UND PETROLEUM ENGINEERING
UNIVERSITY OF NORTH DAKOTA

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

Presented to North Dakota Industrial Commission
Oil & Gas Research Council

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LEADERS IN ACTION

Acknowledgements

- North Dakota Industrial Commission Oil & Gas Research Council
  - Nanoparticle-surfactant EOR project: 05/01/2017-04/30/2020
- UND Post-Doctoral Funding Program
  - One post-doctoral associate for two years: 04/2018-03/2020
  - Tuition waivers
- Bakken crude oil samples from HESS
- Bakken core samples from North Dakota Geological Survey's Wilson M. Laird Core and Sample Library

Outline

- Surfactant Screening and Evaluation
  - -Screening and evaluation
  - -Spontaneous imbibition test using surfactant
- Development of Nanofluids for EOR
  - -Amino-modified silica nanoparticles
  - -Polymer nanoparticles
- Bakken Core Sample Characterization
- Molecular Dynamics Simulation
- Next Steps

Surfactant Screening and Evaluation

Surfactant Screening and Evaluation

Aqueous Stability Test

Surfactant	Supplier	Type	API Brine (8% NaCl + 2% $CaCl_2$)				Bakken formation brine			
			20°C	60°C	80°C	105°C	20°C	60°C	80°C	105°C
SOLOTERRA 938	Sasol	Anionic	√	√	×	×	√	×	×	×
SOLOTERRA 963	Sasol	Anionic	√	√	×	×	√	×	×	×
SOLOTERRA 964	Sasol	Anionic	√	√	×	×	√	×	×	×
SOLOTERRA 982	Sasol	Anionic	√	√	×	×	√	×	×	×
**	**	**	√	√	√	√	√	√	√	√
**	**	**	√	√	√	√	√	√	√	√
**	**	**	√	√	√	√	√	√	√	√
Betaine	Lubrizol	Zwitterionic	√	√	√	√	√	√	√	√
AMPHOSOL CA	Stepan Chemicals	Zwitterionic	√	√	√	√	√	√	√	√
AMPHOSOL CS-50	Stepan Chemicals	Zwitterionic	√	√	√	√	√	√	√	√
MERPOL HCS	Stepan Chemicals	Nonionic	√	×	×	×	√	×	×	×
NEUTRONYX 656	Stepan Chemicals	Nonionic	√	×	×	×	√	×	×	×
CEDEPALTD-403	Stepan Chemicals	Anionic	×	×	×	×	×	×	×	×
Calsoft LPS-99	Pilot	Anionic	×	×	×	×	×	×	×	×
Calimulse PR	Pilot	Anionic	×	×	×	×	×	×	×	×
Macat TAM-2 Betaine	Pilot	Zwitterionic	×	×	×	×	×	×	×	×
SG 3380	Wacker	Silicone surfactant	×	×	×	×	×	×	×	×
SG 3381	Wacker	Silicone surfactant	×	×	×	×	×	×	×	×
LANSURF AEP66	LanKem	N/A	×	×	×	×	×	×	×	×
KEMSURF SBE30	LanKem	N/A	×	×	×	×	×	×	×	×

Note: √ means stable at given conditions for longer than 7 days

**: confidential

Surfactant Screening and Evaluation

IFT and Contact Angle Measurement

Surfactant	Supplier	Type	API Brine (8% NaCl + 2% $CaCl_2$), 20 ℃	
			Bakken oil-Brine Interfacial tension, mN/m	n-octane-Water Water contact angle, ° (original=141.3°)
SOLOTERRA 938	Sasol	Anionic	1.57	131.0
SOLOTERRA 963	Sasol	Anionic	2.05	131.3
SOLOTERRA 964	Sasol	Anionic	2.41	129.7
SOLOTERRA 982	Sasol	Anionic	1.44	132.7
**	**	**	0.78	134.0
**	**	**	0.71	134.3
**	**	**	0.85	133.1
Betaine	Lubrizol	Zwitterionic	0.37	**104.3**
AMPHOSOL CA	Stepan Chemicals	Zwitterionic	0.71	**55.1**
AMPHOSOL CS-50	Stepan Chemicals	Zwitterionic	0.53	**60.4**

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Surfactant Screening and Evaluation

Surfactant Adsorption

Surfactant	Supplier	Type	Adsorption amount, mg/g (Bakken formation brine, rock powder, T=105 ℃)	
			Bakken rock	Berea
**	**	**	12.08	10.32
**	**	**	12.66	6.07
**	**	**	12.83	6.04
Betaine	Lubrizol	Zwitterionic	8.03	3.03
AMPHOSOL CA	Stepan Chemicals	Zwitterionic	8.69	3.36
AMPHOSOL CS-50	Stepan Chemicals	Zwitterionic	11.94	3.40

⇒ (1) Experimental data would be higher than real case because tiny rock powder with high surface area was used;

⇒ (2) The adsorption was still pretty high as compared with the standard (1 mg/g);

⇒ (3) Sacrificial agents or surfactant carriers like nanoparticles maybe necessary.

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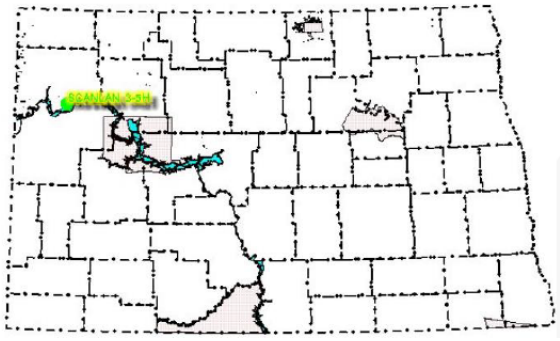
Spontaneous Imbibition Tests Using Surfactant

Properties of Five Bakken Core Plugs (William County)

Test #	Core #	Ø,%	K,md	Length, cm	Diamter, cm	*So, %
1	BTW-1-1	7.28	0.0001	6.8	3.8	84.99
2	BTW-1-2	7.08	0.0006	3.3	3.8	94.78
3	BTW-1-3	7.49	0.0006	3.2	3.8	82.69
4	BTW-1-4	6.55	0.0005	3.1	3.8	95.20
5	BTW-1-5	7.09	0.0005	3.4	3.8	97.32

Note: *So is oil saturation in core plugs after saturating them with Bakken oil for imbibition experiment

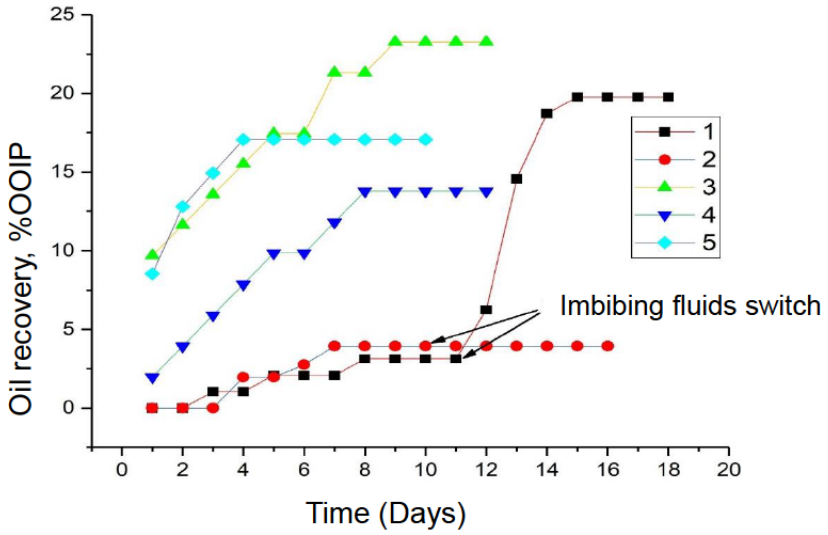
map source: www.dmr.nd.gov



Spontaneous Imbibition Tests Using Surfactant

Results of Spontaneous Imbibition Experiments

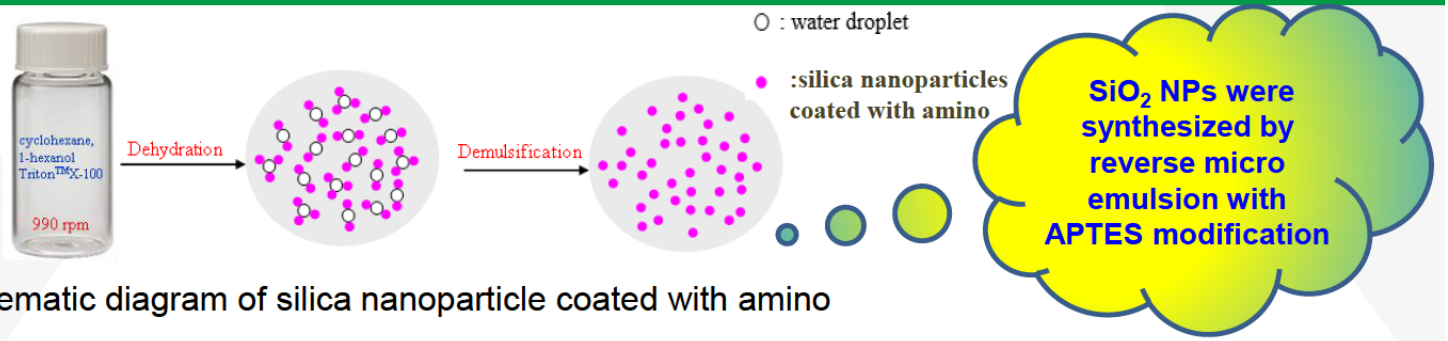
Test #	Core #	Imbibing fluids	Recovery, %OOIP
1	BTW-1-1	16wt% brine initially, changed to 0.1wt%Betaine in16wt% brine, 80°C	19.75
2	BTW-1-2	16wt% brine initially, changed to 0.2wt%Betaine in16wt% brine, 80°C	3.94
3	BTW-1-3	0.1wt%Betaine in16wt% brine, 80°C	23.26
4	BTW-1-4	0.1wt%Betaine in 30wt% brine, 80°C	13.78
5	BTW-1-5	0.1wt%Betaine in16wt% brine, 105°C	17.06



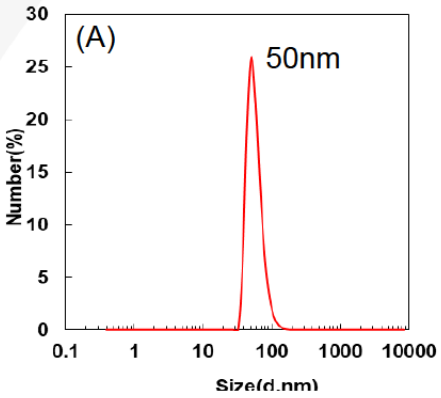
Results of Spontaneous Imbibition Experiments

Development of Nanofluids

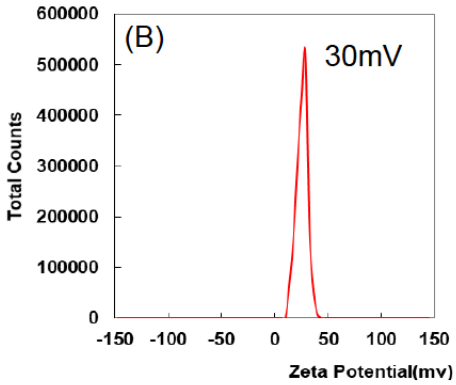
Amino-Modified Silica Nanoparticles



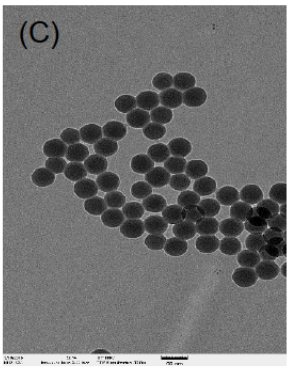
Schematic diagram of silica nanoparticle coated with amino



Particle size spectrum from the DLS method



(B) zeta potential distribution of amino-modified SiO_2 NPs

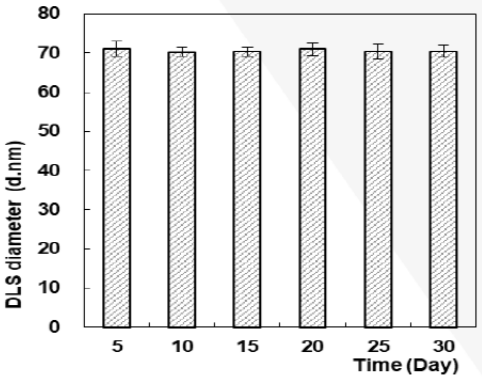


(C) TEM image of amino-modified SiO_2 NPs

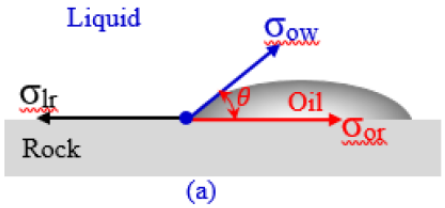
Nanofluid: Amino-Modified Si-NPs + Surfactant

+

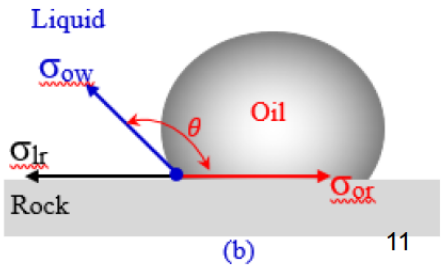
Magnetic stirring for 2hrs Ultrasonic dispersion for 2hrs



Temporal behavior of the average particle size of Nanofluid in 15wt% NaCl brine at 65°C



(a)



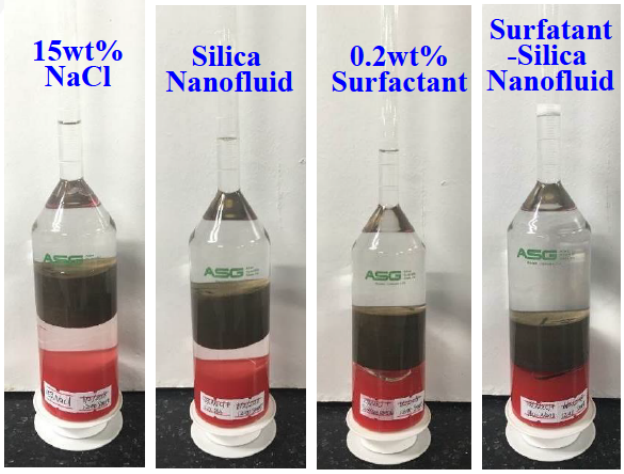
(b)

Spontaneous Imbibition Test

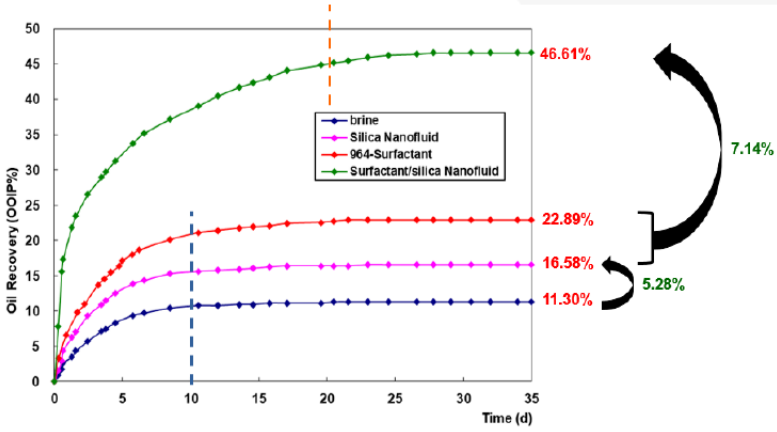
Physical properties of Berea core samples

Core	Imbibing liquid	Ø, %	K, md
B1	15wt%NaCl brine	19.06	90.72
B2	964-surfactant solution	18.01	88.62
B3	Silica nanofluid	18.68	89.27
B4	Surfactant-silica nanofluid	18.25	91.39

Note: 964-Surfactant (Alcohol polyethylene glycol ether carboxylic sodium)



Imbibition experiment at 65°C

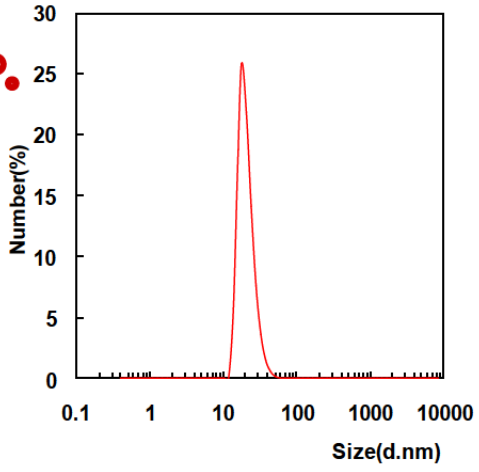


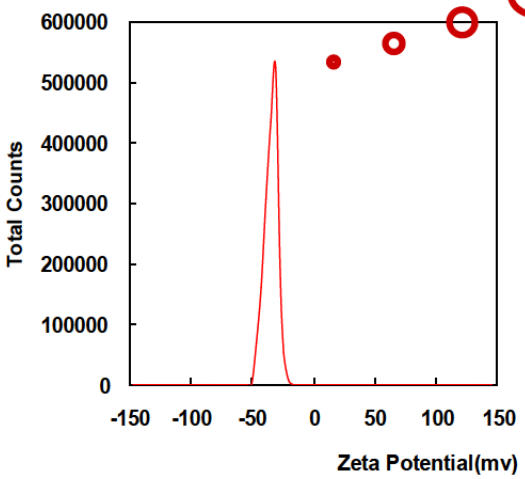
Oil recoveries of spontaneous imbibition

Polymer Nanoparticles

DLS: 15~25nm

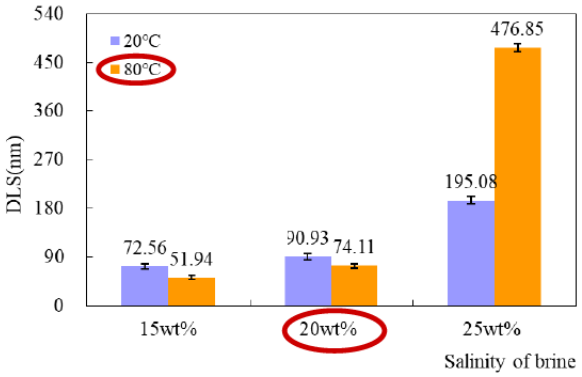
Zeta Potential: -40~-35mv





Particle size and ζ potential distribution of polymer NPs in deionized water

Nanofluid: Polymer NPs + Surfactant (Betaine)



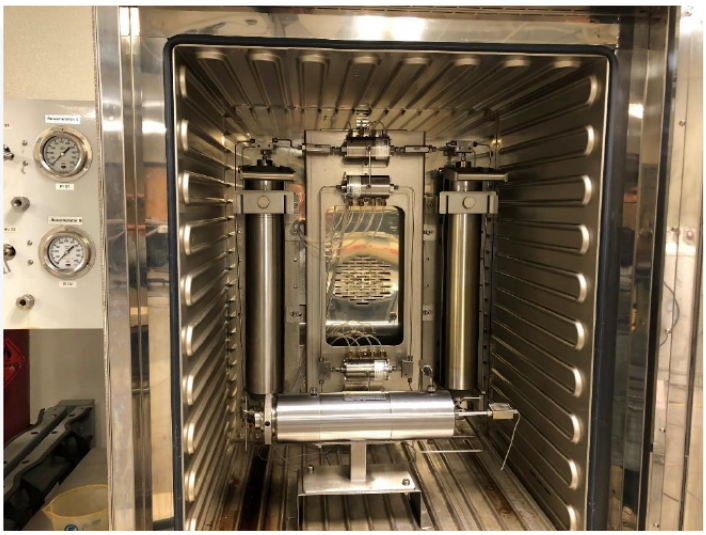
Stability test: effect of temperature and salinity

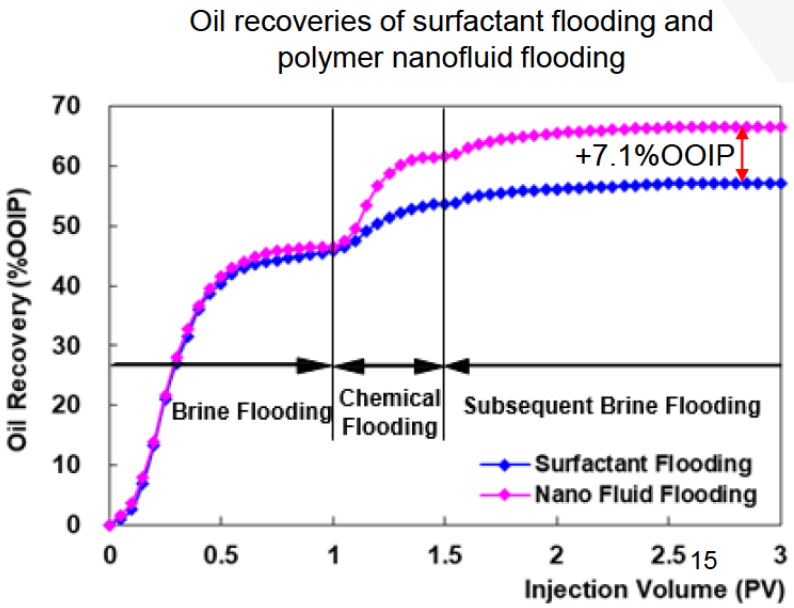
Effect of brine salinity and temperature on particle sizes of polymer nanofluid

Composition of brines

Ions	Na^+	Ca^{2+}	Mg^{2+}	K^+	Cl^-	TDS
mg/L	45639	8258.5	833.5	4340	91338	150,409
	60845	11011	1111	5787	121783	200,537
	76055	13765	1390	7235	152045	250,490

Nanofluid: Polymer NPs + Surfactant (Betaine)

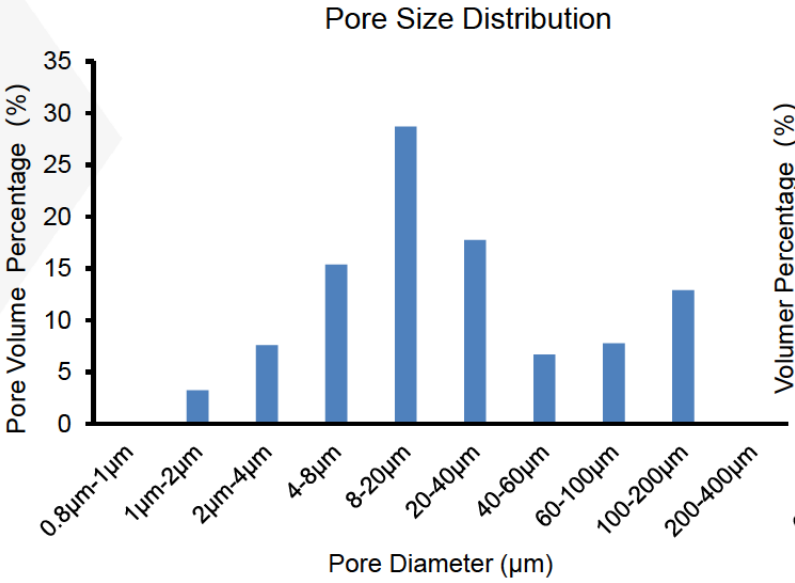


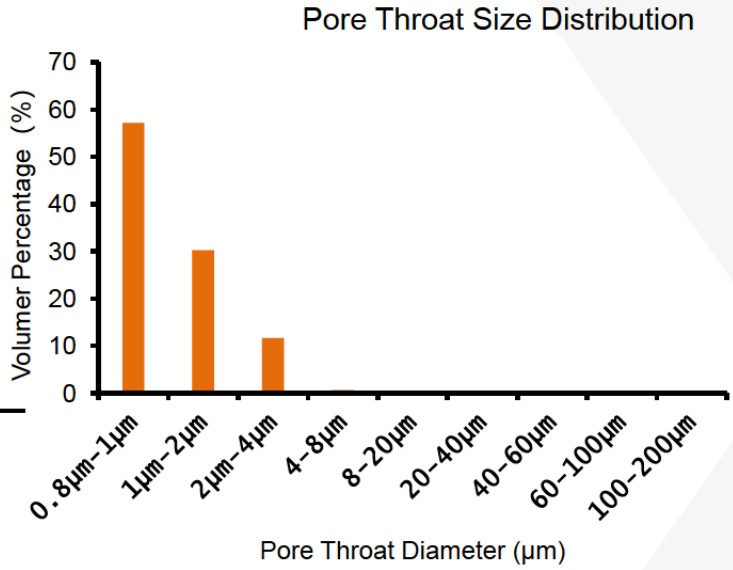


Bakken Core Sample Characterization

Bakken Core Sample Characterization

Pore and throat sizes by digital rock analysis





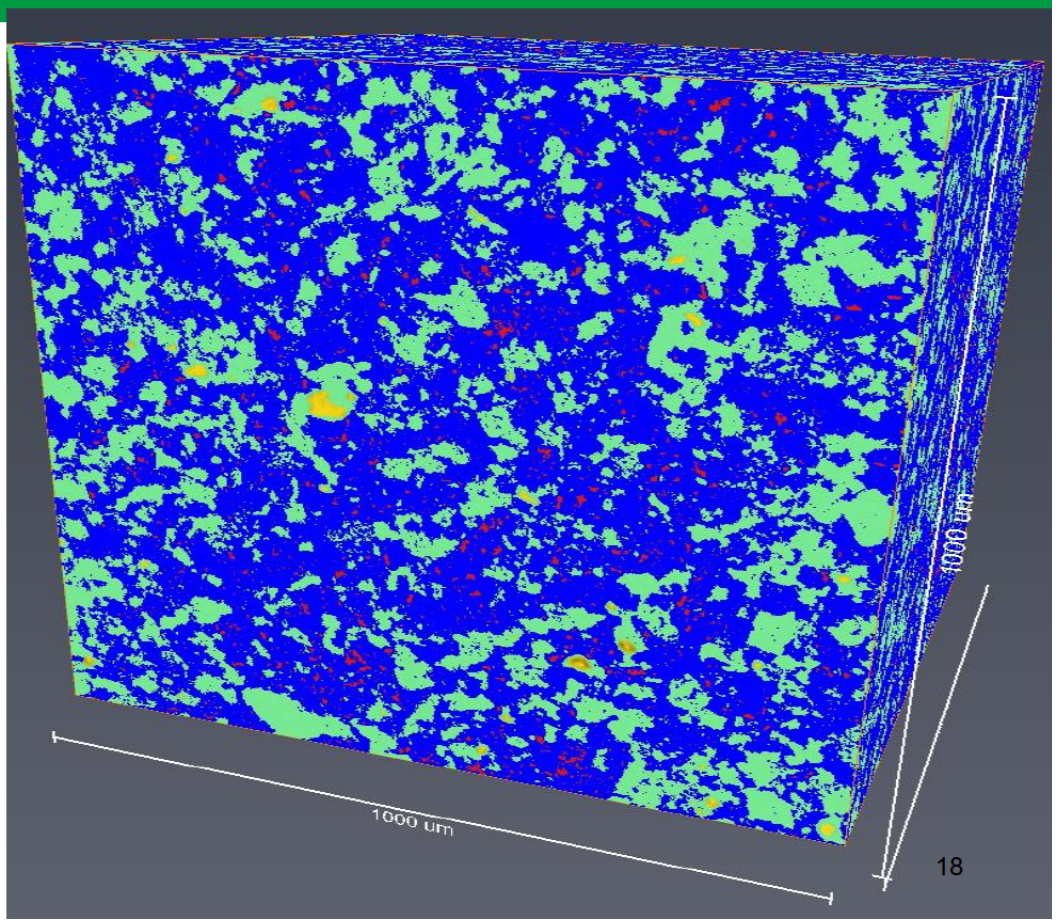
Range of main pores diameters: 4-40μm

Range of main pore throat sizes: 0.8-2μm

Bakken Core Sample Characterization

Micro-CT:

μ-CT Analysis of Bakken Rock (blue: SiO_2 and silt; green: calcite; yellow: heavy minerals; red: pores)



Molecular Dynamics Simulation

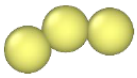
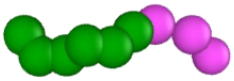
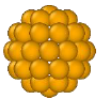
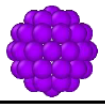
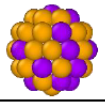
Molecular Dynamics Simulation

Simulation Platform: LAMMPS

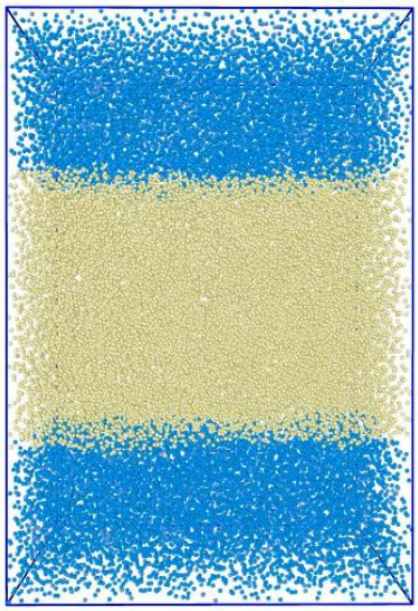
Large-scale atomic/molecular massively parallel simulator (LAMMPS).

- Distributed by Sandia National Laboratories
- A classical molecular dynamics code with a focus on materials modeling.

Models used in the simulations

	Water
	Rock
	Dodecane (C_{12})
	Non-ionic surfactant ($C_{12}E_5$)
	Hydrophilic nanoparticle
	Hydrophobic nanoparticle
	Amphiphilic nanoparticle

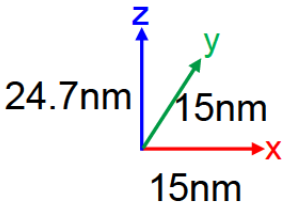
Molecular Dynamics Simulation



Water phase

Oil phase

Water phase



MD simulation of C_{12}/water interface, 300K, 1 atm

(γ_{sim} = 51.30±0.18 , γ_{exp}=52.8 mN/m)

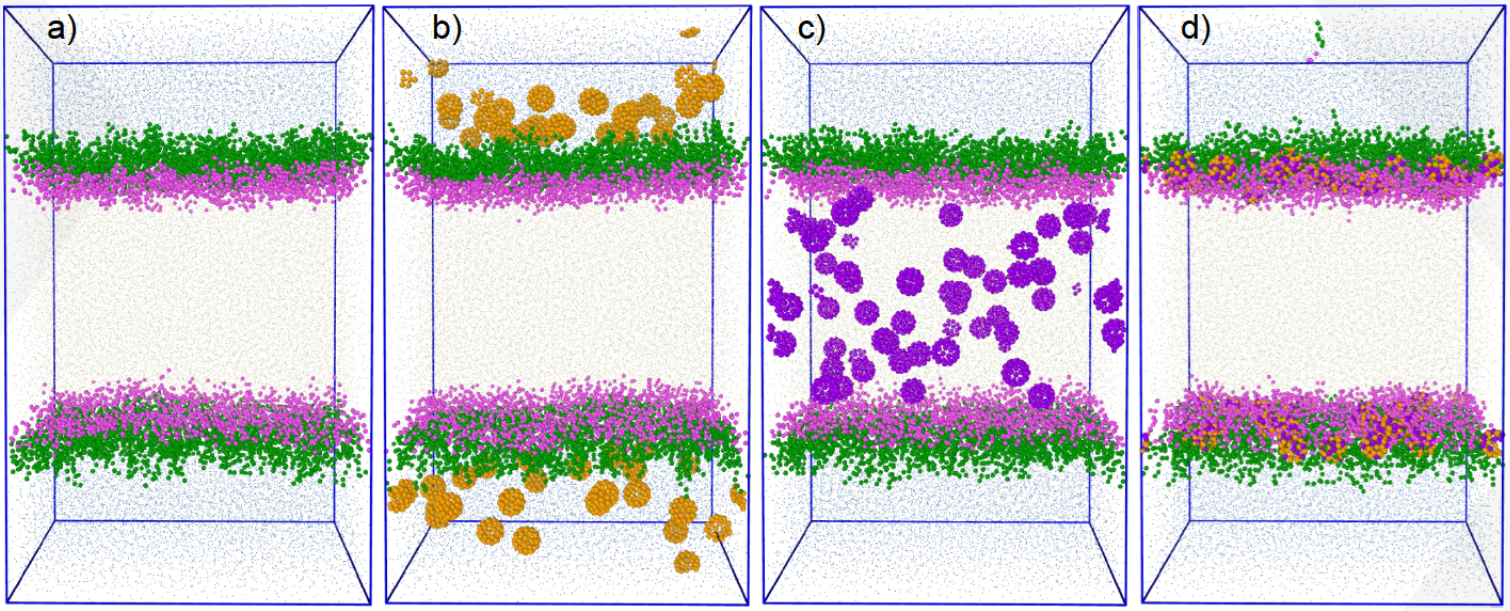
Molecular Dynamics Simulation

a) Surfactants

b) Hydrophilic NPs/surfactants

c) Hydrophobic NPs/surfactants

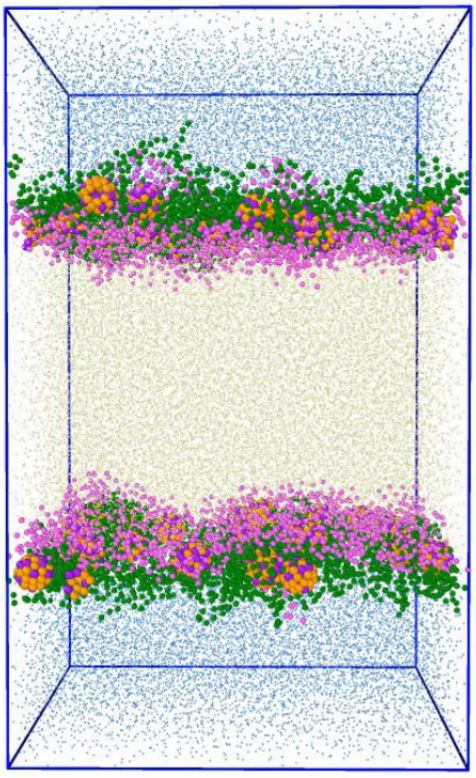
d) Amphiphilic NPs/surfactants

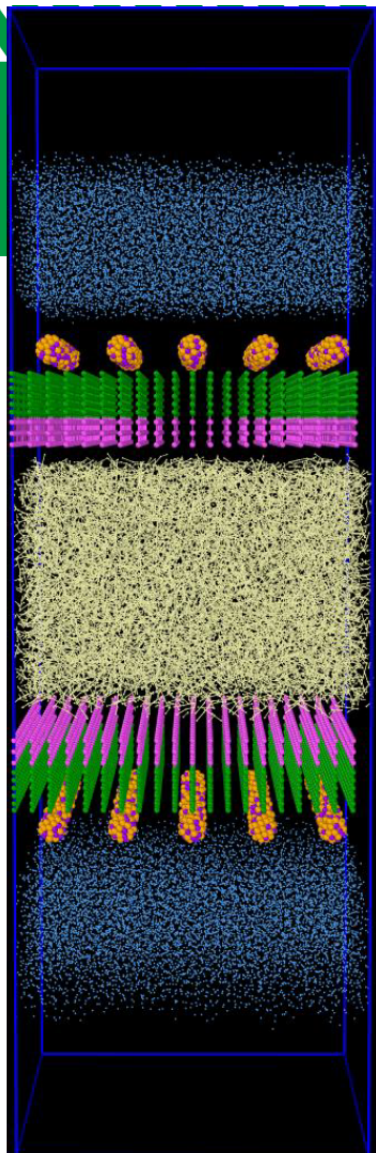


MD simulations of surfactants and NPs/surfactants in the vicinity of the oil/water interface

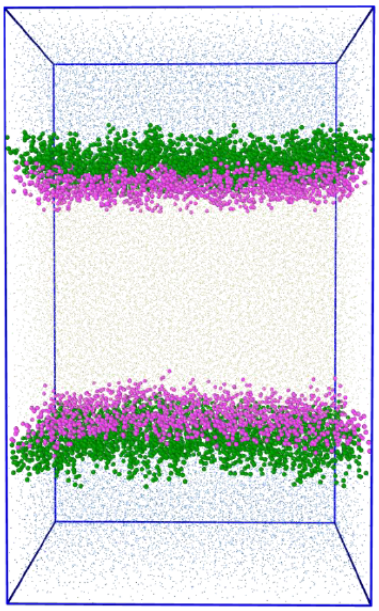
Molecular Dynamics Simulation

Equilibrium condition



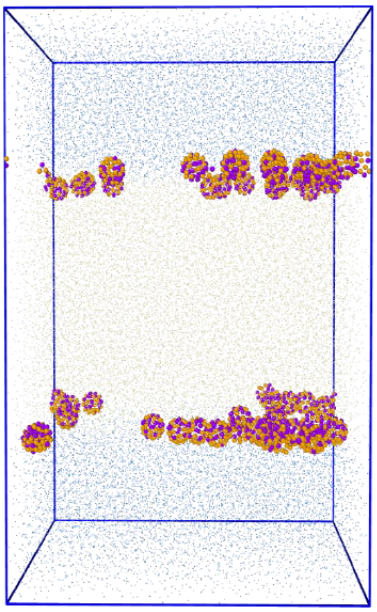


Molecular Dynamics Simulation



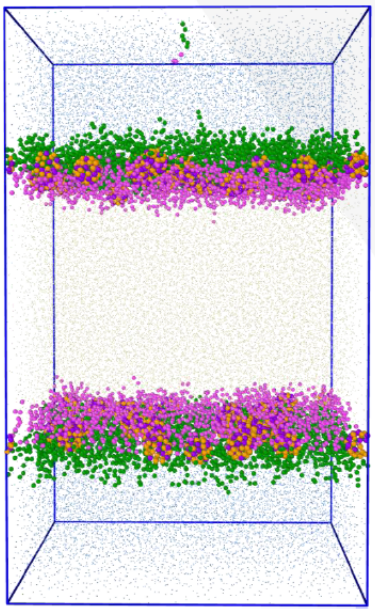
Surfactants

IFTs: 22.10±0.18 mN/m



Amphiphilic NPs

51.32±0.03nN/m



Amphiphilic NPs/Surfactants

19.42±0.13nN/m

Next Steps

- Synthesis of smaller size nanoparticles
- Improve the nanofluid stability under Bakken conditions
- Molecular dynamics simulation of wettability alteration by nanoparticle-surfactant
- Develop nanofluid systems for Bakken EOR

Project Budget

Sponsor	Budget	Expenses as of 12/17/2018	Balance
NDIC OGRP	$678,933	$333,050.57	$345,882.43

- This project is supporting 3 PhD students and 1 master student in Petroleum Engineering Department
  - Chuncheng Li (started Fall 2017)
  - Shaojie Zhang (started Fall 2017)
  - Xun Zhong (started Fall 2017)
  - Runxuan Sun (M.S., started Fall 2017)

- This project is supporting 1 PhD student and 1 Postdoctoral associate in Chemistry Department

Publications (including articles in preparation)

- Xun Zhong, Hui Pu, Yanxia Zhou, Julia Zhao, *Comparative Study on the Static Adsorption Behavior of Zwitterionic Surfactants on Minerals in Middle Bakken Formation*, submitted to *Energy & Fuels* on Nov 19, 2018.
- Xun Zhong, Hui Pu, Yanxia Zhou, Julia Zhao, *SPE-193589 Static Adsorption of Surfactants on Bakken Rock Surfaces in High Temperature, High Salinity Conditions*, *SPE International Conference on Oilfield Chemistry*, 8 - 9 Apr 2019, Galveston, Texas.
- Runxuan Sun, Hui Pu, Wei Yu, Jijun Miao, *Reservoir Simulation Study of Surfactant Injection in Middle Bakken Well*, to be submitted to *Fuel* in January 2019
- Yanxia Zhou, Xu Wu, Xun Zhong, Wen Sun, Julia Zhao, Hui Pu, *Modified Silica Nanoparticle and its Nano fluid for Enhanced Oil Recovery*, to be submitted to *ACS Applied Materials & Interfaces* in January 2019
- Yanxia Zhou, Xu Wu, Xun Zhong, Julia Zhao, Hui Pu, *Self-Assembled Polymer Nanoparticle and Its Nanofluid for Enhanced Oil Recovery in Harsh Formation Conditions*, to be submitted to *ACS Applied Materials & Interfaces* in March 2019

Publications (including articles in preparation)

Abstracts Submitted to SPE Conferences (Under Review)

- Chuncheng Li, Hui Pu, Julia Zhao, *Effect of Nanoparticles and Surfactants on Oil/Water Interfacial Tension: a Coarse-Grained Molecular Dynamics Simulation Study*, abstract submitted to 2019 Unconventional Resources Technology Conference (URTeC), Denver, CO, on Dec 4, 2018).
- Shaojie Zhang, Hui Pu, Julia Zhao, *Experimental and Numerical Study on Spontaneous Imbibition in Bakken Samples: Incorporation of Effect of Bedding Heterogeneity on Recovery*, abstract submitted to 2019 Unconventional Resources Technology Conference (URTeC), Denver, CO, on Dec 4, 2018).
- Xun Zhong, Hui Pu, Yanxia Zhou, Julia Zhao, *Preparation and Evaluation of Novel Nanofluids for Enhanced Oil Recovery Applicable at High Saline Conditions*, abstract submitted to 2019 Unconventional Resources Technology Conference (URTeC), Denver, CO, on Dec 5, 2018).

Questions?

Thanks!