SURFACTANT-INDUCED WETTABILITY ALTERATION

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ABSTRACT

Contact of surfactant solution onto rock surface has an important impact on the wettability alteration of the rock. This phenomenon has widely received attention of researchers on the field of EOR (enhanced oil recovery), at which surfactant solution basically has been used as the main injection fluid. However, there has not yet come up with conclusive findings, which is due to the unique characteristics of surfactant used at the oil fields. Therefore, every surfactant needs a particular laboratory evaluation before injected into a reservoir.

We have evaluated surfactant-induced wettability alteration by means of contact angle measurement. Three kinds of surfactant have been used in this experiment, namely: TFSA (thin film spreading agent), IFT-R (interfacial tension reduction), and Well Stimulator type of surfactants. Two kinds of rocks namely LS (limestone) and SL (sandy limestone) have also been prepared. Both rocks are originally oil wet.

TFSA-LS interaction tend to decrease the oil preferences with time, the contact angle increased 30 degrees after 8 weeks. Whereas TFSA-SL experienced only a little change of contact angle. Contact IFT-R and LS has changed significantly the contact angle to around 51degrees indicating less oil preference. Whereas, IFT-R and SL only changed a bit to less oil wet. The stimulator type of surfactant obviously lessen the oil wet tendency for the both rocks, the contact angles increase from initially around 15 to 35 degrees. In this experiment we found out that all the three surfactants generally tend to change the wettabillity to less oil wet.

Key words: surfactant, wettability change, contact angle

I. INTRODUCTION

Primary and secondary oil recovery processes typically only recover approximately one third of original oil in place, while leaving two-third trapped in the reservoirs as residual oil. The only innovative technology to recover the remaining oil at this stage is EOR methods. Chemical injection is the one that has been implemented in many oil fields with successful results. Chemical injection consists of AS (alkaline-surfactant mixture), SP (surfactant-polymer mixture), and ASP (alkaline-surfactant-polymer mixture) injections. They can be arranged to be injected into a reservoir as a series of order injection fluids but also possibly stand alone fluid injection. Surfactant is an important chemical not only for reducing the interfacial tension of the injected fluid but also for creating wettability changes.

Understanding of the interaction that takes place between crude oil, brine, and rock surface which are collectively represented by the term wettability is very important when chemical injection will be initiated. Rock wettability basically dictates the recovery mechanism during the EOR processes. Moreover, surfactant which consists of polar compounds can make rock wettability alteration. Therefore, a detail study of the wettablity changes in surfactant injec-

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tion is necessary to get the EOR processes implemented successfully.

II. LITERATURE REVIEW

Several papers have been published discussing the effect of surfactant injection on the induced wettability alteration. Experiments conducted to account the wettability changes have been performed to use several methods such as: oil recovery of coreflood experiments, relative permeability constructions, and contact angle measurements. But so far, there are no comprehensive conclusions regarding the relationship between the type of surfactant and wettability nature (oil wet or water wet). The interaction between reservoir fluid/rock and every type of surfactant is very complex and difficult to predict. Therefore, detailed laboratory tests should be done to anticipate the wettability changes at any surfactant injection proposal.

A. *Surfactants*

Surfactants are polar compounds that consist of an amphiphilic molecules with both hydrophilic and hydrophobic parts. The surfactants are classified as; anionic, cationic, amphoteric, nonionic depending upon the nature charge present on the hydrophilic group. The role of surfactants in the EOR processes is not only to lower oil-water interfacial tension but also to alter the reservoir wettability.

The mechanism of surfactant injection to improve oil recovery can be understood through the definition of a dimensionless number called “capillary number”.

Table 1
X-Ray diffraction analysis results

No.	Rock type	Illite	Chlorite	Calcite	Quartz	K-Felds	Plagioclase
1	Limestone	-	-	100	trace	-	-
2	Sandy Limestone	2	5	48	38	5	2

Table 2
Result of water analysis

Constituents	meq/L	mg/L
Sodium	267.49	6,151.50
Calcium	25.45	510.1
Magnesium	5.13	62.4
Iron	0.08	2.3
Barium	0	0
Total Cations (excl. Fe)		6,724.00
Chloride	281.4	9,977.60
Bicarbonate	9.52	580.8
Sulphate	7.15	343.6
Carbonate	0	0
Hydroxide	0	0
Total Anions		10,902.00
Total Equiv. NaCl Conc.		17,067.10
pH		7.45

Table 3
Oil Composition

Component		Mol Percent
Carbon Dioxide	CO_2	0.01
Methane Plus	C_{1+}	3.01
Iso-Butane plus	$i\text{-}C_{4+}$	5.47
Hexanes Plus	C_{6+}	2.23
Heptanes Plus	C_{7+}	89.28
Total		**100.00**
Properties of Heptanes Plus:		
API Gravity @ 60 ^{O}F		37.06
Specific Gravity @ 60/60 ^{O}F		0.8386
Molecular Weight		157.52

Table 4
Oil characteristics

Analysis	Result	Units
Acid number	0.085	mgKOH/g
Pour point	78	^{o}F
Asphaltene content	0.82	%
Resin content	3.04	%
Wax content	25.46	%

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The increasing capillary number of several orders of magnitude can release the residual oil behind the capillary trap and make it flow into the well bore. The other important mechanism of surfactant injection is to change contact angle through wettability alteration.[3] Since wettability strongly influences the distribution and flow of fluid in the reservoir, an accurate estimation of in-situ reservoir wettability is important for successful implementation of improved oil recovery process using chemical injection.

B. *Carbonate Reservoirs Rock*

About half of world's known oil reserves are in carbonate reservoir, and naturally fractured. The recovery from this kind of reservoirs is normally lower, even though water flood has been implemented. Many carbonate reservoirs are mixed-wet or oil wet.[4] One key of EOR process in fractured carbonate reservoir is surfactant solution reversing the wettability of the carbonate surface from oil-wet to water wet conditions. This effect allows the aqueous phase to imbibe into the matrix spontaneously and expel oil bypassed by a water flood, where water flood response typically is poor in this type of reservoirs.[6]

Anionic surfactants normally can change wettability of carbonate rock into intermediate/water wet condition. While cationic surfactants also have been reported capable for altering carbonate rock wettability into more water wet.[4] Nonionic surfactants have been investigated as well for altering the carbonate rock wettability from initially strongly oil-wet to a weakly oil-wet state.[5] More findings reported that nonionic surfactant altered from initially weakly water wet to a mixed wet state, while anionic surfactant can change wettability to a strongly oil wet state.[3] It is generally accepted that adsorption of polar compounds onto rock surface has a significant effect on the wettablity alteration of reservoir rocks.

C. *Sandstone Reservoirs Rock*

Laboratory coreflood conducted using Berea sandstone indicated the ability of both nonionic and anionic surfactants to develop a unique kind of heterogeneous wettablity known as "mixed wettability". This mixed wettability development has resulted in significant oil recovery improvement of about 94% original oil in place in the initially water-wet Berea sandstone.[3] A cationic surfactant has been reported that it can change a water wet reservoir to become oil wet, whereas as anionic surfactant can only cause minor change of its wettability.[2]

Reservoir wettability has profound influence on water flood recovery, and water flood oil recoveries are reported to be significant higher in intermediate as well as mixed wettabiltiy conditions. Alteration of wettability to either mixed or intermediate-wet can improve oil recovery from even water-wet reservoir. For given set of conditions, the higher apparent viscosity required for mobility control in oil-wet vs. water-wet reservoirs mean that greater quantities of chemicals will be needed in oil-wet system.[1] The optimum water flood oil recovery has been found to be associated with a special kind of heterogeneous wettability known as "mixed wettability", in which both oil and water wet rock to form preferential flow paths.

The reservoir wettability is strongly influenced by all the composition effects of rock and fluids existing at the reservoir conditions of temperature and pressure. Hence, simulating reservoir conditions and the use of live reservoir fluids in addition of chemical solution such as surfactant in the laboratory are essential to understand the impact of true in-situ surfactant-induced wettability alteration.

III. EXPERIMENTAL DETAILS

Several experiments have been done to evaluate the effect of surfactant solutions on rocks wettability alteration by means of contact angle measurements. Drop Shape Analysis DSA PD-700 equipment was used in this experiment to measure contact angles created by a drop of water or oil onto the rock surface. Two kind of rock types and three types of surfactants have been prepared for this experiment, in addition to reservoir fluids.

A. *Rock Preparation*

Native core samples were taken from oil field. XRD analysis has been done to determine the composition of the rocks, the detailed results are presented at Table 1. The first rock is carbonate rock (LS) which consist of totally calcite and only trace of quartz minerals. LS1 and LS2 are taken at different depth at a similar formation. The second rock is sandy carbonate (SL) which is composed of 38 percent quartz, 49 percent calcite, and small clay minerals. SL1 and SL2 are similar rock types. The rocks have been cut into small chips which can be immersed in surfactant solutions and having an even surface that a liquid bubble can be dropped on it for measuring the contact angle.

Table 5
Original contact angle measurements of control tests

No.	Rock types	Immersion fluid	Immersion time	Droplet	Contact angle degrees	Wettability
1	LS-1	Reservoir Oil	8 Weeks	Formation Water	89.67	Week Water Wet
2	LS-2	Reservoir Oil	8 Weeks	Formation Water	89.00	Week Water Wet
3	SL-1	Reservoir Oil	8 Weeks	Formation Water	80.83	Week Water Wet
4	SL-2	Reservoir Oil	8 Weeks	Formation Water	81.40	Week Water Wet
5	LS-1	Formation Water	8 Weeks	Reservoir Oil	13.20	Oil Wet
6	LS-2	Formation Water	8 Weeks	Reservoir Oil	14.86	Oil Wet
7	SL-1	Formation Water	8 Weeks	Reservoir Oil	13.08	Oil Wet
8	SL-2	Formation Water	8 Weeks	Reservoir Oil	10.03	Oil Wet

B. *Reservoir Fluids*

Reservoir fluid consists of formation water and crude oil. The formation water contents approximately 17.000 mg/L equivalent NaCl. The detailed result of water analysis is shown at Table 2 which is classified as high salinity and high hardness. The crude oil sample used was first also analyzed for its physical and chemical characteristics. Composition and characteristics of the crude oil are revealed in Table 3 and 4. The oil contents very high C_{7+} indicated as dead oil. Moreover, wax content is very high at the level of 25.46%. In the contrary, the acid number is very low at the level of 0.085 mgKOH/g as understood that this number is generally related to surfactant in situ generation during alkaline injection. Therefore, acid number level may have much more impact to the wettability alteration processes in such kind of experiment.

C. *Surfactant*

Surfactants used in this research are commercial products and bought from market. Three kinds of surfactants have been used in these experiments, firstly is for IFT reduction-type of surfactant, secondly is for thin film spreading agent-type of surfactant, and the third is well stimulator-type of surfactant. A table below is the summary of surfactant types used in this research.

No.	Category	Surfactant Type
1	IFT Reduction	Amphoteric
2	TFSA	Nonionic
3	Well Stimulator	Anionic

IFT reduction type of surfactant (IFT-R) was made of 0.30% content in solution of formation water, and TFSA was prepared only at 0.01%, while the stimulator type of surfactant (stimulator) was made up 0.5%. Those surfactant concentrations in the solutions are similar to those compositions needed in the real field projects.

D. *Procedures*

2 chips of each type of rock were immersed in the surfactants solutions. Several experiments were run in parallel to investigate the effect of time to the intensity of the wettability changes. As controls, both rocks also were immersed in the formation water as well as in the reservoir oil. The experiments were done for 2, 4, and 8 weeks respectively. After the rocks experienced contact with surfactant for as long as those executive time frame, then took out from the solution, and the contact angles begun to measure by mean of dropping a liquid bubble onto the rock surface.

E. *Results*

The control experiments where the rocks were immersed in the formation water and also in the reservoir oil were measured as the original wettability of the rocks. The rocks where immersed in the formation water were measured for its wettablity by means of dropping an oil bubble, while the rocks immersed in the reservoir oil by means of dropping a water bubble onto the rock surface. The result is presented in Table 5 indicating that both rocks (LS and SL) have preferences to oil rather than to water. The

Table 6
Contact angle measurements of LS after immersed in TFSA solution

No.	Rock types	Immersion fluid	Immersion time	Droplet	Contact angle degrees	Wettability
1	LS-1	TFSA - 0.01%	2 Weeks	Reservoir Oil	20.42	Oil Wet
2	LS-2	TFSA - 0.01%	2 Weeks	Reservoir Oil	28.56	Oil Wet
3	LS-1	TFSA - 0.01%	4 Weeks	Reservoir Oil	32.26	Oil Wet
4	LS-2	TFSA - 0.01%	4 Weeks	Reservoir Oil	37.87	Oil Wet
5	LS-1	TFSA - 0.01%	8 Weeks	Reservoir Oil	27.13	Oil Wet
6	LS-2	TFSA - 0.01%	8 Weeks	Reservoir Oil	30.19	Oil Wet

Table 7
Contact angle measurements of SL after immersed in TFSA solution

No.	Rock types	Immersion fluid	Immersion time	Droplet	Contact angle degrees	Wettability
1	SL-1	TFSA - 0.01%	2 Weeks	Reservoir Oil	20.42	Oil Wet
2	SL-2	TFSA - 0.01%	2 Weeks	Reservoir Oil	20.42	Oil Wet
3	SL-1	TFSA - 0.01%	4 Weeks	Reservoir Oil	24.19	Oil Wet
4	SL-2	TFSA - 0.01%	4 Weeks	Reservoir Oil	25.62	Oil Wet
5	SL-1	TFSA - 0.01%	8 Weeks	Reservoir Oil	14.76	Oil Wet
6	SL-2	TFSA - 0.01%	8 Weeks	Reservoir Oil	16.16	Oil Wet

Table 8
Contact angle measurements of LS after immersed in IFT-R solution

No.	Rock types	Immersion fluid	Immersion time	Droplet	Contact angle degrees	Wettability
1	LS-1	IFT-R - 0.3%	2 Weeks	Reservoir Oil	21.60	Oil Wet
2	LS-2	IFT-R - 0.3%	2 Weeks	Reservoir Oil	24.37	Oil Wet
3	LS-1	IFT-R - 0.3%	4 Weeks	Reservoir Oil	37.42	Oil Wet
4	LS-2	IFT-R - 0.3%	4 Weeks	Reservoir Oil	37.28	Oil Wet
5	LS-1	IFT-R - 0.3%	8 Weeks	Reservoir Oil	62.19	Oil Wet
6	LS-2	IFT-R - 0.3%	8 Weeks	Reservoir Oil	50.98	Oil Wet

oil bubbles have angles in the range of 13 to 15 degrees, while the water bubbles 80 to 90 degrees. As examples 2 pictures are exhibited in Figure 1 and 2 for LS-oil bubble and SL-oil bubble respectively.

TFSA solution was examined for 2, 4, 8 weeks for the influence on wettability of rocks. The wettability of the rocks was measured by dropping an oil bubble, where the results are shown in Table 6 and 7. The results reveal that wettability of the both rocks experienced a little change in wettablilty, the

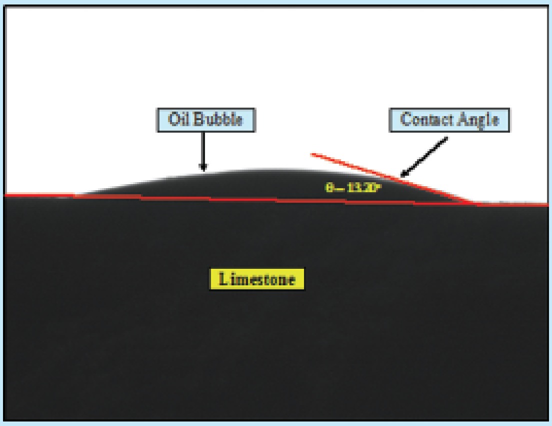

Figure 1
Original contact angle of LS-Oil

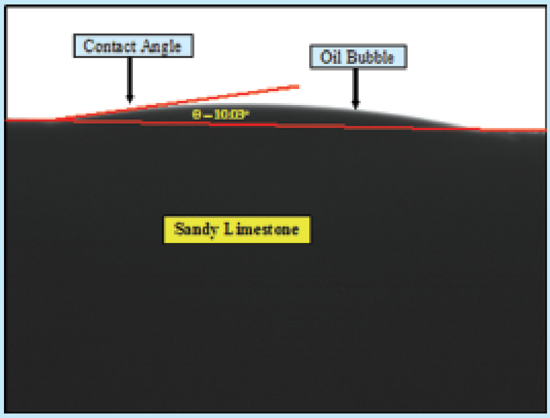

Figure 2
Original contact angle of SL-Oil

Table 9
Contact angle measurement of SL after immersed in IFT-R solution

No.	Rock types	Immersion fluid	Immersion time	Droplet	Contact angle degrees	Wettability
1	SL-1	IFT-R - 0.3%	2 Weeks	Reservoir Oil	17.47	Oil Wet
2	SL-2	IFT-R - 0.3%	2 Weeks	Reservoir Oil	31.50	Oil Wet
3	SL-1	IFT-R - 0.3%	4 Weeks	Reservoir Oil	26.01	Oil Wet
4	SL-2	IFT-R - 0.3%	4 Weeks	Reservoir Oil	26.45	Oil Wet
5	SL-1	IFT-R - 0.3%	8 Weeks	Reservoir Oil	37.50	Oil Wet
6	SL-2	IFT-R - 0.3%	8 Weeks	Reservoir Oil	20.02	Oil Wet

Table 10
Contact angle measurement of LS and SL after immersed in stimulator solution

No.	Rock types	Immersion fluid	Immersion time	Droplet	Contact angle degrees	Wettability
1	LS-1	Stimulator - 0.5%	2 Weeks	Reservoir Oil	29.03	Oil Wet
2	LS-1	Stimulator - 0.5%	4 Weeks	Reservoir Oil	32.01	Oil Wet
3	LS-1	Stimulator - 0.5%	8 Weeks	Reservoir Oil	35.06	Oil Wet
4	SL-1	Stimulator - 0.5%	2 Weeks	Reservoir Oil	27.04	Oil Wet
5	SL-1	Stimulator - 0.5%	4 Weeks	Reservoir Oil	29.07	Oil Wet
6	SL-1	Stimulator - 0.5%	8 Weeks	Reservoir Oil	35.40	Oil Wet

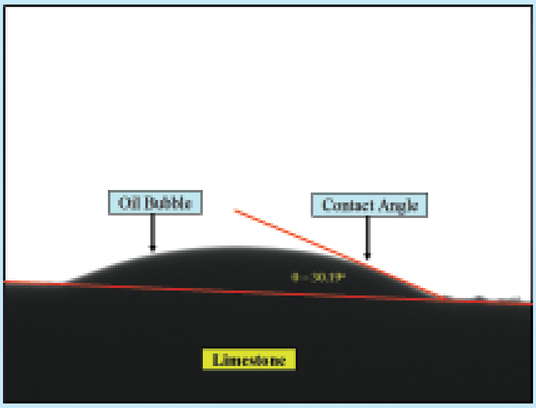

Figure 3
Contact angle of LS-Oil
(After immersed in TFSA for 8 weeks)

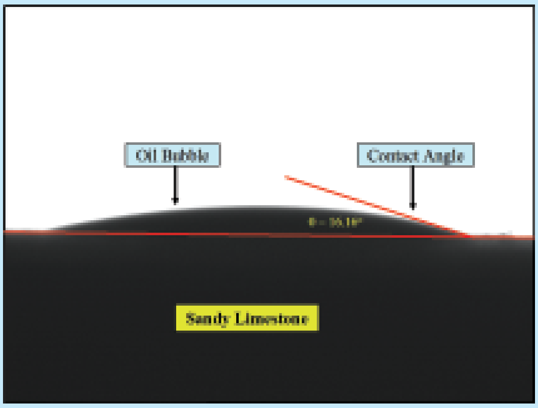

Figure 4
Contact angle of SL-Oil
(After immersed in TFSA for 8 weeks)

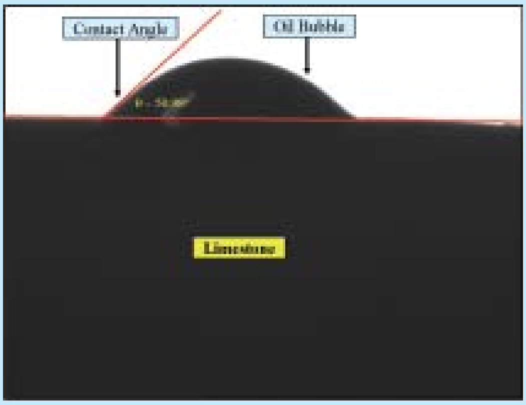

Figure 5
Contact angle of LS-Oil
(After immersed in IFT-R for 8 weeks)

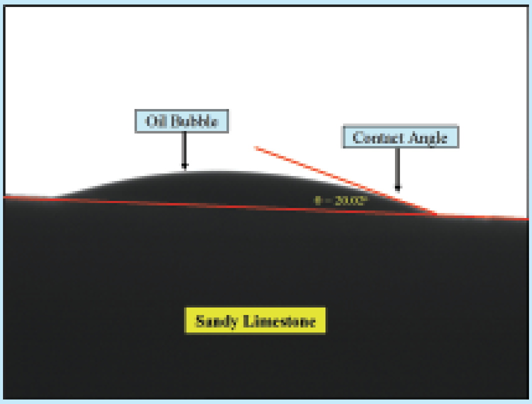

Figure 6
Contact angle of SL-Oil
(After immersed in IFT-R for 8 weeks)

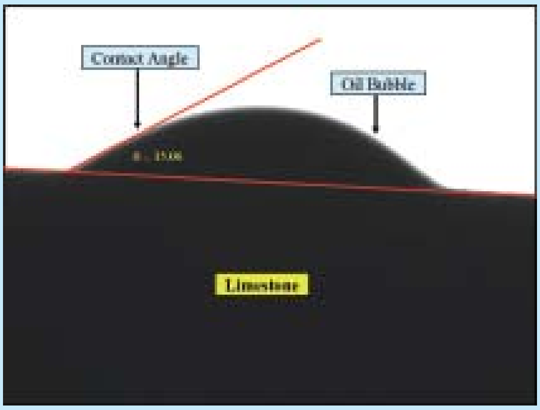

Figure 7
Contact angle of LS-Oil
(After immersed in stimulator for 8 weeks)

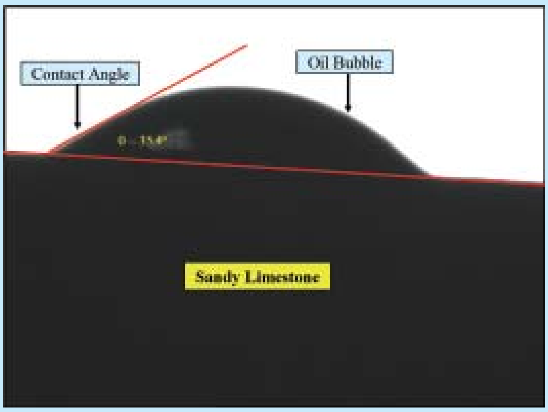

Figure 8
Contact angle of SL-Oil
(After immersed in stimulator for 8 weeks)

LS tend to decrease the oil preferences with time from around 20 degrees after 2 week to around 30 degrees after 8 weeks. Whereas SL experienced a little incremental contact angle to 20 degrees at the beginning of 2 weeks experiment but after that becoming return back to about 16 degrees after 8 weeks time. Two example pictures are presented in Figure 3 and 4 each for LS and SL after 8 weeks immersed on TFSA solution.

IFT-R solutions were also examined for the similar time span. The results are presented in Table 8 and 9 for LS and SL respectively. The contact angle measurements show that the contact angles of LS were changed significantly to 21 degrees after 2 weeks time and becoming 51degrees after 8 weeks indicating less oil preference. On the other hand, measurements on SL identify that the changes were a lttle bit lower eventhough the changes to more water preference still to occur. The average value of the contact angle was around 26 degrees. Figure 5 and 6 show the contact angle for both rocks after 8 weeks immersed in IFT-R solution.

Table 10 is the results of the contact angles of both rocks after immersed in the stimulator type of surfactant as long as 8 weeks. Those results indicate that this kind of surfactant tend to lessen the oil wetness and the contact angles increased from initially around 15 up to 35 degrees. Figure 7 and 8 show the contact angle measurements for both type of rocks.

IV. CONCLUSIONS

Laboratory scale analysis has been done to investigate the effect of the interaction between surfactant solution and carbonate rock. Three kind of surfactants have been used in these experiments, including TFSA, IFT-R, and well Stimulator surfactant types. The conclusions of these works are as follows :

1. Both LS and SL are more oil wet originally than water wet
2. All the three surfactants tend to change the wettabillity to less oil wet
3. Wettability alteration to less oil wet is more obvious in the interaction between LS and IFT-R as well as LS and Stimulator surfactant types
4. SL has only experienced a little wettability changes to less oil wet after contacting with three kind of surfactants
5. It is suggested to perform the experiments longer than 8 weeks or at least 6 months which is the time normally used to evaluate the chemical performance in EOR projects.

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