Effect of Hexadecyl Trimethyl Ammonium Bromide ($C_{16}TAB$) as Cationic Surfactant on Contact Angle and Interfacial Tension of Carbonate Rocks and Oil

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Abstract

Contrary to sandstone reservoirs, carbonate reservoirs have an oil-wetting nature. Water flooding of these fractured reservoirs with low permeability matrix blocks is not recommended unless a wettability alteration process is possible. Imbibition is an oil recovery mechanism for these types of reservoirs, if the rock matrix is water wet and there is enough water in fractures in contact with the matrix. Heavy matrix oil, high interfacial tension (IFT), oil-wet matrix sample, and limited contact area of matrix with water in fractures, requires additional effort to enhance the oil recovery by capillary imbibition. Surfactants can be injected into naturally fractured reservoirs to improve the capillary imbibition recovery performance. A well-known surfactant is Hexadecyl Trimethyl Ammonium Bromide ($C_{16}TAB$), which is an appropriate type of surfactant for these kinds of reservoirs. However, due to its high cost, it is rarely used in the real case studies.

In the present paper a simple and inexpensive method has been proposed for synthesizing this surfactant. Surfactant at different concentrations have been dissolved in high salinity brine, and the interfacial tension (IFT) between the aqueous solution and the oil has been measured by pendent drop method. In addition, the contact angle between the oil and the aqueous solution is measured by sessile drop method, and during the experiment, photos were taken every two seconds in order to analyse the IFT and the contact angle obtained. It has been found that reduction of IFT continues up to critical micelle concentration of the surfactant. Furthermore, a correlation has been obtained to predict the IFT between the oil and the high salinity aqueous solution containing different surfactant concentrations. Finally, the best surfactant concentration is obtained for reservoir case studies.

Keywords: *Interfacial Tension (IFT), Wettability, Cationic Surfactant, Hexadecyl Trimethyl Ammonium Bromide (C16TAB), Contact Angle, Critical Micelle Concentration (CMC)*

1- Introduction

The use of surfactants in enhanced oil recovery has been studied extensively in the past and has been reviewed in several references [1,2]. The use of surfactants in carbonate reservoirs has had limited application due to fractures, low matrix permeability, dead pore volume, high hardness and salinity, heterogeneity, and adsorption.

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There are some methods for IFT prediction, such as Parachor method or scaling laws. In all of these methods the fluids are assumed to be a mixture of pure components with a known exact concentration. Hence, if all the compositions and their exact concentrations of fluid are not clear, these methods cannot be used. Even in the best condition, if all the components with exact concentration are known, it is not recommended to estimate IFT of hydrocarbon-water by these methods, as these correlations can produce highly erroneous results, even for simple binary systems [3,5].

Firoozabadi and Ramey demonstrated IFT between water and pure hydrocarbons over a wide range of temperatures. Their findings are shown in Fig. 1. They have shown IFT function is as follows [6]:

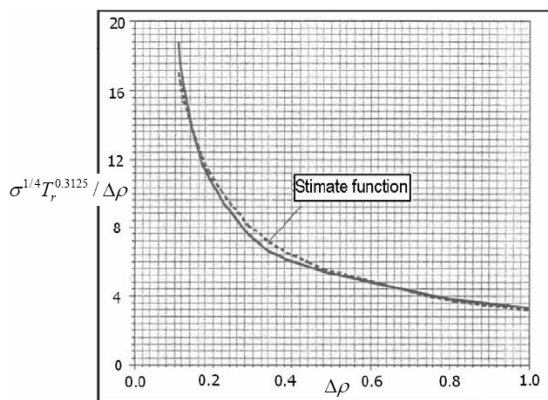$$\text{IFT function} \equiv \sigma^{\frac{1}{4}} T_r^{0.3125} / \Delta\rho \qquad (1)$$

Figure 1. Generalized correlation for water-hydrocarbon interfacial tension [6]

Where, σ is the interfacial tension in mN/m or dyne/cm, T_r is the reduced temperature for hydrocarbon at a temperature of measurement, and $\Delta\rho$ is the density difference in g/cm³. They have correlated data from a number of sources on the interracial tension of pure hydrocarbons and pure water using the correlating parameter $(\sigma^{\frac{1}{4}} T_r^{0.3125} / \Delta\rho)$ on the y-axis and the density difference $\Delta\rho$ on the x-axis, and have demonstrated the reliability of their correlation for various compounds ranging from methane to n-dodecane. The above correlation was evaluated to estimate the oil-water IFT which indicated errors exceeding 30% [7]. The presence of surface active compounds in oil may prohibit the use of any generalized correlation which does not take such effects into account.[7]

Badakhshan has conducted some experiments to determinate the IFT of some pure hydrocarbons and water [8]. In this paper he has indicated that the Firoozabadi/Ramey correlation does not predict the measured values well for some brine systems and aliphatic compounds. For example, the calculated value for cyclohexane at 21°C is 40.5 mN/m, [7] while the measured value is 52.3 mN/m .The values are either above or below the correlation curve, contrary to prediction values. He has claimed that if a wider range of hydrocarbons was measured against the brine solutions, a different correlating line could perhaps be established. However, the correlation may be more apparent than real value because the product of σ and T_r, raised to low exponents, is essentially a constant and the inclusion of $\Delta\rho$ in both the abscissa and ordinate makes the curve essentially the graph of a hyperbola. Finally, it can be concluded that there is no generalized equation for predicting IFT for all hydrocarbons-brine system with different

temperatures and pressures [9, 10].

There are numerous methods to determine IFT [6-8, 11-13]. The pendant drop technique is a common one, based on the fact that small drops or bubbles tend to be spherical due to the predominance of surface forces over the gravitational forces acting on them. In this method, the surface or interfacial tension can be determined from measurements of the shape of the drop or bubble formed [11]. A drop hanging from a tip (or a clinging bubble) elongates as it increases in size because the difference in hydrostatic pressure becomes significant in comparison with that given by the curvature of the drop. If the drop's expansion is stopped before gravity overcomes the interfacial tension (in which case the drop falls or a bubble goes up), and the drop is left undisturbed, a force balance will be attained and the final shape of the drop will depend on its size, the density difference between the drop and its surroundings, and the surface/interfacial tension. In order to use this method, the parameter (S) is defined as follows:

$$S = \frac{D_s}{D_e} \qquad (2)$$

Where, D_e is the equatorial diameter of the drop and D_s is the diameter at a distance from the apex equal to D_e as shown in Fig. 2. There is a new shape dependent variable, H, which is basically a modified Bond number. This allows the interfacial tension to be calculated as:

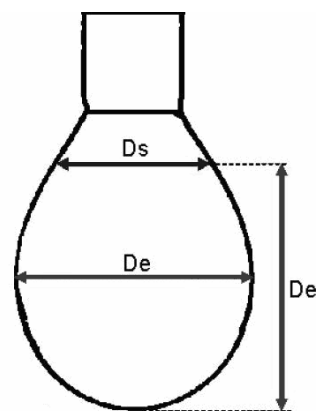$$\sigma = \frac{\Delta \rho g D_e^2}{H} \qquad (3)$$

Figure 2. Drop measurements needed to calculate shape factor S

The relationship between H and S was determined experimentally, and a set of 1/H values versus S should be obtained. Extensive and reasonably accurate tables of such values are found in the literature [7, 14]. Therefore, the only information needed to calculate the interfacial tension from the drop's image are D_e, D_s and $\Delta\rho$ [14].

2- Experimental procedure

We have used the simplest possible chemical route to synthesize the desired cationic surfactant ($C_{16}TAB$). At first alkyl halides (R-Br) is synthesized by reacting hexadeconol alcohol (Merck Chemical Co. brand, with purity of 99%) with red phosphor, and also by adding bromide dropwise to the mixture. 1-bromo hexadecane formed is then reacted with trimethylamine (Merck Chemical Co. brand, with 99% purity) in the presence of acetonitrile and refluxed for 24 hours. The desired surfactant produced was in the form of white crystals which were then washed with alcohol and dried for 24 hours at room

temperature. The surfactant was then dissolved in alcohol and prepared for further investigation on contact angle and IFT.

In order to investigate the effect of $C_{16}TAB$ on IFT, the pendent drop experiment is done. Captive drop instrument, manufactured by the Alberta Research Center (ARC), is used for this purpose. During this experiment the pendent drop cell was filled with aqueous solution with different $C_{16}TAB$ solution concentrations, and an oil/brine transfer vessel was filled with kerosene. Kerosene was injected through a micro pump into the

pendent drop cell at a very low rate. Although this low flow rate makes the process time consuming, it allows the surfactant monomers and micelles to reach equilibrium between the two fluids. Choosing this low rate also guarantees that the oil drop separation from the tip is the result of density difference, not the flow rate of injection. A camera which is mounted on the instrument took a photo every 2 seconds during drop formation. The process of a drop formation can be observed in Fig. 3.
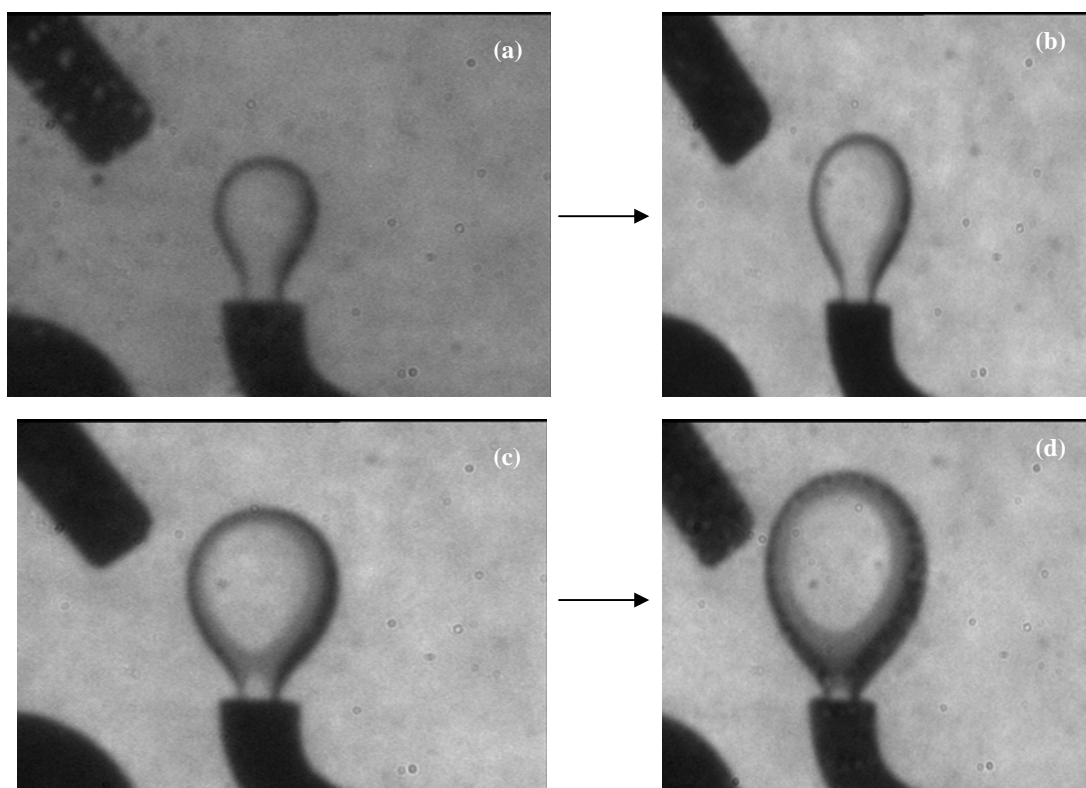

Figure 3. The process of a drop formation (a- d) in pendent drop method.

In order to calculate the real drop size from the taken photos, calibration of the drop photos is essential, because all drop size calculations are based on pixel size. For converting these pixels to metric dimension, a photo should be taken from the calibration ball with a known exact diameter. It should be noted that the camera's zoom and its position was unchanged during the experiments; so the calibration process was not required for further experiments. The taken photos are digitized by ARC edge detection program. In order to calculate D$_s$, D_e, and IFT, a program is written in DELPHI 7 which uses digitized photos results. This program is able to use drop size and factors that are used in pendent drop method like D_e and D_s in order to calculate IFT.

3- Results and discussion

It should be mentioned that kerosene was selected as the oil phase and high salinity brine with variable surfactant concentration as the aqueous phase in this project. The reason for choosing kerosene instead of crude oil was to ignore the effect of asphaltene and other surface active agent's effects which may be present in crude oil.

Brine used in this project was made by dissolving 150000 ppm NaCl in distilled water. Working with this high salinity brine was extremely difficult; however, it was chosen because of its similarity to south Iranian oil reservoir brine salinity.

In order to measure contact angle the real reservoir rock sample must be used, ideally. Since the original wettability alteration due to exposing rock samples to the aqueous solution during the experiment can produce

some errors, fresh rock samples must be used in each test. It is known that a piece of polished calcite should be used as a representative of carbonate reservoir in the sessile drop method and a piece of polished quartz as a representative of the sandstone reservoir theoretically; however, these pieces cannot be real representatives of reservoirs because of the existence of some heterogeneity in the reservoir rock like fractures, clay and roughness, that cannot be applied to these pieces.

As carbonate reservoirs was the issue in this project, according to the literature it is expected that a piece of polished calcite be used in sessile drop experiment. But due to a lack of availability of polished calcite with an appropriate roughness (2 micron), homogenous smooth Plexiglas pieces were used as captive drop surfaces instead for polished calcite. The main reason for selecting Plexiglas was its oil-wetness behavior, enabling a better understanding of wettability alteration, and also knowing that surfactants result in increasing water-wetness of the surfaces.

It should be noted that the reported contact angle measured is the average of both the right and left angles. Although they should be the same, averaging reduces the errors.

Because of the interaction of the oil drop and the aqueous solution, as time passes the contact angle changes until equilibrium between the two phase surfaces is achieved. In the sessile drop experiment, it was noted that, as the time passed the correct contact angle can be accessible just after equilibrium point is achieved. This change can be explained by moving monomers and micelles from water to oil and against it. Contact

angles of the mixture of oil and different surfactant concentrations at equilibrium point are measured and the obtained results are shown in Fig. 4.

As one can notice from Fig. 4, generally the same trend is observed for all drops in aqueous with different solution surfactant concentrations, but the time to reach equilibrium point for contact angle is different for different surfactant concentrations. On the other hand, the oil drop in the brine solution did not follow the same trend. It should be emphasized that the dynamic behavior of the contact angle is due to surfactant monomers and micelles transfer between two phases. Small changes in the primary points refer to the establishment of the drop on the surface. Various drops contact angle in different aqueous solutions are given in Table 1.

Table 1. Equilibrated contact angle for different surfactant concentrations, measured by sessile drop method (T=25°C , P =1 atm.)

Surfactant solution (ppm)	Equilibrate contact angle (Degree)
0	116.4706
100	79.11765
150	70.00110
200	51.47058
250	39.11765
300	32.94117
350	20.29411
375	10.00185
400	14.11764

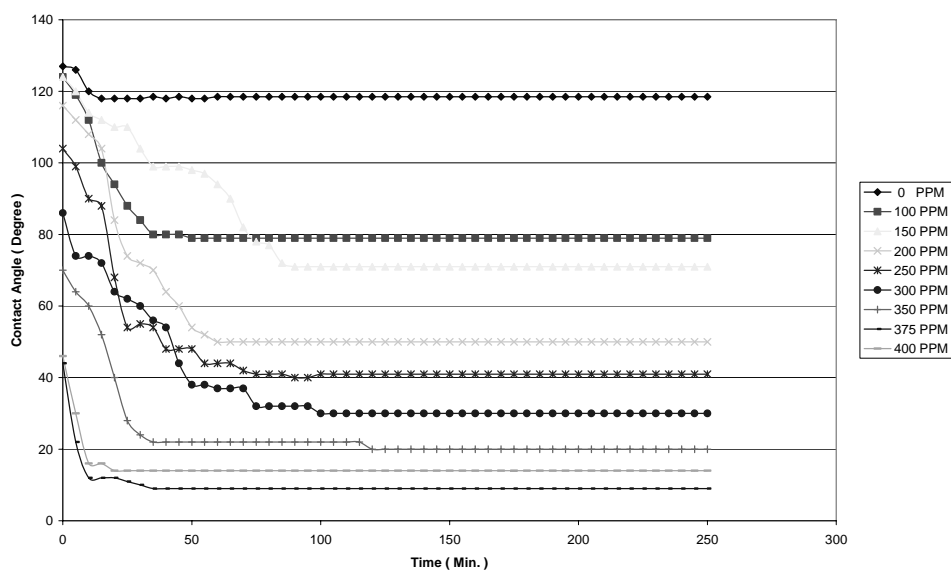**Figure 4.** Variation of contact angle versus time for different amounts of surfactant concentrations in sessile drop method (T= 25°C, P= 1atm)

As mentioned earlier, in order to evaluate the effect of surfactant on interfacial tension, pendent drop method was employed. A pendent drop cell was filled with aqueous solution with different surfactant concentrations and an oil/brine transfer vessel was filled with kerosene. Kerosene was injected through an ISCO pump into the pendent drop cell at a very low flow rate. Although this low flow rate makes the process time consuming, it will allow the surfactant monomers and micelles to reach equilibrium between two layers of oil and brine. Choosing a low flow rate, guarantees that the oil drop separation from the tip is the result of density difference, but not forces involved due to the injection of kerosene. A camera took a photo every 2 seconds during drop formation.

In order to ensure the results obtained are correct, IFT between some materials that are known and reported in the literature was calculated. Results of IFT measured by the equipment mention earlier and their related values reported in the literature are shown in Table 2. From the results obtained it can be concluded that all IFT measured should be multiplied by a correction factor of 1.15. The

main reason for this difference may refer to the digitizing process and light source adjustments.

In order to investigate the effect of C$_{16}$TAB on IFT reduction between kerosene and brine with a salinity of 150000 ppm NaCl at $30\,^{o}C$; a written program was used to determine IFT of each oil drop and aqueous solution. It should be added that this program is able to show drop size and factors that are used in pendent drop method like D_{e} and D_{s}. The points that are used to measure the IFT of the oil drop is shown graphically in Fig. 5.

As mentioned before, there is a parameter (1/H) in the pendent drop equation which is determined by Anderson given in a form of a table [7]. In this program (1/H) is defined as a function of (S). In order to find this function, we have plotted all available data for (1/H) given in Anderson's table versus their related (S), and by using "SIGMAPLOT" software, from which the best curve was determined. The results of this finding can be observed in Fig. 6, and the obtained function is:

$$1/H = 0.3153 \cdot S^{-2.6071} \tag{4}$$

Table 2. Comparison between IFT measured and those reported in the literature.

| Fluids	Measured IFT(mN/m)	Literature Value (mN/m)	Needed Coefficient	Relative Difference (%)
Water/Air (25°C)	62.05922	71.99	1.161621	13.7947
Acetone/Air	19.10975	22	1.151245	13.1375
n-hexane/Air	14.83441	17	1.145984	12.7387
Methanol/ Air	19.13533	22.07	1.152364	13.2971
Toluene/ Air	24.07078	27.93	1.160328	13.8175
Water/Toluene	27.74902	32	1.153194	13.2843
Water/CCl4	39.08643	45	1.151295	13.1413
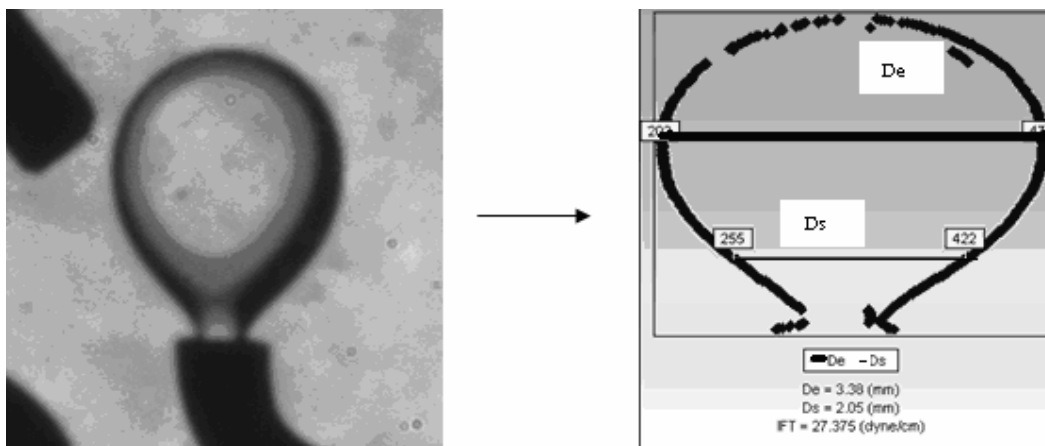
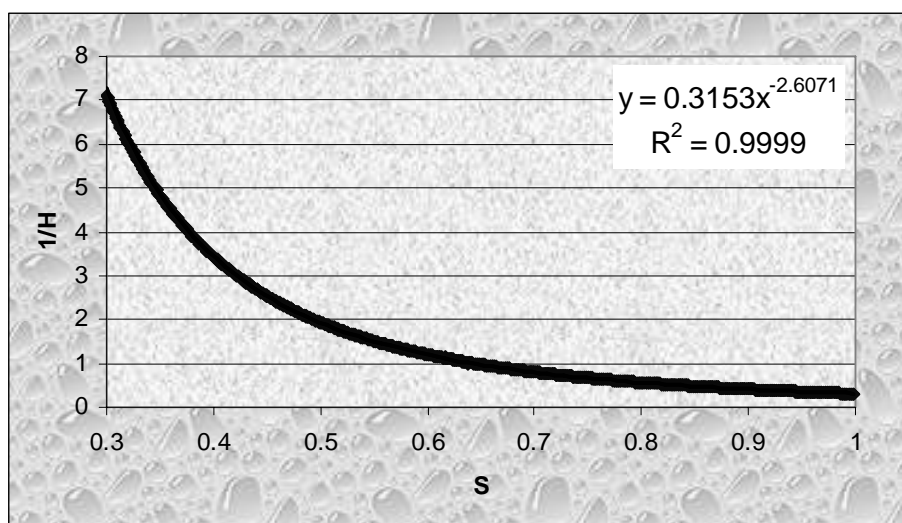**Figure 5.** A drop formed in pendent drop experiment and the related one in the output of the program.

Figure 6. curve obtained for 1/H versus S.

In each point of the figures, 7 is representative of IFT between the surfactant solution and the kerosene drop in the given temperature and is the average of more than five values (it should be pointed out, all tests were conducted at a pressure of 1 atmosphere). Maximum care was taken with all tests in order to minimize the possible error. For this reason each test has been repeated at least three times.

Interfacial tension of $C_{16}TAB$ aqueous solution reaches the lowest point around the solution concentration of 345 ppm. This concentration, which is shown with a legend of square point, is called the critical micelle concentration (CMC) of $C_{16}TAB$ aqueous solution. After CMC, the interfacial tension remains constant or slightly increased.
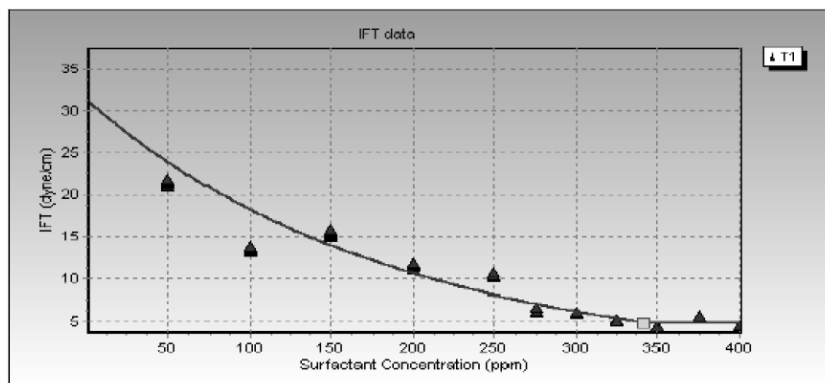
Figure 7. Variation of IFT with surfactant concentration (T=30 °C, P = 1atm.)

As Badakhshan has reported, interfacial tension can be considered as a linear function versus temperature in constant surfactant saturation [7]. Therefore, for each tested surfactant concentration, we have modeled a linear correlation between temperature and interfacial tension. The correlation for all surfactant concentration is the same ($IFT = A_1T + A_2$), where A_1 and A_2 are constants that differ for each concentration. To estimate A_1 and A_2 we have used the least squares method in this program, after finding the average of the measured data for each temperature in the given surfactant concentration. So A_1 and A_2 can be found easily in the given conditions. Table 3 shows the values obtained for these obtained constants.

Another result worth mentioning is the development of a correlation to predict IFT in different temperatures and surfactant concentrations. Through the experiments, pressure was atmospheric pressure. The pressure sensitivity was not investigated, because as mentioned, the oil used in this research was not live and contained no

solution gas. In addition, pressure changes have no considerable effect on IFT[6]. Note that surfactant concentration must be in the range of 0 to 400 ppm for IFT prediction by this program. Some predicted IFT for different surfactant concentrations are shown in Table 4.

Table 3. The obtained constants in function (IFT=A_1T+A_2) calculated by written program.

Surfactant concentration (ppm)	A1	A2
0	-0.06	38.51
50	-0.1	24.86
100	0.01	12.73
150	-0.07	17.66
200	-0.1	14.29
250	-0.05	12.33
275	-0.04	8.19
300	-0.08	8.8
325	-0.04	6.53
350	-0.04	5.6
375	-0.07	8.69
400	-0.04	5.89

Table 4. Predicted IFT by the written program.

Surfactant concentration (ppm)	A1	A2	Temperature	Predicted IFT
25	-0.07	31.23	55	27.38
45	-0.09	25.76	45	21.71
120	-0.01	14.59	50	14.09
225	-0.08	13.23	35	14.09

4- Conclusions

1) Hexadecyl Trimethyl Ammonium Bromide ($C_{16}TAB$) has been synthesized in a much cheaper way and it can be considered a good issue for case study injection.

2) A correlation is obtained to predict IFT between oil and brine containing different amounts of surfactant concentrations. Note that brine salinity is considered as a fixed parameter (150000 ppm) and temperature and surfactant concentrations are considered as variable parameters. It is easily possible to predict IFT for any temperature and surfactant concentration.

3) Use of a small amount of cationic surfactant ($C_{16}TAB$), along with oil, has reduced the contact angle up to critical micelle concentration formation of the surfactant. Even though the tests are not applied on carbonate rocks, one can conclude that by using this type of surfactant the contact angle of the mixture and carbonate rocks will also be reduced.

4) It has been shown that the contact angle increases after CMC.

5) Interfacial tension (IFT) also decreases with increasing surfactant concentration up to CMC value, and after this concentration it remains constant or slightly increased.

6) The recommended surfactant concentration for reduction of IFT is near critical micelle concentration.

5- Acknowledgment

6- Nomenclature

D_e equatorial diameter, mm

D_s diameter at distance from apex, mm

H   modified bond number

S   ratio of D_s/D_e

T_r reduced temperature

ΔP density difference, g/cm^3

σ interfacial tension, mN/m

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