during the time period of this report. The report notes the following summary:

During the past quarter, our primary goals are to study the morphology and characteristics of rock samples of Middle Bakken formation of five wells through scanning electron microscope (SEM) analysis. Meanwhile, we self-made Hele Shaw cell to simulate the fractures in the formation. Spontaneous imbibition experiments using different solutions were carried out. The optimization of the nanoparticle-surfactant hybrid for enhanced oil recovery (EOR) was evaluated. Also the phase behaviors under several salinities and temperatures were tested. With respect to nanomaterial preparation, we fabricated a series of small polymer nanoparticles for testing.

We mainly focused on the following tasks:

- 1) Comparison of morphology and characteristics of Middle Bakken rock samples using SEM;
- 2) Design and Construction of Hele Shaw cell by ourselves;
 - a) Hele Shaw cell gap determination
 - b) Designing of gap style
 - c) Construction of Hele Shaw holder

- 3) Spontaneous Imbibition Experiments
 - a) Core samples with different permeability in imbibition brine with same salinity
 - b) Core samples with same permeability in imbibition brine with different salinity
- 4) Evaluation and Optimization of the Nanoparticle-surfactant Hybrid for EOR
 - a) Surfactants stability experiments
 - b) Interfacial tension determination of superior surfactants
 - c) Contact angle determination of superior surfactants
 - d) Preliminarily testing the adsorption of surfactant on rock in the addition of nanoparticle
- 5) Phase Behavior
 - a) Phase behaviors testing for PEG 6000, PEG 8000, and 58N surfactants
 - b) Searching new surfactants for enhanced oil recovery
- 6) Nanoparticles preparation
 - a) Synthesis of small polymer nanoparticles
 - b) Size and Zeta potential characterization of polymer nanoparticles

Quarterly Report for the period of May 1, 2018 through August 1, 2018 received. It has been posted on the Oil and Gas Research Program website and includes detailed results of the tasks completed during the time period of this report. The report notes the following summary:

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

Quarterly Report for the period of August 1, 2018 - November 1, 2018 received. It has been posted on the Oil and Gas Research Program website and includes detailed results of the tasks completed during the time period of this report. The report notes the following summary:

During the past quarter, our primary goals were to test the oil recovery of novel nanofluid by physical simulation and to analyze flow mechanisms of Middle Bakken formation by numerical simulation. Specifically, we tested the performances of surfactant-coated silica nanofluid at high salinity brine, carried out spontaneous imbibition experiment of Berea and numerical simulation of tight Bakken formation. We also studied the NMR characteristics of tight Bakken core samples.

We mainly focused on the following tasks:

- 1) Performance of surfactant coated silica nanofluid at high salinity brine
 - a) Interfacial tension change
 - b) Contact angle change
- 2) Spontaneous imbibition test of Berea
- 3) Evaluation and optimization of the nanoparticle-surfactant hybrid for EOR
- 4) Numerical simulation of spontaneous imbibition in tight Bakken core samples
- 5) NMR study of tight Bakken formation

Quarterly Report for the period of November 1, 2018 – February 1, 2019 received. It has been posted on the Oil and Gas Research Program website and includes detailed results of the tasks completed during the time period of this report. The report states in part:

1. Synthesis of polymer nanoparticle

Summary and discussion

Figure 1 shows the DLS (dynamic light scattering) and zeta potential distribution of the polymer nanoparticles in distilled water. The hydrodynamic diameter distribution of particle sizes was mostly between 15~25nm. The zeta potential was between -40~-35mv.

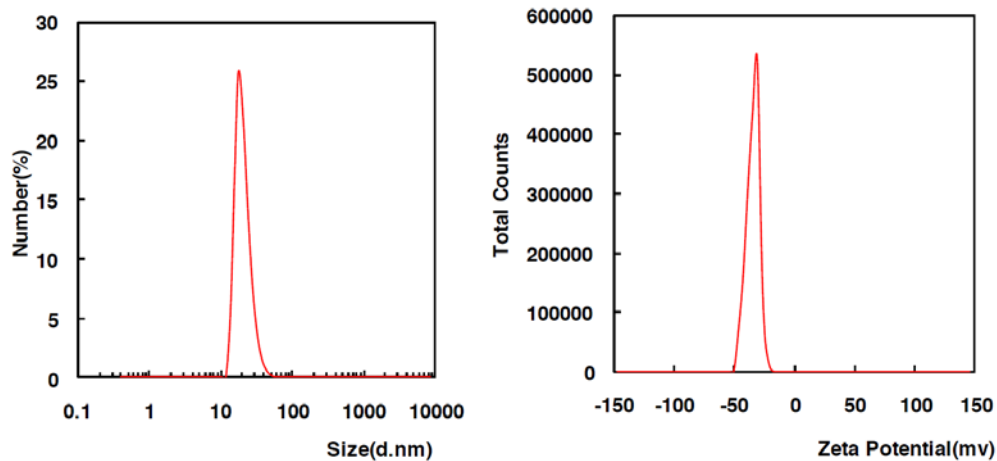


Figure1. DLS and zeta potential distribution of polymer nanoparticles

2. Stability test of surfactant-based polymer nanofluid

Summary and discussion

The surfactant-based polymer nanofluid is stable in all of the tested brines, including in 300,000 mg/L brine. Figure 2 shows the particle size results obtained from the stability experiment. Because the pore size of the Bakken formation is around 100nm, so in the follow up experiments, the 20wt% brine was chosen.

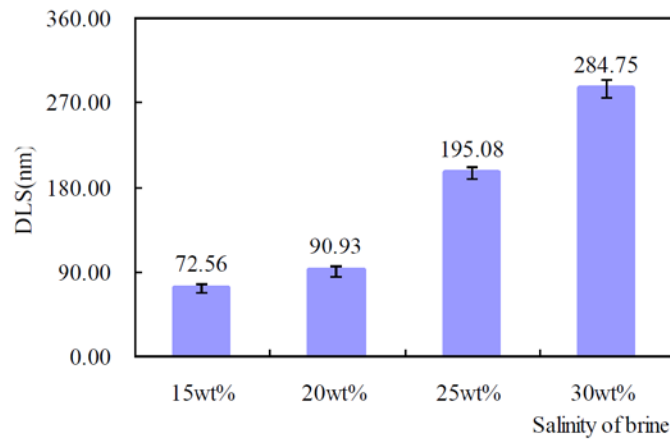


Figure2. DLS of polymer nanoparticles in different salinity brines

3. Core flooding experiment using polymer nanofluid

Summary and discussion

Figure 3 shows the oil recovery profiles of surfactant flooding and surfactant-based nanofluid, both injected 0.5PV of solutions. It can be seen that comparing with brine flooding, surfactant flooding can enhance oil recovery by 7.91%OOIP, while surfactant-based nanofluid flooding yields an incremental oil recovery of 15.03%OOIP. These encouraging coreflooding results indicate that the incremental oil recovery by surfactant-based nanofluid flooding is 7.12%OOIP higher than that of surfactant flooding. Moreover, in the subsequent water flooding, the ultimate recovery from nanofluid-flooded sample is 1.44%OOIP higher than that of surfactant flooded core plug.

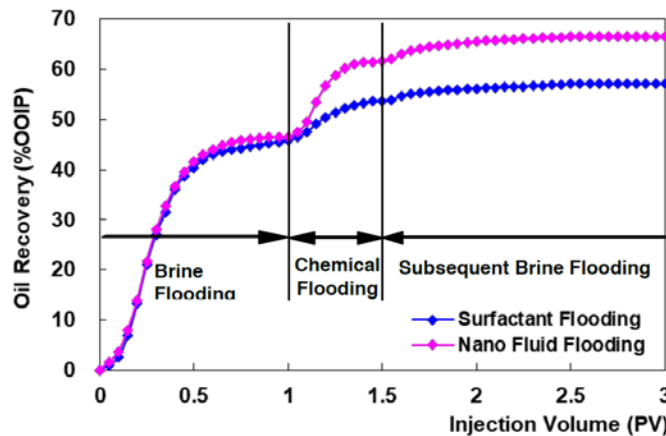


Figure 3. Oil recovery of surfactant flooding and surfactant-based nanofluid flooding

4. Molecular dynamics simulation of oil transport through nano pores

Summary and discussion

The transport behaviors of n-octane through quartz nano pore (Figure 4) and graphene nano pore (Figure 6) are studied by molecular dynamics simulation. The simulations are carried out at 383K, 35Mpa. The octane molecules lie dominantly parallel to the solid surface in the near-wall region. The mass density profiles (Figure 5, Figure 7) are symmetric with respect to the central plane ($z=0$) of the two rock surfaces. Dense octane layers exist in the near-wall region. From the spacing between two successive troughs, we determined the thickness of each monolayer ~ 0.45

nm). The density tends toward a constant (the bulk density at the same pressure and temperature) when it is farther away from the solid surface.

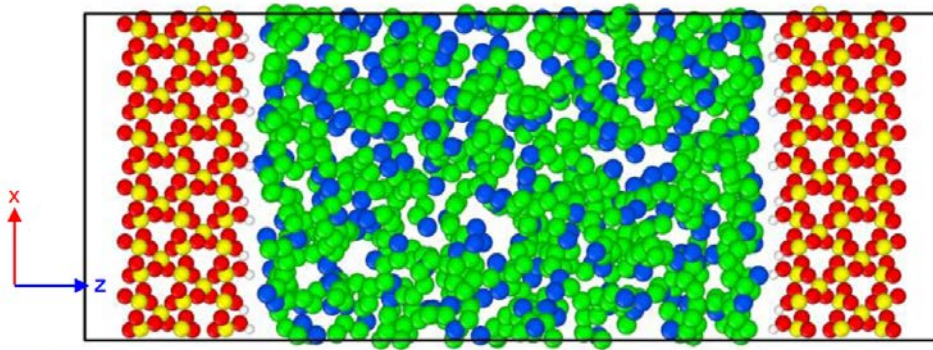


Figure 4. Simulation snapshot of n-octane flow through a 4.76nm hydroxylated quartz nanopore (Color code for atoms: red, oxygen; white, hydrogen; yellow, silicon; Blue and green, methyl (-CH₃) and methylene (-CH₂) groups in n-octane).

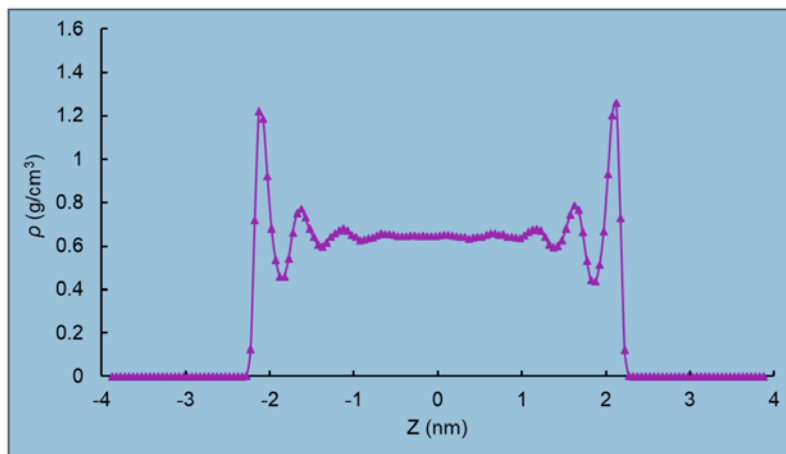


Figure 5. Mass density profile of n-octane confined in a 4.76nm quartz nanopore (383K, 35Mpa).

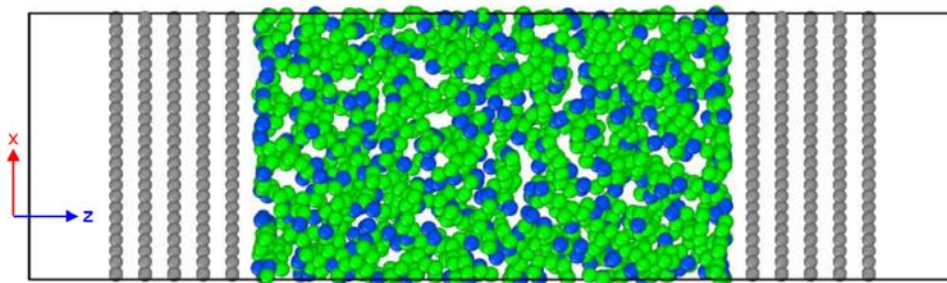
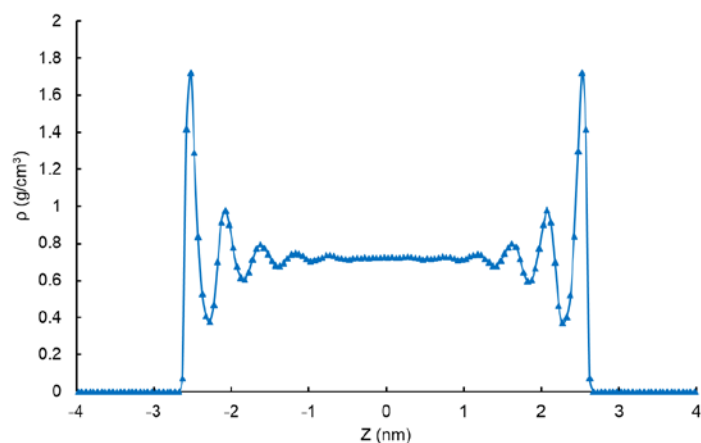


Figure 6. Simulation snapshot of n-octane flow through a 5.80 nm graphene nano pore (Color code for atoms: grey, carbon; Blue and green, methyl (-CH₃) and methylene (-CH₂) groups in n-octane).



By comparing the mass density profiles of n-octane confined in quartz and graphene nano pores, we can find that for each dense layer, the peak density of octane in graphene pores is much greater than that in quartz, indicating strong interactions and preferential adsorption of liquid hydrocarbons within carbonaceous material. In order to increase the mobility of oil in nano pores, it is crucial to alter core wettability from oil-wet to water-wet.

5. Molecular dynamics simulation of NPs/surfactant at the oil/water interface

Summary and discussion

The IFTs of C12/water and C12E5/C12/water systems are calculated by molecular dynamics simulation (Figure 8). All simulations are carried out at 300 K and 1 atm. The IFT of C12/water in our simulation is 51.30 ± 0.18 mN/m which is in good agreement with the experimental value (52.8 mN/m). When the surfactant concentration is increased to an interfacial area of 56.25 \AA^2 per C12E5, the IFT can be reduced to 22.10 ± 0.18 mN/m.

NPs/C12E5/C12/water systems (Figure 9) are also constructed to investigate the influence of various types of NPs on the ability of surfactants in term of interfacial tension (IFT) reduction. Figure 9 shows the distribution and organization of NPs and surfactants at the oil/water interface. The hydrophilic or hydrophobic NPs can only stay in a single phase. The hydrophilic or hydrophobic NPs can hardly affect the IFTs. Amphiphilic NPs can stay at the oil/water interface and the IFT is reduced to 19.42 ± 0.13 mN/m.

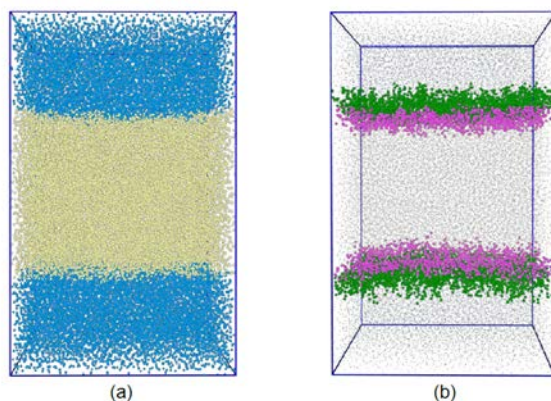


Figure 8. Simulation snapshots of (a) C₁₂/water interface and (b) C₁₂E₅ in the vicinity of C₁₂/water interface (Color code for atoms: yellow, C₁₂; blue, water; pink, hydrophobic tail of C₁₂E₅; green, hydrophilic head of C₁₂E₅).

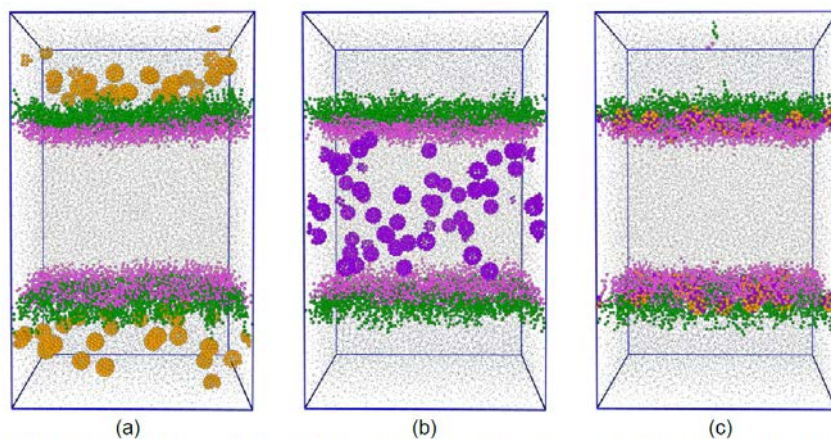


Figure 9. Simulation snapshots of NPs/ $C_{12}E_5$ in the vicinity of C_{12} /water interface: (a) hydrophilic NPs, (b) hydrophobic NPs, (c) amphiphilic NPs. (Color code for atoms: gold, hydrophilic bead; purple, hydrophobic bead).

Figure 10 shows the organization of NPs and NPs/surfactants in the vicinity of the oil/water interface. Without surfactants, NPs tend to aggregate and form a big cluster. With surfactants added, the NPs are evenly distributed.

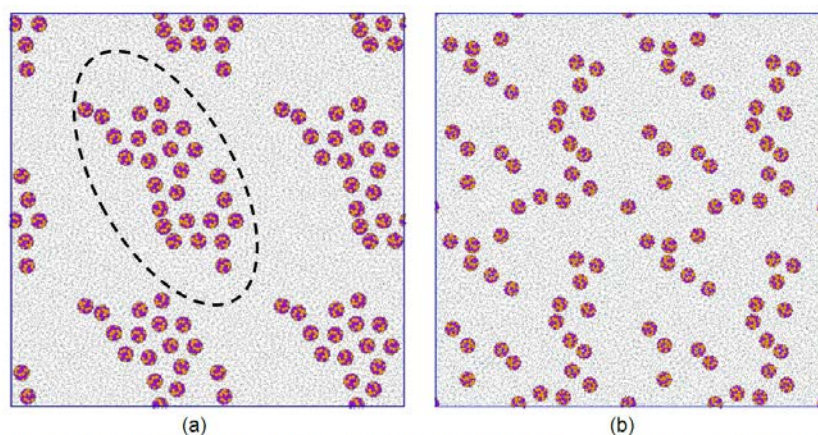


Figure 10. MD simulation of (a) NPs and (b) NPs/surfactants ($C_{12}E_5$ molecules are omitted) in the vicinity of the C_{12} /water interface (top view).

Quarterly Report for the period of February 1, 2019 - May 1, 2019 received. It has been posted on the Oil and Gas Research Program website and includes detailed results of the tasks completed during the time period of this report. The report states in part:

During the past quarter, our primary goals were to develop one type of nanofluid which can reduce water/oil interfacial tension (IFT) and change wettability of Middle Bakken rocks.

We mainly focused on the following tasks:

1. Commercial silica nanoparticle size distribution test.
 - a. The commercial nanofluid used in the study is a colloidal silica obtained from NYACOL company. After it was dispersed in distilled water homogeneously, its size distribution was tested using dynamic light scattering (DLS) technique.
 - i. The silica nanoparticles can be used in oil recovery of Bakken Formation because their sizes are small enough to transport through the nanopores of the formation.

2. Measurement of IFT between Bakken oil and nanofluid.
 - a. This nanofluid is mainly comprised of surfactant and silica nanoparticles, with an expectation of utilizing the synergy between silica nanoparticles and surfactants to enhance the oil recovery¹. The nanoparticle used is above mentioned. The surfactant is an anionic surfactant obtained from Sasol.
 - i. The interfacial tension (IFT) decreased dramatically with the addition of nanoparticles to the concentration of 0.1 wt%. Above this concentration (0.1 wt%), the IFT changed slightly and plateaued. The experimental results also indicate that the IFT of nanofluid with 0.4 wt% surfactant is higher than that of nanofluid with 0.1 wt% surfactant. This may be due to aggregation of nanoparticles caused by the higher surfactant concentration. The aggregation of nanoparticles will decrease its capability in reducing the IFT.
3. Measurement of Bakken oil-nanofluid contact angles of Middle Bakken rock surfaces.
 - a. In order to evaluate the effect of nanofluids on Bakken oil-nanofluid contact angles of Middle Bakken rock surfaces, the dynamic contact angles as a function of both time and nanoparticle concentrations were both measured.
 - i. Contact angle increases significantly as nanoparticles concentrations increase from 0 to 0.1 wt%. Then contact angle changes slightly with further increase of nanoparticle concentration. The reason for contact angle increase is possibly that the nanoparticles were adsorbed at rock surface and changed the wettability.

Additional details are available in the full report.

Quarterly Report for the period of May 1, 2019 - August 1, 2019 received. It has been posted on the Oil and Gas Research Program website and includes detailed results of the tasks completed during the time period of this report. The report states in part:

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.