Evaluation of nano-CTAB surfactant for the purpose of enhancing oil recovery in an Iranian carbonate reservoir

M. Abuzaryan, H. A. Akhlaghi Amiri*, A. Ahmadpour, R. Mohammadi Pour
Chemical Engineering Department, Faculty of Engineering, Ferdowsi University of Mashhad, Mashhad, Iran
ha.akhlaghi@um.ac.ir

Abstract
In this research, Cetyltrimethylammonium Bromide (CTAB) nano-emulsions were prepared at 0.05 and 0.1 wt% and evaluated in comparison with conventional CTAB emulsions. Particle size analysis showed that average CTAB nano-surfactant particle size was approximately 60 nm, much lower than that of the CTAB emulsions. Zeta potential analysis was used to evaluate the stability of the emulsion and demonstrated that CTAB nano-surfactant was more stable than the normal surfactant. CTAB Nano-surfactant also showed lower interfacial tension with the crude oil sample, in comparison with CTAB surfactant. The interfacial tension was more decreased by increasing the surfactant concentration. Wettability tests with carbonate rock powder, oil and CTAB emulsion/nano-emulsion showed that these surfactants are able to alter the rock wettability toward more water-wet condition. Spontaneous imbibition tests were performed at 50 ^{0}C on the oil saturated carbonate core samples with brine, surfactant and nano-surfactant, respectively. However, stable emulsions of oil in the aqueous phase made estimating the amount of oil recovery impossible.

Keywords: CTAB, Nano-Surfactant, enhanced oil recovery, spontaneous imbibition.

Introduction
Although demanding for petroleum supplies is growing rapidly, the potential of oil reservoirs is decreasing. In this respect, it's essential to efficiently produce more oil from the reservoirs through advanced techniques. Enhanced oil recovery methods are those techniques which help to increase oil recovery, whenever primary and secondary recoveries are declining [1]. Changing the rock wettability, oil-water interfacial tension (IFT) and mobility ratio are the main mechanisms used to produce additional oil from rock matrices. Surfactants [2], nanoparticles [3], polymer [4], and alkali [5] are popular chemical agents used to improve conventional water-flooding processes. Literature offers numerous reports on the study of different parameters related to oil production using chemical agents.
Imbibition experiments with core plugs, both 100% oil-saturated and containing initial water, using anionic, nonionic and cationic surfactants were carried out by Babadagli and Boluk in 2005. They observed that in the case of 100% oil saturation, nonionic IGEPAL and the cationic CTAB had better results at low concentrations [6]. Jarrahian et al. (2012) studied the effect of nonionic (Triton X-100), cationic (C12TAB) and anionic (SDS) surfactants on the wettability of dolomite cores. Their experiments showed that C12TAB change the wettability toward

water-wet conditions more efficiently than other surfactants [7]. Karimi et. al. investigated wettability and spontaneous imbibition of DTAB surfactant in different brine formulations. It was revealed that diluted brine changed the limestone core wettability to a more water-wet state. As a result, much more oil could be recovered [8]. Samantha in 2017 [9] showed that increasing C16TAB surfactant concentration maintain the oil-wet characteristic of the limestone sample, nevertheless, the oil recovery increases due to less adsorption of surfactant molecules on the rock surface.
Obviously, the smaller the particle and/or nanoparticle, the more the surface area and activity. Dehaghani (2018) synthesized CTAB nano-surfactants and examined their effects on interfacial tension and enhanced oil recovery before and after treatment by a magnetic field with different intensities through core flooding tests in 2018. He concluded that increasing both concentration and temperature can reduce IFT to small values. Although increasing CTAB concentration promotes oil recovery, it is barely affected by higher magnetic field intensities [10].
In the present work, Cetyltrimethylammonium Bromide (C16TAB) nano-surfactant was prepared successfully and its effect on an Iranian tight carbonate reservoir with heavy oil was investigated. Also, the performance of C16TAB and Nano-C16TAB are compared.

Experimental

Material

Cetyltrimethylammonium Bromide (CTAB) of 99% purity, which is a cationic surfactant, and NaCl of 99.9% purity were purchased from Merck, Germany. Kerosene and Heptane with 99% purity were prepared from Dr Mojlali Company.
Three carbonate cores, mostly limestone, from an Iranian oil field, supported by National Iranian South Oil Company (NISOC), were used for the experiments. One of them was crushed and powdered, for wettability test; and the other two cores were used for spontaneous imbibition tests. The cores had moderate porosity, which their properties are listed in Table 1.
Crude oil was prepared form the same oil field, supported by NISOC, with density of 0.85 g/cm^3 (^{O}API=34). The crude oil was centrifuged (12000 rpm) and filtrated through Millipore filter to eliminate contamination and particles.

Methods

1-Homogenizing

For the preparation of CTAB emulsion, 0.05 wt% and 0.1wt% of surfactant emulsions were mixed in the brine with 30000 ppm (NaCl) salinity. The samples then were agitated for 105 minutes using ultrasonic homogenizer to make CTAB nano-emulsion. Homogenizing was done at a frequency of 20 kHz at a temperature of 20-30 ºC [11].

2-DLS tests

The dynamic light scattering (DLS) test was conducted by Particle Size Analyzer model Vasco3 made by Cordouan Company. The tests were carried out on CTAB and nano-CTAB surfactant with 0.05% and 0.1%wt concentration at the presence and absence of NaCl at 50 oC.

3-Zeta Potential

Zeta Compact was used to measure the zeta potential of the samples. First, 10 ml of CTAB emulsion and nano-emulsion were added to different bottle tests. Then, they were heated up to 50 oC in an oil bath for two days.

4-IFT Measurement
The IFT measurements between oil and brine containing surfactant were performed at ambient temperature (22.5-25.2 °C) by using a ring tensiometer model KRUSS-K100. The IFT measurements were performed using brine with different surfactant and nano-surfactant concentrations, keeping the total salinity constant at 30000 ppm by adjusting NaCl concentration.

5-Wettability Measurements
5 ml of the prepared samples (brine and emulsion/nano-emulsion with 0.05 wt% CTAB) were added to different vials containing 2.5 grams of the carbonate rock powder. Then, they were mixed in a magnetic stirrer for 24 hrs at ambient temperature. Afterwards, 5 ml of oil were added to each vial and the mixture was stirred for 48 hrs. Finally, the vials were placed stationary on a flat surface to become stable and ready for analysis.

Table 1. Carbonate core properties, used for spontaneous imbibition test.

Core	Length (mm)	Diameter (mm)	Porosity (%)
1	89.83	24.44	18.48
2	64.42	24.22	19

6-Core handling
In order to obtain homogeneous wetting conditions, the cores were handled according to the procedures described by Standnes and Austad [12]. Mild cleaning of the core was performed by Kerosene and n-heptane, to displace the kerosene, and finally with DIW, using Soxhlet extractor. The core was then dried at 90 oC to a constant weight.

7-Core Saturation
The dry core was 100% saturated with oil under vacuum, placed in a desiccator saturation setup at room temperature. The saturated cores were left immersed in oil for at least 1 days. Porosity and pore volume were determined from the change in weight.

8-Core Aging
The cores were aged, immersed in oil, in a stainless-steel aging cell at 90 ^{o}C for 2 weeks.

9-Spontaneous imbibition test
After the aging process, the cores were placed in Amott cells for spontaneous imbibition studies at 50 ^{o}C. The cells were filled with the actual imbibing fluid (first brine and then surfactant emulsions) in each step, and the amount of oil produced (% OOIP) was recorded with time on a graded scale.

Result and discussion
DLS test was conducted on CTAB emulsions. Figure 1 and 2 show the particle size of emulsions made by 0.05%wt and 0.1%wt CTAB concentrations, respectively. The effects of salinity (NaCl) and temperature (50 ˚C) were studied. CTAB in both concentrations has the peak in particle size in the range of 200 to 800 nm. CTAB particle size was slightly increased by salinity and temperature, may be caused by molecular collisions and interactions between sodium-chloride ions and CTAB particles. Also, the thickness of the electrically permeable

layer at the presence of salt is reduced with increasing electrolyte concentration in the solution [13].

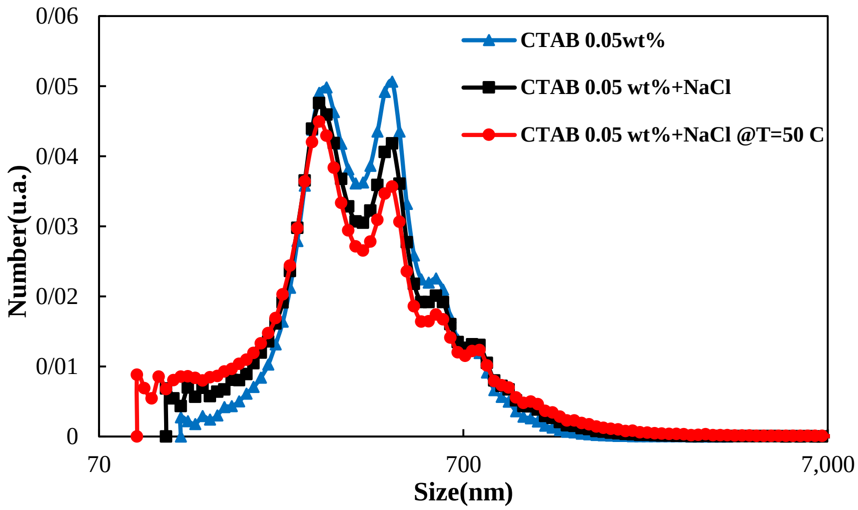


Figure 1. Particle size of CTAB at 0.05wt% at different salinity and temperatures.

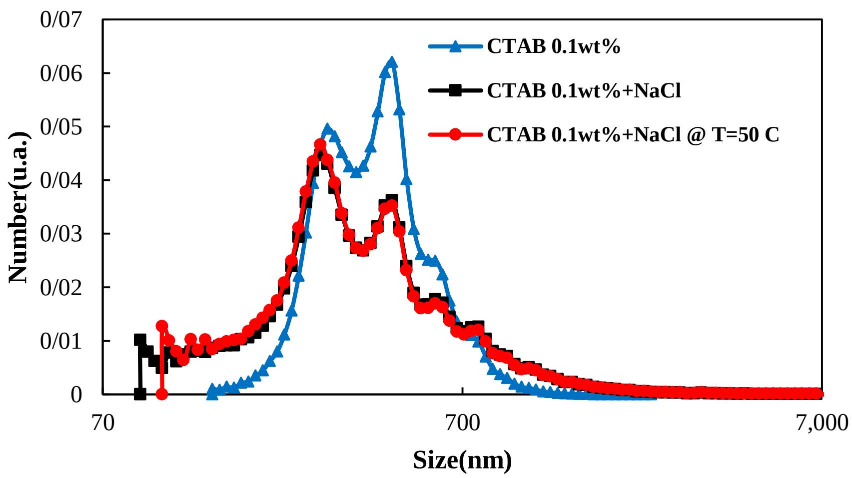


Figure 2. Particle size of CTAB at 0.1wt% at different salinity and temperatures.

Figure 3 and 4 show the particle size of emulsions made by 0.05%wt and 0.1 % wt nano-CTAB surfactant. The effects of salinity and temperature were also studied. As shown in Figures 3 and 4, the peak of nano-CTAB particle size is decreased to about 30 nm, due to the homogenizing process that confirmed the nano-scale size of the particles. Nano-CTAB samples with concentrations of 0.05 wt% and 0.1 wt% include 92% and 86% of the particles that were less than 100 nm, respectively. The three peaks in the 0.05 wt% CTAB nano-emulsion diagram (Figure 3) shows that the particles with the sizes of 32, 39 and 45 nm are the most abundant. The average particle size was reported in the range of 61 nm, in this case. In the 0.1 wt% nano-CTAB emulsion (Figure 4), most of the particles have the sizes of 32, 37, 42 and 49 nm, with the average particle size of 74 nm. In the presence of salt (30000 ppm NaCl) and then exposed to 50 ^{o}C, nano-CTAB particle sizes were less affected. Due to the smaller particle sizes, the electrostatic forces and molecular interactions are less pronounced in the case of the nano-CTAB emulsions.

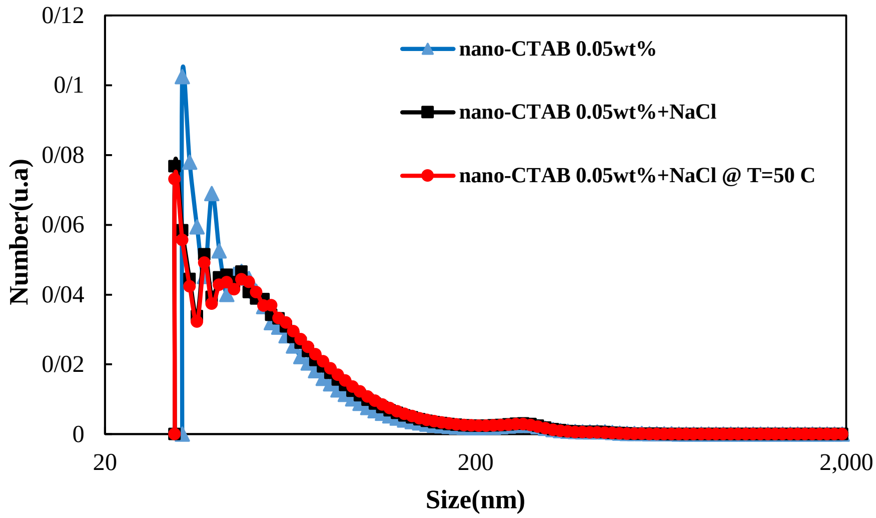


Figure 3. Particle size of nano-CTAB at 0.05 wt% at different salinity and temperatures.

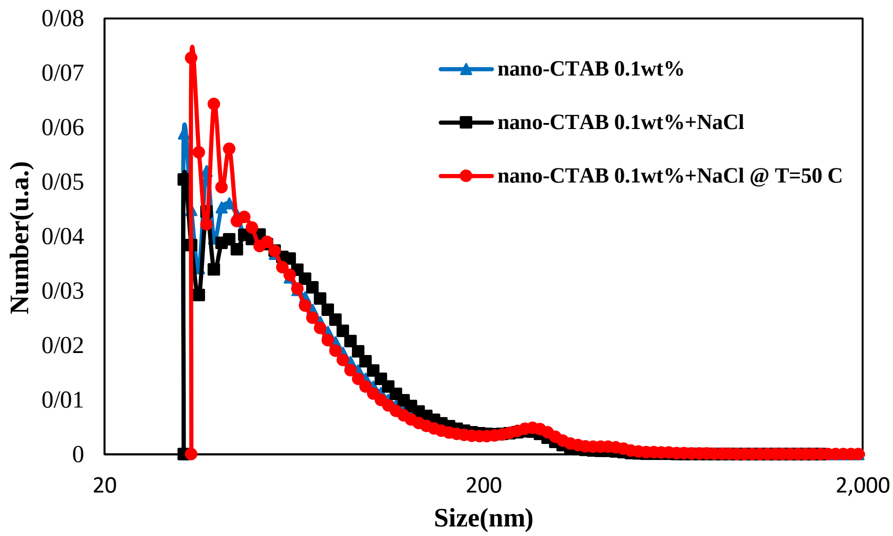


Figure 4. Particle size of nano-CTAB at 1 wt% at different salinity and temperatures.

Figure 5 shows the zeta potential results for CTAB and nano-CTAB emulsions at two concentrations. Charge of the particle, whether negative or positive, corresponds with a negative or positive zeta potential. The positive sign of the measured zeta potentials confirms the cationic nature of the CTAB surfactant [14]. In 0.05 wt% CTAB emulsion, the mean zeta potential value was 7 mV, while in 0.1 wt %, it was slightly increased to 9 mV. It's probably due to strong electrostatic repulsion between particles as a result of increased steric hindrance. In the case of nano-emulsion zeta potential was increased from 18 to 19 mV, by increasing concentration. As it clear in figure 5, the mean zeta potential in the CTAB nano-emulsions is considerably higher than that of the CTAB emulsions. It could be attributed to the influence of gravity that becomes negligible on nanoparticles; thus, the dispersion stability and the mean zeta potential was increased.

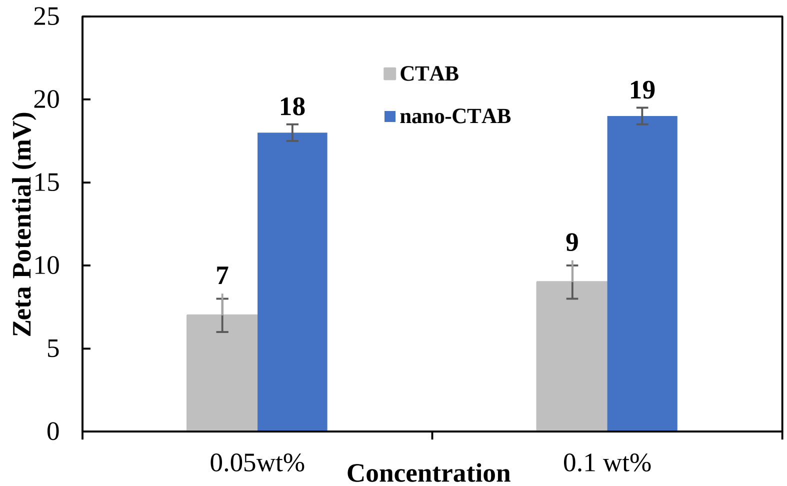


Figure 5. Zeta potential analysis of CTAB and nano-CTAB at different concentrations.

The lower the tensile force at interfacial of an oil-in-water emulsion, the easier the movement of the molecules present at the oil surface and thus the easier the oil droplet to deform [5]. According to Table 2, the IFT between oil and the surfactant emulsions (containing NaCl) was decreased by an increase in the concentration of both surfactant and nano-surfactant. The IFT between oil and pure brine was 26.2 mN/m; which employing CTAB at 0.05 and 0.1 wt% reduced this value to 1.17 and 0.53 mN/m, respectively. In the case of CTAB nano-surfactant, the values of 0.74 and 0.27 mN/m were obtained by increasing concentration. More surface area and thus more surface activity of the CTAB nano-surfactant compared with CTAB surfactant may be the reason for this further IFT reduction [15].

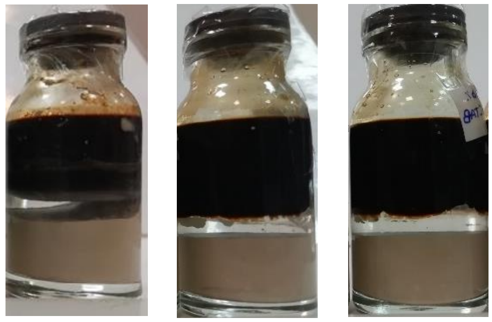
Table 2. Interfacial tension of brine and CTAB emulsion/nano-emulsion with crude oil.

Sample	IFT (mN/m)
CTAB 0.05wt% - oil	1.17
nano-CTAB 0.05wt% - oil	0.74
CTAB 0.1wt% - oil	0.53
nano-CTAB 0.1wt% - oil	0.27

In the wettability test (shown in Figure 6), as the fluids became stable, the water column was surrounded by the water/oil interface in one side and the water/rock interface at the other side. As Figure 6 shows, the water column was thickened in the presence of CTAB emulsion/nano-emulsion compared to the pure brine. The cationic CTAB surfactant interacts with negatively carboxylate groups in oil, thus may reduce their tendency to carbonate powders' surface, which have positive charge. Therefore, CTAB surfactant (and nano-surfactant) may be capable of altering the rock wettability toward more water-wet condition.

Table 3. Spontaneous imbibition process and recovery on the two cores.

Test	Core	Oil recovery by synthetic brine	Second Imbibing fluid
(A)	1	4.3	CTAB 0.05 wt%
(B)	2	5.4	Nano-CTAB 0.05 wt%
(C)	1	4.4	CTAB 0.1 wt%
(D)	2	5.4	Nano-CTAB 0.1 wt%



(A) (B) (C)

Figure 6. Wettability test in presence of (A) brine, (B) CTAB emulsion and (C) CTAB nano-emulsion.

Table 3 shows the process and the oil recovery by spontaneous imbibitions method of synthetic brine and CTAB emulsions/nano-emulsions with 0.05 wt% and 0.1 wt% concentration at 50 ˚C. The oil recovery in the core 2 with the brine was slightly higher than core 1 in both tests; which is attributed to the cores' characterizations. After imbibition test by synthetic brine, the cores were immersed in CTAB emulsions/nano-emulsions in Amott cells, as shown in Table 3. However, stable oil in water emulsions were formed during all conducted imbibition tests in presence of CTAB emulsions/nano-emulsions. So, estimating the amount of oil recovered was impossible. Considering wettability tests, this behavior may be explained by higher temperature (^{o}50) that leads to greater reduction of interfacial tension to ultra-low values [16].

Conclusion

In this study, CTAB nano-emulsions at 0.05 and 0.1 wt% were prepared and their effect on the recovery of crude oil from an Iranian carbonate cores was tested, in comparison with conventional CTAB surfactant emulsion. Particle size analysis showed that the particle size of the CTAB nano-surfactants were approximately 60 nm. So, it was in nano-scale size. Zeta potential analysis confirmed that nano-surfactants are more stable than the surfactants. Also, the CTAB surfactant concentration improved stability of the enhanced oil recovery fluid. The interfacial tension of brine-oil was lower in the presence of CTAB surfactants, which led to a further decrease by increasing the concentration and the use of nano-surfactants. Also, CTAB surfactant is capable of altering the rock wettability toward more water-wet condition Spontaneous imbibition tests in the presence of the CTAB surfactant and nano-surfactant in the second stage provided emulsions of oil in the aqueous phase that made estimating the amount of oil recovery impossible even after a long time.

Reference

[1] Bahadori, A., Fundamentals of enhanced oil and gas recovery from conventional and unconventional reservoirs, Australia, (2018)

[2] Chen, S., Liu, H., Sun, H., Yan, X., Wang,G., Zhou, Y. and Zhang, J., "Synthesis and physiochemical performance evaluation of novel sulphobetaine zwitterionic surfactants from lignin for enhanced oil recovery," J. Mol. Liq., 249, 73–82, (2018).

[3] Peng, Z., Zhang, B., Luo, L., Wang, J., Ding, P., Zeng, B. and Cheng, M., "A review of nanomaterials for nanofluid enhanced oil recovery," RSC. Adv., 7, (2017).

[4] Firozjaii, H.R. and Saghafi, A.M., "Review on chemical enhanced oil recovery using polymer flooding: Fundamentals, experimental and numerical simulation," Petroleum, (2019).

[5] Olajire, A.A., "Review of ASP EOR (alkaline surfactant polymer enhanced oil recovery) technology in the petroleum industry: Prospects and challenges," Energy, 77, 963–982, (2014).

[6] Babadagli, T. and Y. Boluk, "Oil recovery performances of surfactant solutions by capillary imbibition," J. Colloid Interface Sci., 282, 162–175, (2005).

[7] Jarrahian, K., Seiedi, O., Sheykhan, M., Sefti, M.V., and Ayatollahi, S., "Wettability alteration of carbonate rocks by surfactants: A mechanistic study," Colloids Surfaces A Physicochem. Eng. Asp., 410, 1–10, (2012).

[8] Karimi, M., Al-Maamari, R.S., Ayatollahi, S., and Mehranbod, N., "Wettability alteration and oil recovery by spontaneous imbibition of low salinity brine into carbonates: Impact of Mg2+, SO42− and cationic surfactant," J. Pet. Sci. Eng., 147, 560–569, (2016).

[9] Santanna, V.C., Castro Dantas, T.N., Neves, A.M., Lima, J.R.D., and Nóbrega Pessoa, C., "Recovery of oil in limestone with cationic surfactant: investigation of the adsorption, wettability, and spontaneous imbibition," J. Pet. Sci. Technol., 8, 72–80, (2018).

[10] Dehaghani, A.H.S. and Badizad, M.H., "Effect of magnetic field treatment on interfacial tension of CTAB nano-emulsion: Developing a novel agent for enhanced oil recovery," J. Mol. Liq., 261, 107–114, (2018).

[11] Standnes, D.C. and Austad, T., "Wettability alteration in chalk: 1. Preparation of core material and oil properties," J. Pet. Sci. Eng., 28, 111–121, (2000).

[12] Esmaeeli, J., Kharrat, R., Barati, N. and Sobhani, A., "Stability of silica nanoparticle dispersion in brine solution: an experimental study," Iran. J. Oil Gas Sci. Technol., 3, 26–40, (2014).

[13] Mcelfresh, P.M., Wood, M. and Ector, D., "Stabilizing nano particle dispersions in high salinity, high temperature downhole environments," SPE Int. Oilf. Nanotechnol. Conf. Exhib., 2012.

[14] Sun et al., X., "Application of nanoparticles in enhanced oil recovery: a critical review of recent progress", Energies, 10, 1-33, (2017).

[15] Hou, B.F., Wang, Y.F. and Huang, Y., "Study of spontaneous imbibition of water by oil-wet sandstone cores using different surfactants", J. Dispers. Sci. Technol., 36, 1264–1273, (2015).

[16] Liu, Q., Dong, M. and Ma, S., "Alkaline/surfactant flood potential in western canadian heavy oil reservoirs", SPE/DOE Symp. Improv. Oil Recovery. (2006).