Experimental Study of Anionic and cationic surfactants effects on reduce of IFT and wettability alteration in carbonate rock

Elyas Golabi[1]. Fakhry Seyedeyn Azad[2]. Sayed Shahabuddin Ayatollahi[3]. Sayed Nooroldine Hosseini[1]. Mjid Dastanian[1].

Abstract: The oil recovery by water flooding from carbonate reservoir is not effective because of the capillary forces in naturally fractured oil-wet carbonate formations. Alkaline/surfactant solution is recommended to enhance the spontaneous imbibition between fractures and matrix by both the wettability alteration and ultra-low interfacial tensions. In this work, the effects of anionic surfactant (SDBS), and a cationic surfactant (C_{12}TAB), on the interfacial tension (IFT) between oil and water and wettability alteration of limestone core samples were investigated. The understudied oil and limestone core were obtained from Aghajari reservoir, in the south-western part of Iran. The experimental results showed that the minimum amount of IFT achieved are using 0.5 wt% SDBS with 0.6 mol/lit NaOH, 1.5 wt% Na_2CO_3 and 5wt% NaCl at 70 ^{o}C. At 0.4 wt% and 70 ^{o}C, C_{12}TAB mostly altered the wettability toward water wet.

Key words: Fracture Carbonate Reservoir, Wettability Alteration, Surfactant, Oil-Wet, Water-Wet.

1 INTRODUCTION

The oil recovery methods generally used are pressure depletion and water flooding. The residual oil left after water flooding in fractured oil-wet reservoir has been reported to be very high [Chen et al., 2000]. This has been mostly due to the preferential flow of water, as the non-wetting fluid, in the fractures leaving most of the oil saturated Matrices completely unswept. The water imbibition into the Matrices is hindered by the negative capillary pressure in the Matrices. After a conventional water flooding process, the residual oil in the reservoir is trapped as a discontinuous phase in form of oil drops by capillary forces [Dosher et al., 1976]. On average, water flooding leaves approximately two third of the original oil in place (OOIP) as residual oil which is the target of further EOR recovery [Wardlaw, 1996].

Surfactants flooding system aims at producing the residual oil after secondary oil recovery with water flooding or gas injection. Creation of ultra- low interfacial tension and wettability alteration are the most important mechanisms for oil recovery by surfactant flooding. Establishment of positive capillary pressure of reservoir rock and displacement of oil in the porous media by surfactant flooding have been reported [Golabi et al., 2012, Yu, 2009, Hatiboglu et al., 2007, Somasundaran et al., 2006, Babadagli, 2003, Standnes et al., 2003, Graue et al, 2002, Touhami et al., 2001, Babu et al., 1986, Xie et al, 2005, Austad et al., 2003,, and Ramakrishnan, 1983]. Many flooding systems, especially surfactant-enhanced alkaline systems have been investigated [Ramakrishnan et al., and Almalik et al.]. It has been reported that the alkaline addition into many flooding systems plays an important role in reduction of interfacial tension. On the other hand, the alkaline can react strongly with the rock in the layer. So, a great quantity of alkaline can be consumed, and the layer can also be destroyed simultaneously. Therefore, a high potential of achieving maximum oil recovery exist, with using a properly designed surfactant formulation.

Liu et al. performed a study on using alkaline/surfactant flooding for Western Canadian heavy oil reservoir. They used Na_2CO_3 and NaOH as alkalines and alkyl sulfate, alpha olefin sulfonate, linear alkyl benzene sulfonate, alkyl benzene sulfonate and alkyl ether sulfate as surfactants. Their experimental results showed that the dynamic interfacial tension of oil/water could be lowered by using a combination of Na_2CO_3 and NaOH solutions at low concentrations of the surfactant.

Spontaneous imbibition tests in oil-wet dolomite cores were carried out by Hirasaki and Zhang. No spontaneous imbibition was observed with brine for 8 months, while with alkaline/surfactant solution, spontaneous imbibition was initiated within an hour. However, no conclusion was made toward what factor and to what extent contributed mostly to the observed oil recovery. Nedjhioui et al. investigated the effect of using a combination of two anionic surfactants (SDS and Marlon ARL), on water solubility of biopolymer (Xanthan gum) and alkaline (NaOH) at various concentrations by measuring their electrical conductivity, as well as surface and interfacial tensions. They concluded that the mixture of different compounds has important effects on the conductivity and interfacial tension of these systems and the crude oil/water system. Lorenz and Peru reported that interfacial tension was decreased by adding sodium hydroxide, sodium carbonate and sodium carbonate alkaline compounds. The amount of decrease was de-

Corresponding Author: E-mail addresses: elyas.golabi@iauo.ac.ir (Elyas Golabi)

1. *Department of Petroleum Engineering, Omidiyeh Branch, Islamic Azad University, Omidiyeh, Iran.*
2. *Department of Chemical Engineering, University of Isfahan, Isfahan, Iran.*
3. *EOR Research Center, School of Chemical and Petroleum Engineering, Shiraz University, Shiraz, Iran.*

ISSN 2229-5518

clining going from sodium hydroxide to sodium carbonate alkaline compounds.

Mohanty investigated wettability alteration and imbibition of West Texas oil reservoir. He used anionic surfactants Alfotera, and cationic surfactant DTAB. His results showed that anionic surfactants could reduce IFT more than the cationic surfactant but in wettability alteration, the cationic surfactant was more powerful than the anionic surfactants. He also showed that the cationic surfactant was more appropriate than the anionic surfactants for oil recovery at the core after 48 hours.

It was reported that thermal and miscible tertiary recovery techniques were not effective in fractured carbonate reservoirs [Spinler et al.]. Regarding to special properties of such reservoirs, surfactant flooding is a promising method for enhanced oil recovery. Alkaline surfactant solutions are used to recover oil from these types of reservoirs by enhancing the imbibition of water between fracture and the matrix by both wettability alteration and interfacial tension reduction. Aghajari reservoir is one of these types of reservoirs. Thus, chemical flooding seems to be a suitable method for increasing oil recovery from the reservoir if the surfactant formulation for the oil recovery is properly designed and the formulation is properly controlled. This work is committed to quantify the effects of the anionic and cationic surfactants on the oil-water IFT reduction in the presence of alkaline as well as the wettability alteration of the reservoir rock from the Aghajari, oil reservoir.

2. Experimental

2.1. Materials The anionic surfactant, cationic surfactant and alkaline used in this study were sodium dodecylbenzene sulfonate ($CH_3(CH_2)_{11}C_6H_4SO_3Na$) with molecular weight 347.48 gr/mol, Critical Micelle Concentration (CMC) at 25 ^{0}C is 0.526 wt% and grade ≥ 80% (the structure is shown in Fig. 1). Cationic surfactant $C_{12}TAB$ ($C_{12}N(CH_3)_3Br$) with molecular weight 308.34 gr/mol, Critical Micelle Concentration (CMC) at 25 ^{0}C is 0.418 wt% and grade ≥ 98% (The structure is shown in Fig. 2). These surfactants were obtained from Sigma-Aldrich Company. NaOH and Na_2CO_3 were purchased from Merck Company. The oil and core samples that were used in this study were obtained from Aghajari reservoir that was located in south west of Iran. The oil properties and composition and reservoir brine composition are given in table 1 to 2. Core data regarding porosity, permeability and compressibility are presented in table 4.

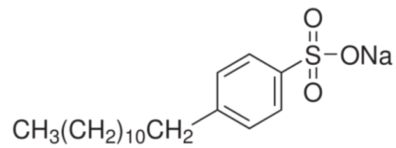

Fig 1: Chemical structure of SDBS

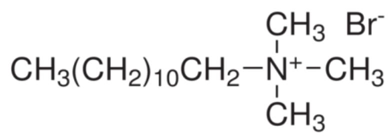

Fig 2: Chemical structure of $C_{12}TAB$

Table 1: Oil properties

Viscosity (cp)	API	Compressibility (Psi^{-1})	Density at 25 ^oC (g/ml)	Asphaltene (wt%)	Oil volume Factor (RB/STB)	Acid number (mg KOH/g oil)
0.570	34.3	2.81×10^{-5}	0.845	0.25	1.4	1.16

2.2. Interfacial tension measurement

The prepared anionic solution with reservoir brine contained anionic surfactant at 0.5 wt% (CMC concentration), NaOH at 0 to 0.6 mol/lit and Na_2CO_3 at 0.5, 1 and 1.5 wt%,

Corresponding Author: E-mail addresses: elyas.golabi@iauo.ac.ir (Elyas Golabi)

1. *Department of Petroleum Engineering, Omidiyeh Branch, Islamic Azad University, Omidiyeh, Iran.*
2. *Department of Chemical Engineering, University of Isfahan, Isfahan, Iran.*
3. *EOR Research Center, School of Chemical and Petroleum Engineering, Shiraz University, Shiraz, Iran.*

ISSN 2229-5518

while the cationic solution with reservoir brine at 0.1 to 0.5 wt%.

In order to investigate equilibrium phase behavior of oil and surfactant-brine aqueous solution, the prepared solutions were mixed with the reservoir oil in a test tube in 1:1 volume ratio. The test tube was shaken and then left for at least five days to achieve phase equilibrium. The IFT between the top oil layer and the bottom brine-surfactant solution layer and then was measured using tensiometer SITE 100 model.

Table 4: core data

Permeability (md)	Porosity	Compressibility (Psi^{-1})	Rock Type
160.136	0.15	4×10^{-6}	Limestone

2.3. Wettability alteration

In order to study of the effects of these two types of surfactants at CMC concentration and different temperature on wettability alteration, the limestone core adapt to parts with dimensions 3.25 × 5 cm. Firstly, they were saturated with the reservoir brine and after that were saturated with oil sample. Each segment was first immersed in brine-surfactant solutions inside the experimental cell and then oil bubble was injected through an orifice at the bottom cell.

In addition, the wettability alteration was verified by comparing the contact angle between the oil drop and the rock after aging the rock at the specified temperature and concentrations of the surfactants. The contact angle was measured by imaging system (Figure 3).

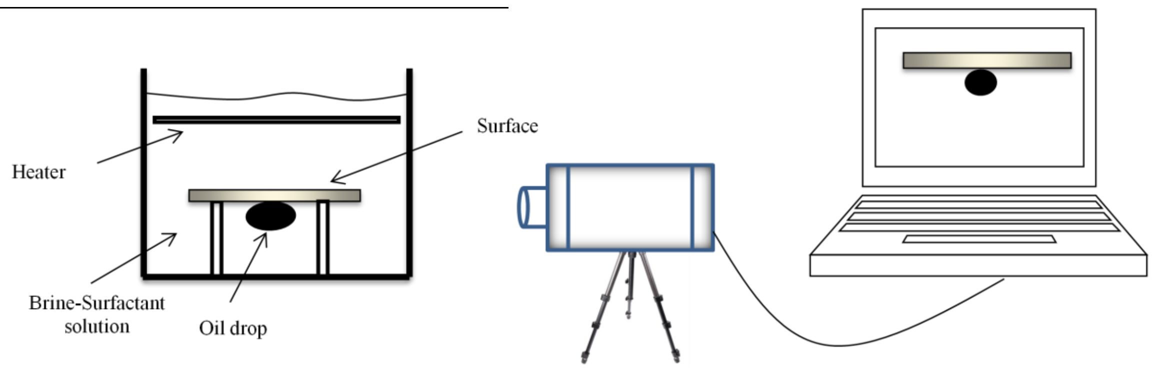

Fig 3: Experimental cell and imaging system for contact angle measurement

Table2: Composition of Oil

Corresponding Author: E-mail addresses: elyas.golabi@iauo.ac.ir (Elyas Golabi)

1. *Department of Petroleum Engineering, Omidiyeh Branch, Islamic Azad University, Omidiyeh, Iran.*
2. *Department of Chemical Engineering, University of Isfahan, Isfahan, Iran.*
3. *EOR Research Center, School of Chemical and Petroleum Engineering, Shiraz University, Shiraz, Iran.*

ISSN 2229-5518

Component	Mol Fraction
H_2S	**0.13**
N_2	**1.13**
CO_2	**3.55**
CH_4	**3.20**
C_2H_6	**2.08**
C_3H_8	**6.00**
$i\text{-}C_4H_{10}$	**1.84**
$n\text{-}C_4H_{10}$	**4.74**
$i\text{-}C_5H_{12}$	**3.43**
$n\text{-}C_5H_{12}$	**6.41**
C_6H_{14}	**12.27**
C_{7+}	**55.22**

Ion	Concentration (g/l)
Na^+	**57.13**
K^+	**1.16**
Ca^{2+}	**6.8**
Mg^{2+}	**1.94**
Cl^-	**106.5**
SO_4^{2-}	**0.8**
HSO_3^-	**1.22**
Total Dissolved Solid (TDS)	**175.55**

Table 3: Composition of Brine

Corresponding Author: E-mail addresses: elyas.golabi@iauo.ac.ir (Elyas Golabi)

1. *Department of Petroleum Engineering, Omidiyeh Branch, Islamic Azad University, Omidiyeh, Iran.*
2. *Department of Chemical Engineering, University of Isfahan, Isfahan, Iran.*
3. *EOR Research Center, School of Chemical and Petroleum Engineering, Shiraz University, Shiraz, Iran.*

3 Results and Discussions

Interfacial tensions between the oil sample and brine-surfactant solution containing 0.5 wt% CMC concentration SDBS surfactant and 0.5 to 1.5 wt% Na_2CO_3 were measured at 30, 50, and 70 °C for various NaOH concentrations. The results obtained at 30, 50, and 70 °C are shown in Figures 4, 5, and 6 respectively.

Figure 4 indicates that by increasing NaOH concentration, an initial dramatic decline occurs in IFT until 0.1 mol/liter and after that reduction of IFT get slightly slope. The minimum amount of IFT was obtained at 1.5 wt% Na_2CO_3 and 0.6 mol/lit NaOH solution at 30 °C. The amount of IFT decreased more at 1.5 wt% of Na_2CO_3 compared to two other concentrations.

Although the trend of IFT reduction at 50 °C (Figure 5) is similar to the IFT behavior at 30 °C (Figure 4), the amount of IFT reduction is more at 50 °C compared to that at 30 °C for all concentrations of Na_2CO_3.

The same results of IFT reduction are shown in Figure 6 for 70 °C. This indicates that the optimum temperature for the minimum IFT at the SDBS concentration of 0.5 wt% at the mentioned conditions is 70 °C. As we can see from Figure 7, the higher concentration of Na_2CO_3, causes the lower amount of IFT.

Figures 4, 5, and 6 indicate that at 1.5 wt% Na_2CO_3 the minimum amount of IFT was obtained at lower concentration of NaOH (0.6 mol/lit) compared with the amount of IFTs obtained at 0.5 wt% of Na_2CO_3. This suggests that NaOH is more effective than Na_2CO_3 to reduce IFT, as minimum amount of IFT can be achieved at a lower concentration of NaOH solution when the concentrations of Na_2CO_3 are relatively high.

The effect of cationic C_{12}TAB surfactant concentration on the oil-brine IFT was also examined at the temperatures of 30, 50 and 70 °C (Figure 8). By increasing surfactant concentration, an initial decrease of IFT to its minimum followed by slight increase was observed. The minimum amount of IFT for this surfactant was obtained for 0.4 wt% surfactant at 70 °C. As can we see at each temperature with 0.4 wt% (CMC concentration) the minimum value of IFT were obtained and after that change of IFT relatively stayed stable. Operating temperature of 70 °C was found to be more appropriate in comparison with temperatures of 30 and 50 °C, however it doesn't mean this is definitely the optimum temperature for surfactant as the experiment was not carried out at higher temperatures because of reservoir temperature is around of 70 °C.

According to Figures 4, 5, 6, and 8, anionic SDBS surfactant decreases the IFT at CMC concentration in comparison with C_{12}TAB and therefore it is a more appropriate surfactant.

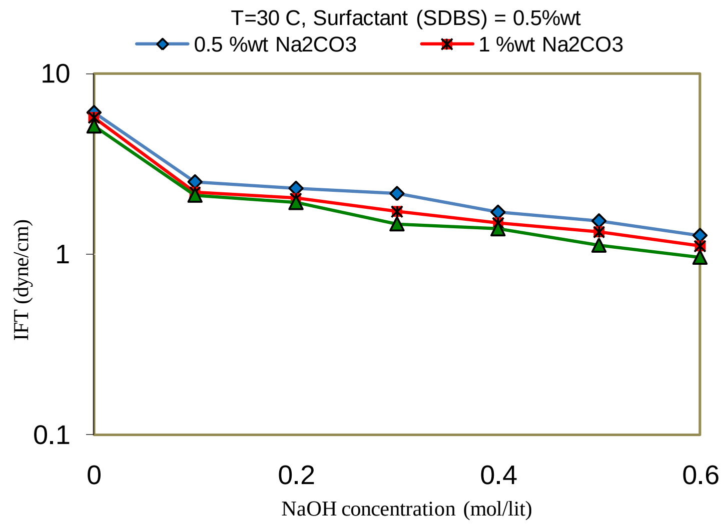

Figure 4: Oil-Water IFT reduction for the solution of 0.5 wt% SDBS, 0.5 to 1.5 wt% of Na2CO3, and 30 oC at different NaOH concentrations

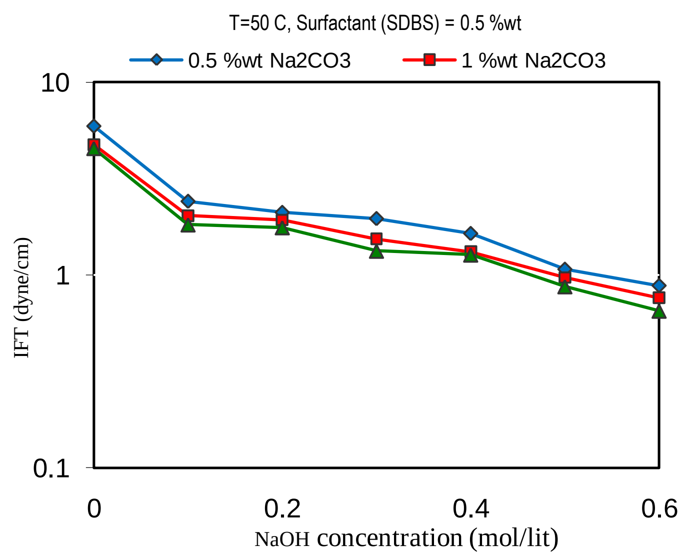

Figure 5: Oil-Water IFT reduction for the solution of 0.5 wt% SDBS, 0.5 to 1.5 wt% of Na2CO3, and 50 oC at different NaOH concentrations

Corresponding Author: E-mail addresses: elyas.golabi@iauo.ac.ir (Elyas Golabi)

1. *Department of Petroleum Engineering, Omidiyeh Branch, Islamic Azad University, Omidiyeh, Iran.*
2. *Department of Chemical Engineering, University of Isfahan, Isfahan, Iran.*
3. *EOR Research Center, School of Chemical and Petroleum Engineering, Shiraz University, Shiraz, Iran.*

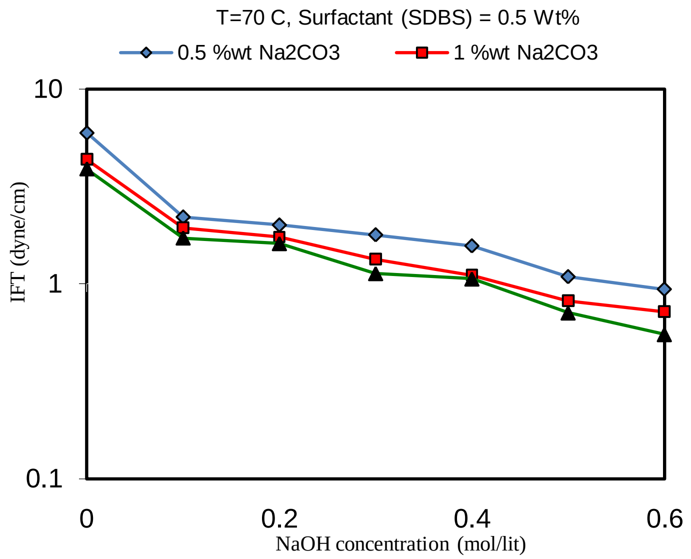

Figure 6: Oil-Water IFT reduction for the solution of 0.5 wt% SDBS, 0.5 to 1.5 wt% of Na2CO3, and 70 oC at different NaOH concentrations

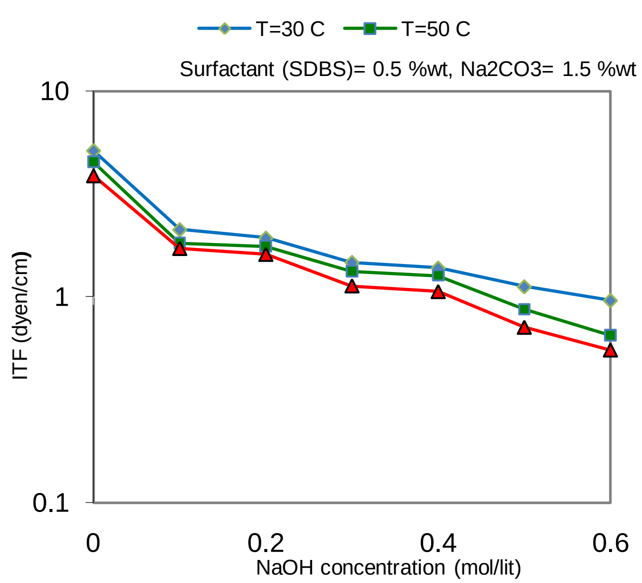

Figure 7: Oil-Water IFT reduction for the solution of 0.5 wt% SDBS, 1.5 wt% of Na2CO3, and 30, 50 and 70 oC at different NaOH concentrations

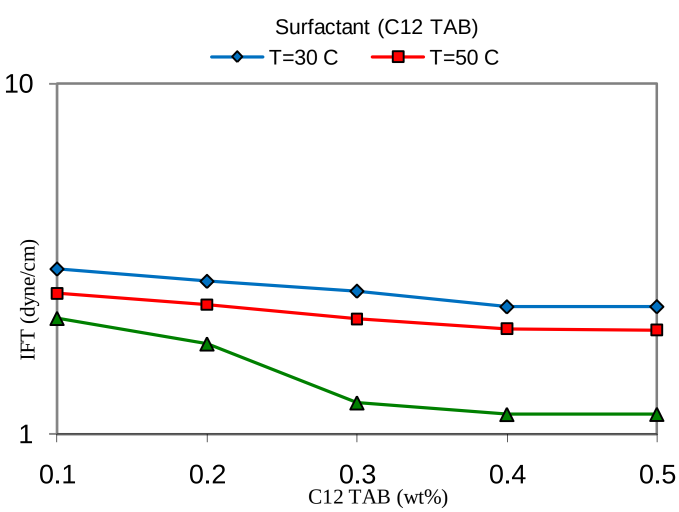

Figure 8: Oil-Water IFT reduction for the solution of 0.05 wt% C12TAB,

Corresponding Author: E-mail addresses: elyas.golabi@iauo.ac.ir (Elyas Golabi)

1. *Department of Petroleum Engineering, Omidiyeh Branch, Islamic Azad University, Omidiyeh, Iran.*
2. *Department of Chemical Engineering, University of Isfahan, Isfahan, Iran.*
3. *EOR Research Center, School of Chemical and Petroleum Engineering, Shiraz University, Shiraz, Iran.*

ISSN 2229-5518

3.1. Wettability Alteration Measurements Using Contact Angle Method

The contact angle measurement was applied to find the tendency of the specified reservoir rock to the oil and water solution. The oil and limestone core were used in this part of study were obtained from Aghajari reservoir.

First part measured the contact angle of reservoir rock in the presence of brine. According to droplet shape and the contact angle between oil droplet and the reservoir rock saturated with oil, the rock demonstrated as oil-wet (58 degree).

Table 5 shows the variation of the reservoir rock wettability in the presence of brine-surfactant solution containing 0.5 wt% surfactant SDBS, 1.5 wt% Na_2CO_3 and 0.6 mol/lit NaOH at 25, 30, 50 and 70 ^oC. According to table 5, SDBS solution was able to make a remarkable wettability alteration of reservoir rock to water-wet. Therefore an increase in temperature had positive effect on the degree of wettability so the higher temperature was seen the most effectiveness on the wettability alteration.

Table 6 demonstrates the reservoir wettability in the presence of brin-surfactant solution composed of 0.4 wt% (CMC concentration) surfactant $C_{12}TAB$ and brine, at 25, 30, 50 and 70 ^oC. The appearance of droplet and the contact angle between the droplet and the rock indicates that $C_{12}TAB$ has remarkably altered the reservoir rock wettability. Increasing solution temperature also led to more alteration towards to water-wet condition.

According to the contact angle between the oil drop and the rock (Table 5 and 6), surfactant $C_{12}TAB$ has altered the reservoir rock wettability more than SDBS at the same temperature.

Table 5: Variation of the contact angle between reservoir rock and droplet of surfactant SDBS

Temperature (^oC)	25	30	50	70
Contact Angle at 0.5 wt%	98	102	109	113

Table 6: Variation of the contact angle between reservoir rock and droplet of surfactant C12TAB

Temperature (^oC)	25	30	50	70
Contact Angle at 0.4 wt%	105	108	115	119

4. Conclusion

1- At lower concentrations, more IFT reductions were obtained by anionic surfactant SDBS compared with $C_{12}TAB$.
2- Surfactant $C_{12}TAB$ alters the reservoir rock wettability more than SDBS surfactant at the same temperatures.
3- Increasing of temperature is effective parameter at reduction of IFT and wettability alteration toward water wet.
4- In use of SDBS surfactant, presence of alkaline cause more reduction of IFT.
5- $C_{12}TAB$ at CMC concentration showed minimum IFT value and after this concentration the variation of IFT was constant.

5. References

[1] Almalik, M. S., Attia, A. M., 1997. Effects of alkaline flooding on the recovery of Safaniya crude oil of Saudi Arabia, J. Pet. Sci. Eng. 17, 3–4, 367-376
[2] Austad, T., Standnes, D. C., 2003. Spontaneous imbibition of water into oil-wet carbonates, J. Pet. Sci Eng., 39(3-4), 363-376.
Babadagli, T., 2003. Evaluation of EOR methods for heavy-oil recovery in naturally fractured reservoirs, J. Pet. Sci Eng 37, 25-37.
[3] Babu, D.R., Hornof, V., Neale, G.H., 1986. Evaluation of aqueous chemical systems for heavy oil recovery processes, Fuel, 65, 4–7.
[4] Chen, H.L., Lucas, L.R.,. Nogaret, L.A.D, Yang, H.D., Kenyon, D.E., 2000. Laboratory monitoring of surfactant imbibition using computerized tomography, SPE 59006 Presented at the SPE International Petroleum Conference and Exhibition in Mexico, Villa Hermosa, Mexico.
[5] Dosher, T.M., Wise, F.A., 1976. Enhanced crude oil recovery potential-an estimate. Paper SPE 5800, J. Pet. Technol. 575-585.
[6] Golabi, E., Seyedeyn Azad, F., Ayatollahi, S. Sh., Hosseini, S. N., Akhlaghi, N., 2012. Experimental Study of Wettability Alteration of Limestone Rock from Oil-Wet to Water-Wet using Various Surfactants, SPE 157801.
[7] Graue, A., Aspenes, E., Bogno, T. , Moe, R. W., Ramsdal, J., 2002. Alteration of wettability and wettability heterogeneity, J. Pet. Sci Eng 33, 3-17.
[8] Hatiboglu, C. U., Babadagli, T. 2007. Oil recovery by counter-current spontaneous imbibition: effect of matrix shape factor, gravity, IFT, oil viscosity, wettability, and rock type, J. Pet. Sci Eng 59, 106-122.
[9] Hirasaki, G.J., Zhang, D.L., 2004. Surface chemistry of oil rrecovery from factured, oil-wet, carbonate formations, SPE J. 9 (2), 151–162.
[10] Li, J., Wong, W., GU, Y., 2004. Dynamic interfacial tension phenomena and wettability alteration of crude oil-rock–alkaline-surfactant solution systems, SPE 90207, SPE Technical Conference, Houston.
[11] Liu, Q., Dong, M., Ma, S., 2006. Alkaline/surfactant flood potential in western Canadian heavy oil reservoirs, SPE 99791.

Corresponding Author: E-mail addresses: elyas.golabi@iauo.ac.ir (Elyas Golabi)

1. *Department of Petroleum Engineering, Omidiyeh Branch, Islamic Azad University, Omidiyeh, Iran.*
2. *Department of Chemical Engineering, University of Isfahan, Isfahan, Iran.*
3. *EOR Research Center, School of Chemical and Petroleum Engineering, Shiraz University, Shiraz, Iran.*

[12] Lorenz, P.B., Peru, D.A., 1989. Guidelines help select reservoir for NaHCO3 EOR, Oil & Gas J., 87, 37, 53-57.
[13] Martin, F.D., Oxley, J.C., Lim, H., 1985. Enhanced recovery of a "J" sand crude oil with a combination of surfactant and alkaline chemicals, SPE 14293.
[14] Mohanty, K.K., 2003. Dilute surfactant methods for carbonate formations, Quarterly Progress report, DE-FC26-02NT 15322, U.S. Department of Energy.
[15] Morrow, N. R., 1990. Wettability and its effect on oil recovery, J. Pet. Technol., 1476-1484.
[16] Nedjhioui, M., Moulai-Mostefa, N., Morsli, A., Bensmaili, A., 2005. Combined effects of polymer/surfactant/oil/alkali on physical chemical properties, Desalination 185, 1-3, 543–550.
[17] Ramakrishnan, T. S., Wasan, D. T., 1983. A model for interfacial activity of acidic crude oil/caustic systems for alkaline flooding, SPEJ 23:4, 602-612.
[18] Somasundaran, P., Zhang, L. 2006. Adsorption of surfactants on minerals for wettability control in improved oil recovery processes, J. Pet. Sci Eng 52, 198-212.
[19] Spinler, E.A., Zornes, D.R. Tobola, D.P., Moradi-Araghi, A., 2000. Enhancement of oil recovery using a low concentration of surfactant to improve spontaneous and forced imbibition in Chalk, SPE 59290.
[20] Standnes, D. C., Austad, T., 2003. Nontoxic low-cost amines as wettability alteration chemicals in carbonates, J. Pet. Sci Eng 39, 431-446.
[21] Tadros, T., 2005. Applied Surfactants: Principles and applications, Phase behavior of surfactant systems (Chapter 3), John Wiley & Sons, United Kingdom.
[22] Touhami, Y., Rana, D., Neale, G.H., Hornof, V., 2001. Study of polymer-surfactant interactions via surface tension measurements, Colloid Polym. Sci. 279, 297–300
[23] Wardlaw, N. C., 1996. Factors effecting oil recovery from carbonate reservoirs and predication of recovery, in G. V. Chilingarian, S. J. Mazzullo, H. H. Rieke, eds., in carbonate reservoir characterization: A Geologic-Engineering Analysis, Part II: Elsevier, New York, Development in Petrolium Science 44, 867-903.
[24] Xie, X., Weiss, W.W., Tong, Z., Morrow, N.R., 2005. Improved oil recovery from carbonate reservoirs by chemical stimulation, SPE 89424, 276-285.
[25] Yu, L. 2009. Spontaneous imbibition of seawater into preferentially oil-wet chalk cores experiments and simulation, J. Pet. Sci Eng 66, 171-179.

Corresponding Author: E-mail addresses: elyas.golabi@iauo.ac.ir (Elyas Golabi)

1. *Department of Petroleum Engineering, Omidiyeh Branch, Islamic Azad University, Omidiyeh, Iran.*
2. *Department of Chemical Engineering, University of Isfahan, Isfahan, Iran.*
3. *EOR Research Center, School of Chemical and Petroleum Engineering, Shiraz University, Shiraz, Iran.*