Applicability evaluation of a natural surfactant on the wettability alteration of oil reservoirs' rocks

F. Navaei, E. Esmaeilnezhad*
Department of Petroleum Engineering, Hakim Sabzevari University, Sabzevar, Iran
E.esmailnezhad@hsu.ac.ir

Abstract
Surfactant flooding is a suggested enhanced oil recovery (EOR) method in the oil reservoir that wettability alteration mechanism is effective. A new natural-based surfactant derived from Acanthophyllum tree trunk (Chuback) was proposed here to change the wettability of rock faces to water wet for more oil production purpose in the oil reservoir. The results of oil and water contact angle measurement proved that the proposed surfactant has this ability to be used as a surfactant in porous media. The response surface method was also utilized to investigate the effect of surfactant concentration, salt concentration and salt types on the goal responses, water and oil contact angle. According to the results, the optimum Chuback concentration is around 0.75 wt%.

Keywords: Enhanced oil recovery, Wettability alteration, Natural surfactant, Chuback.

Introduction
Surfactant flooding that is one of the effective Enhanced Oil Recovery (EOR) methods subordinate in chemical EOR, recovers the holdover trapped oils by reduction of interfacial tension between oil and aqueous phases [1] and moreover, wettability alteration of the reservoir rock faces byways of adsorption process [2]. Note that throughout surfactant flooding, surfactant losses onto reservoir rock surfaces have a massive consequence in the practicability of the addressed process and must be inspected consistently before dealing with displacement issues [3]. The natural surfactants have been evolving in recent years towards the development of more environmentally friendly products [4]. The high flow volumes of wastewaters containing conventional surfactants and the pollution caused by these substances or their degraded products have led to the replacement of these surfactants in natural surfactants by non-ionic surfactants which are highly biodegradable, non-toxic, and made from natural sources [5].
Wettability of surfaces is preferred to be hydrophilic or hydrophobic depending on the type of the application. This can be achieved using different techniques such as increasing the roughness of these surfaces [6]. Another methodology to modify surface wettability is coating these surfaces with low surface energy materials that can be used to render them super-hydrophobic [7]. In petroleum reservoirs, the term wettability alteration usually refers to the process of restoring the original reservoir wettability, which is presumed to be water-wet [8]. An early study showed that altering the wettability toward more water-wet increases EOR [9].

The crucial function of reservoir wettability on primary oil recovery methods like water drive was recognized by early research [10]. Secondary recovery via water flooding is directly related to the wettability of the oil reservoir too [11]. For instance, previous studies declared that oil recovery with water flooding for an oil-wet reservoir may be less by 15% compared with the water-wet reservoir. Most of the reservoirs, from another point of view, exhibit some degree of oil-wetness for which surfactant flooding is suggested. If the reservoir has a similar affinity to oil and water, the wettability is defined as neutral [12], and when some parts of the reservoir show different wettability state into other parts, the term mixed-wet is used [13]. The effect of wettability on oil recovery during water injection was tested and deduced that ultimate oil recovery reaches its maximum near the neutral-wet state. Sharma and Mohanty demonstrated that reservoirs with mixed wettability can have a higher oil recovery during water flooding than water-wet reservoir [14]. Although there is a general assenting that wettability alteration of the strongly oil-wet reservoir is favorable [15], no irrefutable statements can be made about the extent of the alteration that would induce the optimum oil recovery.

To the best of the author's knowledge and considering previous articles, very few researches have investigated the performance of different natural surfactants in wettability alteration and measuring contact angel of different rocks. In this study, considering the above points, the adsorption behavior of a new natural surfactant onto carbonate rock surfaces at different conditions such as various salt concentration, variant surfactant concentration and finally dissimilar surfactant solution concentration, the performance and benefits of the natural surfactant extracting from Acanthophyllum tree trunk (Chuback) in wettability alteration were investigated. Furthermore, qualitative wettability experiments such as contact angle measurements were implemented to demonstrate the total effects of the mentioned surfactant on the carbonate rock sample wettability. The following sections illustrate the details of each experiment procedures along with relevant gained experimental results.

Experimental

Materials and Methods:

Chuback natural surfactant powder, extracted and provided from the Acanthophyllum tree trunk was used in this investigation. Acanthophyllum is a genus of flowering plants in the family Caryophyllaceae. It is a tree that is small, shrubby perennial plants with spiny leaves, generally grown in warm and dry parts of Iran and Africa and included a high concentration of saponins with high quality. Crude oil (32^0 API, 0.832 gr/cm^3 @ 15^0 C) from one of Iranian oil reservoir and salts including NaCl and $CaCl_2$ (Merck Co., Ltd. Germany) for making ready different concentrations of the droplets of brine solution, were used to drop onto slabe samples. Several slabs from carbonate rock with sizes of 5×2×0.3 cm were cut and polished based on a common procedure [16].

Before aging the slab samples, the plugs were dried in the oven in the 122 ◦F for 30 hours to constant weight. The function of the natural surfactant at various salt concentration (0, 5000 and 10000 ppm), different salt types (NaCl and $CaCl_2$), variant surfactant concentration (0.75, 1.5 and 3 wt%) was applied for measure the contact angle and then determining about wettability alteration of core samples from oil-wet state to water-wet state. In order to observe the impact of surfactants on wettability alteration, each rock sample was aged with previously prepared surfactant solution for 2 days. Direct images of drops on the slabs were taken using a Samsung camera, then the pictures of droplets contact angles were analyzed carefully using ImageJ software.

Results and discussion

Instead of changing just one factor at a time, the individual effect of each factors, including Chuback concentration (0.75, 1.5 and 3 wt%- Factor A), salt concentration (0, 5000 and 10000 ppm- Factor B) and different salt types (NaCl and $CaCl_2$- Factor C), was employed by response surface methodology (RSM) and then contact angles of water and oil were the goal functions of the problem in the phrase of those factors. Design Expert software along with analysis of variance (ANOVA) was applied to recognize based P-value that the changes in the levels of factors are meaningful. Table 1 lists the matrix of factors along with the corresponding answers.

Table 1: Experimental design matrix with corresponding responses.

Std	Run	Factors			Contact Angle	
		A	B	C	Water	Oil
10	1	0.75	5000	NaCl	0	30.87
1	2	0.75	5000	$CaCl_2$	0	29.5
12	3	1.5	5000	NaCl	6.71	30.34
13	4	1.5	5000	$CaCl_2$	9.16	29.15
7	5	3	5000	NaCl	0	27.53
4	6	3	5000	$CaCl_2$	5.28	36.45
18	7	0.75	10000	NaCl	0	28.05
14	8	0.75	10000	$CaCl_2$	0	31.26
8	9	1.5	10000	NaCl	0	25.24
6	10	1.5	10000	NaCl	7.5	40.28
9	11	3	10000	NaCl	0	35.66
11	12	3	10000	$CaCl_2$	5.97	32.63
15	13	0	0	NaCl	20.38	4.02
3	14	0	0	$CaCl_2$	20.38	4.02
2	15	0	10000	NaCl	35.73	40.46
5	16	0	10000	$CaCl_2$	21.16	33.47
16	17	0	5000	NaCl	31.69	29.19
17	18	0	5000	$CaCl_2$	37.1	26.54

As it can be seen in figure 1, our samples are oil-wet, with increasing surfactant concentration, contact angle of the water and oil droplets decreases (from 20.38^0 to 0^0) and increases (from 4.02^0 to 39.15^0), respectively.

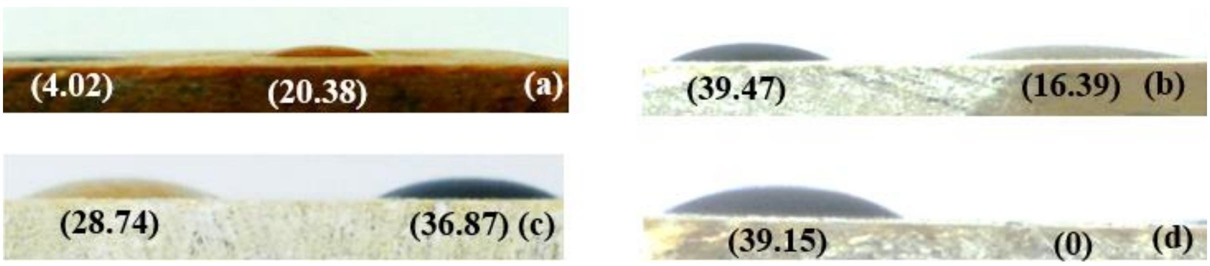

Figure 1: Contact angles of water and oil at different Chuback concentration. (a): 0 wt%, (b): 0.75 wt%, (c):1.5 wt%, (d): 3 wt% Chuback.

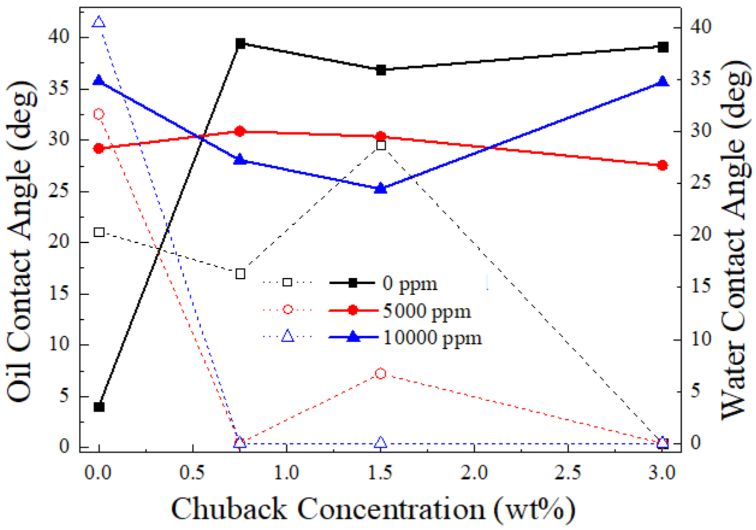

Figure 2: Contact angles of water (open) and oil (closed) at different concentration of NaCl and Chuback.

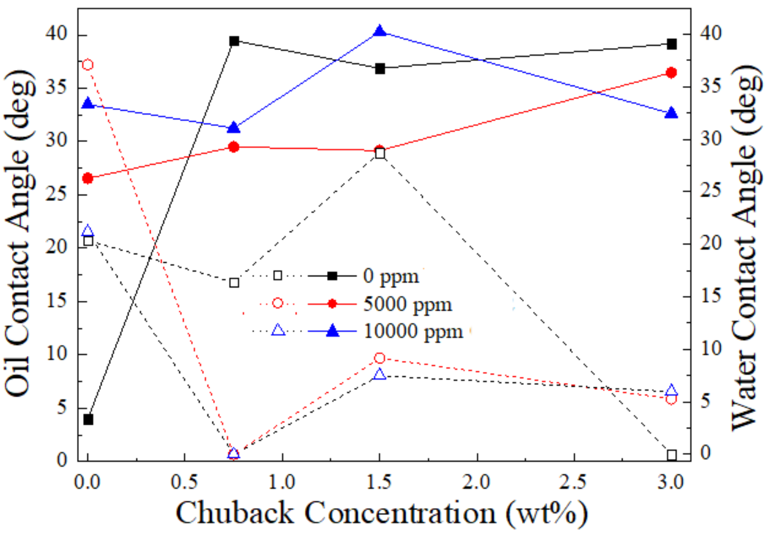

Figure 3: Contact angles of water (open) and oil (closed) at different concentration of $CaCl_2$ and Chuback.

The results of the experiments are shown in figures 2 and 3. As the results show, at zero concentration of Chuback, by increasing the concentration of NaCl and $CaCl_2$, the contact angle of water and oil increases slightly. After adding Chuback, an inverse effect is found, so as with increasing the concentration of both types of salts, contact angle of water and oil decreases, although this effect is compensated with increasing the Chuback concentration. Generally, It can be inferred from figures 3 & 4 that adding the Chuback changes the wettability of rock, even though it seems the optimum concentration for Chuback is around 0.75 wt% because in this concentration, the figures reach to a threshold and adding more Chuback doesn't have great impact on the contact angle of water and oil.
According to the P-value of table 2, it can be concluded that the surfactant which was used in this experiment, Chuback, had a sensible effect on water contact angle and can alter the wettability of reservoir rock from oil-wet to water-wet. Furthermore, Chuback concentration, salt concentration and also interaction of them had an extraordinary effect on the reduction of contact angles of the oil droplets. This effects and changes in water contact angle mean that after flooding or aging rock with Chuback, the reservoir rock wettability can change from oil-

wet to water-wet, therefore the proposed surfactant can be used in porous media as a surfactant flooding method.

Table 2: The results of ANOVA for oil and water contact angle.

Water Contact Angle							Oil Contact Angle					
Source	**Sum of Squares**	**df**	**Mean Square**	**F Value**	**p-value Prob> F**		**Source**	**Sum of Squares**	**df**	**Mean Square**	**F Value**	**p-value Prob> F**
Model	1292.57	6	215.43	1.50	0.3020		Model	1472.14	6	245.36	13.48	0.0016
A- Chuback con.	1039.46	1	1039.46	7.24	0.0310		A- Chuback con.	137.21	1	137.21	7.54	0.0287
B-salt con.	24.21	1	24.21	0.17	0.6935		B-salt con.	178.71	1	178.71	9.82	0.0165
C-salt type	36.38	1	36.38	0.25	0.6300		C-salt type	3.35	1	3.35	0.18	0.6806
AB	0.39	1	0.39	0.002	0.9601		AB	174.12	1	174.12	9.57	0.0175
AC	67.38	1	67.38	0.47	0.5152		AC	43.73	1	43.73	2.40	0.1650
BC	14.09	1	14.09	0.098	0.7631		BC	29.74	1	29.74	1.63	0.2418
Residual	1004.35	7	143.48				Residual	127.37	25	18.20		
Cor Total	2296.92	13					Cor Total	1599.52	31			

Conclusions

It is worth mentioning that the cost of natural surfactant is several times less than the other surfactants; therefore, using natural surfactant at higher concentrations is still economical. In this study, a natural surfactant, Chuback, was proposed as an alternative for chemical surfactant in the EOR method. The results showed that the proposed surfactant can alter wettability of surfaces toward more water-wet condition, which represented that chuback as a natural and biodegradable with an optimum concentration around 0.75 wt% can be considered as a potential alternative for synthetic surfactants in EOR methods. RSM was utilized to be sure that the concentration of the proposed surfactant along with salt concentration and slat type have meaningful effect on the wettability alteration of oil and water based P- value.

References

[1] Zargartalebi, M., Kharrat, R. and Barati, N. ," Enhancement of surfactant flooding performance by the use of silica nanoparticles", Fuel 143 21-27 (2015).

[2] Nasralla, R. A. and Nasr-El-Din, H. A. ," Double-layer expansion: is it a primary mechanism of improved oil recovery by low-salinity waterflooding?", SPE Reservoir Evaluation & Engineering 17(01) 49-59 (2014).

[3] Salari, Z. and Ahmadi, M. A. ," Experimental studies of ionic surfactant adsorption onto carbonate rocks, Energy Sources, Part A: Recovery", Utilization, and Environmental Effects 38(4) 549-554 (2016).

[4] De, S., Malik, S., Ghosh, A., Saha, R. and Saha, B. ," A review on natural surfactants", RSC advances 5(81) 65757-65767 (2015).

[5] Mondal, M. H., Malik, S., Roy, A., Saha, R. and Saha, B. ," Modernization of surfactant chemistry in the age of gemini and bio-surfactants: a review", RSC Advances 5(112) 92707-92718 (2015).

[6] Amin, J. S., Nikooee, E., Ayatollahi, S. and Alamdari, A. ," Investigating wettability alteration due to asphaltene precipitation: Imprints in surface multifractal characteristics", Applied Surface Science 256(21) 6466-6472 (2010).

[7] ShamsiJazeyi, H., Miller, C. A., Wong, M. S., Tour, J. M. and Verduzco, R. ," Polymer-coated nanoparticles for enhanced oil recovery", J. Appl. Polym. Sci. 131(15) (2014).

[8] Khishvand, M., Alizadeh, A., Kohshour, I. O., Piri, M. and Prasad, R. ," In situ characterization of wettability alteration and displacement mechanisms governing recovery enhancement due to low-salinity waterflooding", Water Resour. Res. 53(5) 4427-4443 (2017).

[9] Hou, B. f., Wang, Y. f. and Huang, Y. ," Mechanistic study of wettability alteration of oil-wet sandstone surface using different surfactants", Appl. Sur. Sci. 330, 56-64 (2015).

[10] Agbalaka, C. C., Dandekar, A. Y., Patil, S. L., Khataniar, S. and Hemsath, J. ," The effect of wettability on oil recovery: A review", SPE Asia Pacific Oil and Gas Conference and Exhibition, SPE, (2008).

[11] Gamage, S., Hasanka, P. and Thyne, G. D. ," Comparison of oil recovery by low salinity waterflooding in secondary and tertiary recovery modes", SPE Annual Technical Conference and Exhibition, SPE, (2011).

[12] Sheshdeh, M. J. ," A review study of wettability alteration methods with regard to nano-materials application", SPE Bergen One Day Seminar, SPE, (2015).

[13] Alhammadi, A. M., AlRatrout, A., Singh, K., Bijeljic, B. and Blunt, M. J. ," In situ characterization of mixed-wettability in a reservoir rock at subsurface conditions", Sci. rep 7(1) 10753 (2017).

[14] Sharma, G. and Mohanty, K. ," Wettability alteration in high-temperature and high-salinity carbonate reservoirs", SPE J. 18(04) 646-655 (2013).

[15] Al-Anssari, S., Arif, M., Wang, S., Barifcani, A., Lebedev, M. and Iglauer, S. ," Wettability of nanofluid-modified oil-wet calcite at reservoir conditions", Fuel 211 405-414 (2018).

[16] Teklu, T. W., Alameri, W., Kazemi, H. and Graves, R. M. ," Contact angle measurements on conventional and unconventional reservoir cores", Unconventional Resources Technology Conference, San Antonio, Texas, pp. 2297-2311 (2015).