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New Anionic and Cationic Surfactants and their Effects on Relative Permeability Curves and wet ability Alteration in EOR Process

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ABSTRACT

C12TAB and C10TAB are most efficient in spontaneously displacing the oil from the oil-wet core material. In this paper we presented the results from a study regarding wettability alteration oil-wet to water-wet in low permeability chalk using water-soluble surfactants. Fourteen different surfactants were tested for spontaneous imbibition into oil-wetchalk cores. In an irreversible way, Cationic surfactants of the type $R-N^+(CH_3)_3$ desorbed organic carboxylates from the chalk surface. This was accomplished by aging crude oil-saturated chalk cores for different time intervals and atdifferent temperatures. The wettability of the chalk wasevaluated by their ability to spontaneously imbibe synthetic brine. Crude oils with high ANhave a greater potential to turn the chalk oil wet. By cleaving the core and taking pictures, we investigated the fluid distribution inside the core. Also, in this research, the influence of chemical cationic surfactant Hexadecyl-tri Methyl Ammonium Bromide and anionic new surfactant Hexadecyl-Amino-Benzene Sulfonic Acid on wettability alteration and oil recovery in carbonate rocks are investigated. CMC-value, hydrophobic property, IFT-value, and steric effects close to the N-atom have a great influence on the efficiency of the surfactant. In an irreversible way, Anionic surfactants were not able to desorb anionic organic carboxylates from the crude oil. To involve the formation of a water-wet bi-layer between the oil and the hydrophobic chalk surface we have suggested the brine imbibed non-uniformly, and the mechanism

Keywords: Permeability curves, EOR process, amphoteric surfactants, cationic Surfactants, oil recovery

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I. INTRODUCTION

Wettability alteration of the rock from oil wet to water wet has been suggested as the primary mechanism for increased oil recovery during low salinity water flooding in carbonates ^{[1][2][3]}. Oil recovery is generally greater in water wet reservoirs because of the higher oil mobility owing to its lower affinity to rock surfaces. Water breakthrough is typically slower in water-wet rocks compared to oil-wet reservoirs. In addition, in fractured rocks, a water-wet matrix allows for water imbibition and counter current flow of oil. Most carbonate reservoirs are not completely oil wet; instead the

rocks usually have mixed wettability depending on the nature of the mineral surface, oil properties, and fluid-rock interactions [1][4][5]. The relative proportion of oil-wet and water-wet surfaces determines the overall capillary pressure, relative permeability, and residual oil saturation, which ultimately control oil recovery ^{[1][6][7][8]}. Oil recovery by water flooding is one of the most important methods applied to maintain the reservoir pressure above the bubble point pressure in order to increase oil sweep efficiency ^[9] Mechanism of oil recovery by water is in such a way that when water is located next to the rock, spontaneous imbibition of water in to the matrix occurs and oil is extracted ^[10]. Most of the Iranian reservoirs which are fractured carbonate reservoirs are oil wet [11]. In this type of reservoir, water cannot spontaneously imbibe in to the matrix due to the low and negative capillary pressure [3]. Maximum oil recovery is obtained after the wettability alteration of reservoir rock^[12].

A proper method of increasing the sweep efficiency in this type of reservoirs is to maintain oil swelling, reduce the oil viscosity, lowering the interfacial tension and changing the wettability of the rock ^[13]. Hence, wettability alteration of the oil wet rocks to water wet is crucial to enhance oil recovery of this type of reservoir. In other to improve oil recovery in fractured carbonate reservoirs, some different method have been reported in the literature including adding а certain amount of surfactants^{[14][15]}, thermal processing, microbial flooding and [16][17]. In order to change the wettability using surfactants, three different types of surfactants including anionic surfactant^{[18][19]}, non-ionic surfactants ^[14]and cationic surfactants were employed ^[20]

The goal of this study is to investigate the effect of the cationic surfactant Hexadecyl-tri Methyl Ammonium Bromide and amphoteric new surfactant Hexadecyl-Amino-Benzene Sulfonic Acid on wettability alteration and oil recovery in carbonate reservoirs. The results of them are comprised to each other. In the current thesis, the following test was performed to investigate the mentioned goals:

- Conductivity, IFT measurement, in order to finding CMC.
- Absolute permeability measurements.
- Contact angle measurements by VIT 6000 apparatus in order to wettability alteration investigation.
- Surfactant flooding in critical micelle

concentration to perform relative permeability curves.

- Quantitative (contact angle) and qualitative (relative permeability Curves) wettability alteration method to investigate the effect of two surfactants.
- Oil recovery measurement by three flooding process, (water, CTAB and HABSA injections).

2. EXPERIMENTAL APPARATUS AND PROCEDURE

2.1. Materials

2.1.1. Carbonate Core Sample and Solid Polished Surfaces

Carbonate core samples were taken from babakoohi field outcrop in Fars state (Iran). After taking plugs from these cores, some pellets (flat polished surface) has been taken from carbonate plugs for contact angle measurement. Figure 1 shows the carbonate plug and pellets that prepared for this study.



Figure 1: Carbonate plugs and aged pellets 2.1.2. Oil phase

Kerosene was used in IFT measurements and crude oil was used in core flooding tests and sample aging.

Table 1: Oil phase specification

Crude oil	Crude	Kerosene
density(gr/cm ³)	oil API	density(gr/cm ³)
0.8	35	0.84

2.1.3. Aqueous Phase

Distilled water with different concentration of cationic surfactant Hexadecyl-Tri Methyl Ammonium Bromide and amphoteric surfactant Hexadecyl- Amino Benzene Sulfonic Acid has been used as aqueous phase in this study.

2.2. Experimental Setup

2.2.1. Soxhlet (Core Cleaning Systems)

For many core analysis measurements, samples are cleaned out of pore fluids and contaminants then either measured in a dry state or with partial or full re-saturation. Cleaning and drying of rock samples can be achieved using many different techniques; Sox let is the fastest method. Hot Sox

let solvent extraction can be used to rapidly clean samples. In the Sox let apparatus, the sample soaks in hot solvent that is periodically siphoned off, distilled and returned to the sample. The process continues until the siphoned-off solvent becomes clear. This may take from a few, to several hundred hours depending upon permeability and the viscosity of the oil in the pores. It is possible to obtain the initial water saturation and water composition from preserved core and core plugs through distillation extraction. A complete unit consists of an electric heating mantle, boiling flask, thimble for holding the sample, trap or calibrated sidearm, and condenser.



Figure 2: Sox let Extractor

2.2.2. IFT & Contact angle Measurement System Drop shape analysis (pendant drop method) is a convenient way to measure surface tension. Pendant drop enhanced densitometry, bv video-image analysis, has been considered as a very accurate method for measuring the IFT of fluid/fluid interface for a wide range of IFT values (Figure 3.3). In this method, video images of pendant drops are digitized to determine the interface loci, then measuring the IFT through the solution of the Young- Laplace equation. The pendant drop technique, as other interfacial tension measurement techniques, requires extreme cleanliness to obtain good quality and reproducible results. Here, the needle used for hanging the drop should be well cleaned and the climbing of the interface over the outer surface of the needle should be avoided. Figure 3.4 describes a schematic of the instrument which is used to measure the interfacial tension (IFT) of aqueous surfactant solutions and kerosene. The method involves injection of a drop of fluid (such as crude oil) into a second immiscible phase to determine the IFT between the two phases^[21].

The VIT 6000 consisted of following compartments:

- Two Manual pumps equipped with gauges for monitoring the pressure inside the manual.
- Visual cell equipped with sapphire glasses can tolerate high pressure.
- PT-100 thermometer for monitoring the temperature of the system.
- A vibration-free base.
- Electrical heaters for generating heat for increasing the temperature of the system.
- Pressure transmitter for 700 bar and indicator for monitoring the pressure through the experimentation.
- Video system: 1 CCD color camera 4 M pixel, 1 macro zoom lens, 1 panel light, stands for mounting camera.
- Support for camera with micrometers motion
- tables (rotation & translation).
- Computer



Figure 3: Pendant Drop Interfacial Tension Measurement Apparatus (VIT-6000)



Figure 4: Schematic Image of Contact angle Measurement Apparatus.

2.2.3. Core Flooding Apparatus

In general terms, a core flood system is a system that flow a fluid (gas or liquid) through a core sample at controlled pressure and temperature conditions and measures or monitors flow

parameters. These systems are used for a wide variety of experimental research in the laboratory to develop, evaluate or prove concepts in the laboratory that will improve oil recovery and production in the field.

Core flooding system is the main part of any petroleum laboratory in the academic or the research institutes. Different types of experiments could be conducted using this apparatus such as; conventional fluid injection, chemical flooding, gas injection, acidizing, porosity and permeability measurement and many other tests required in the reservoir condition. Figure 3-5 and 3-6 shows the schematic core flood setup and the core holder with sample accumulators respectively.

Main compartments of the core flooding apparatus include:

- Core holder (Hassler).
- Fluid accumulators.
- Constant temperature Oven.
- High pressure precision pump.
- Digital data logging.
- Rosemount Pressure Transmitter.
- Back Pressure Regulator.
- Hydraulic Pump.
- Stainless Steel Material



Figure 5: Schematic of core flood experimental setup



Figure 6: Core holder and accumulators

2.2.4. Vacuum & Saturating Apparatus

This set consists of a vacuum pump, some air connection lines, burette and desiccator. As observed in figure 3.7 this equipment is used for saturating the plugs.

Workmanship of this set is in this way:

At first put the plug inside the desiccator and after closing its door and connecting the lines, vacuum pump will be turned on and suction out the air inside the desiccator and plug. After 2 or 3 hours that the air inside the plug completely was suctioned out, open the valve under the burette and wait to plug quietly sinking in the fluid. Then we give enough time to plug saturation.



Figure 7: Vacuum and saturation apparatus 2.2.5. Conductivity Measurement Apparatus Conductivity detector which was applied for experiments is from Jenway Company (JENWAY-4510) as shown in Fig. 3.8. At first Conductivity detector should calibrated with standard solution. In all of experiments electrode was washed up with distilled water. This is so necessary for accuracy of solutions conductance and immersing the probe of conductivity meter in solution.



Figure 8: JENWAY-4510 apparatus for measuring conductivity Experimental Procedure

2.3. Core Cleaning

In order to compare the effectiveness of different treatments on the same core and being able to "restore" the core state, it is important that the core can be cleaned to a repeatable initial state^[22]. Restored state analysis requires that the core be cleaned to the water-wet state that existed before oil accumulated in the formation. The core is then saturated with crude oil to a capillary pressure typical of the formation and the system allowed to equilibrate or "age" under formation conditions. The traditional method for cleaning core samples is Dean-Stark extraction, which usually involves boiling toluene [23]. In this method, toluene is brought to a slow boil in a Pyrex flask; its vapors move upwards and the core becomes engulfed in the toluene vapors (at approximately 110 °C). Eventual water within the core sample in the thimble will be vaporized. The toluene and water vapors enter the inner chamber of the condenser; the cold water circulating about the inner chamber condenses both vapors to immiscible liquids. Re-condensed toluene together with liquid water falls from the base of the condenser onto the core sample in the thimble; the toluene soaks the core sample and dissolves any oil with which it come into contact.

When the liquid level within the Soxhlet tube reaches the top of the siphon tube arrangement, the liquids within the Soxhlet tubes are automatically emptied by a siphon effect and flow into the boiling flask. The toluene is then ready to start another cycle.

2.3.1. Pore volume Measurement

Pore volume of the core sample is obtained from difference between dry weight and wet weight divided to density of distilled water. For measuring the core pore volume, fallowed the below steps:

- Cleaning the plug by sox let and toluene.
- Dry plug by oven in 100° C
- Weight plug and note it.
- Vacuuming and saturating the plug by vacuum pump and core flooding
- Weight the wet plug and note it
- Subtract the wet and dry weight and divided the result to density of distilled water

2.3.2. Absolute Permeability Measurements

For characterization of absolute permeability, pressure drops are measured across the core sample at various flow rates of water injection. Absolute permeability of core plug can be deduced from slope of pressure drop versus flow rate. Figure 3-9 shows dual gas permeability and porosity measurement apparatus.



Figure 1: a- dual gas permeability measurement apparatus. b- Gas porosity measurement apparatus.

By using below Darcy equation the absolute permeability can be obtained.

 $Q = \frac{KA\,\Delta P}{\mu L}$ (1)

q = flow rate through the porous medium, cm3/sec A = cross-sectional area across which flow occurs, cm2

 $\mu =$ viscosity of the flowing fluid, cp

L = Length of the carbonate plug (cm)

2.3.3. Aging

The carbonate plug and pellets for being oil wet immersed in the crude oil. After that this samples placed in the drying oven at elevated temperature (around 60 C) for at least 100 hours^[24] ^[25]. The drying oven is shown in Figure 3-10.



Figure 10: Drying Oven

2.3.4. Interfacial Tension Measurement

Kerosene was selected as oil phase and distilled water with variable surfactant concentration as aqueous phase in interfacial tension measurement experiments. The reason of choosing kerosene instead of crude oil was ignoring asphaltene and other surface active agent effects in crude oil and its cleanness. In order to evaluate the interfacial

tension between aqueous solution with different surfactant concentrations and kerosene the pendant drop method is used. In this work, the densities of aqueous solution with different surfactant concentrations and kerosene were measured using DMA-5000 apparatus.

Another part of tests is pendent drop experiment to investigate the effect of two surfactants on IFT reduction. During this experiment pendent drop cell filled with kerosene and transfer vessel was filled with aqueous solution with different surfactant concentrations. Aqueous solution with different surfactant concentrations injected through ISCO pump into the pendent drop cell with the very low flow rate. Although this low flow rate makes the process time consuming, but it will allow the surfactant monomers and micelles reach to the equilibrium between two layers of oil and brine. Choosing this low rate, guaranties that the aqueous phase separation from the tip is result of density difference not flow rate of injection. According to the above-mentioned method, the IFT between aqueous solution with different surfactant concentrations and kerosene was determined. IFT results were used for CMC determination.

2.3.5. Contact ang<mark>le M</mark>easurement

The wettability alteration was verified bv measuring and comparing the contact angle between the water drop and a single, flat polished rock piece which is aged at the concentrations of the surfactants. Before aging the rock pieces in the different concentration of surfactants solution, these pieces aged in the crude oil for two weeks to completely become oil wet. In this study we choice the kerosene as a bulk fluid and distilled water as dropping fluid. Contact angle was measured by a VIT6000 system. The water drop was dispersed on the rock piece and the angle is measured from denser fluid (water) to the lighter fluid (kerosene) and the contact angle was measured (Figure 3-11). Contact-angle measurements give a general qualitative indication of the wetting tendencies of thesurfaces and fluids.



Figure 11: contact angle measurement

Water and Surfactant Flooding

The containers should be filled with selected fluid and put in their place.

- Put the core in core holder slowly.
- The core should be in the center of core holder.
- Use the spacer in order to fill the empty space.
- Close the oven door and wait till receive the objective temperature.
- Opening the confining pressure valve and injection with hydraulic pump apply the
- Loading pressure to the core.
- Back pressure valve should be set on the objective pressure.
- Touch screen shows the information during the experiments.
- If the core is not pre-saturated, at first it should be saturated otherwise, fluids can be directly injected.
- Injection of brine until the core is saturated.
- The amount of injection and production water should be measured accurately.
- Oil injection begins after water saturation and continues till the steady state.
- In this step the injection and production oil and water should be measured.
- Open the solution chamber valve and inject the fluid to the core.
- In all of the steps note the maximum pressure and injection rate.

Relative Permeability Measurement

The water drive displacement technique of testing is essentially an unsteady-state flow process. The sample is originally saturated with wetting phase, and instead of both oil and water being injected; only one phase is injected in to the core. The water drive technique then is an unsteady state process in that only one fluid is entering the core and two fluids are leaving. The water displacement process for determining relative permeability is dependent upon the frontal advance fluid-flow concept. The procedure for performing a water-displacement test is relatively simple and fast. The procedure is essentially as follows: an approximately homogenous sample is selected and its physical properties of permeability, bulk volume and porosity are determined. The sample is properly mounted in a holder and saturated with the wetting phase, which is normally water. Then oil is flooded in to the sample and the initial water saturation was measured. The sample is de-saturated by injecting water at one end and producing both oil and water at the other end of the

small sample. In the calculation of the data obtained from such a test, three necessary condition or assumptions which must be satisfied. First the pressure drop across the core sample must be large enough to make any capillary end effect negligible. Second, the water saturation can be described at a mean value of pressure defined as:

$$\overline{P} = \frac{P_i + P_o}{2} \tag{2}$$

Where P_i represents the pressure at the injection end of the core and P_0 represents the pressure at the production end of the core. Third, flow is horizontal and the core sample is small enough and the test time is short so that all effects of gravitational forces can be neglected. If these three conditions are satisfied, then it is necessary to measure only the following quantities during the test: 1- the cumulative water injected as a function of time and 2- the cumulative oil produced as a function of time. With these two measured quantities and with the pressure at the injection and production ends remaining constant, the relative permeability ratio of water respect to the oil can be calculated. From the measured data, the cumulative volume of water injected in term of mean pressure is expressed as a multiple of the total pore volume of the sample and can be calculated by the following equation:

$$(Q_i)_{pv} = \frac{2Q_{ic}p_i}{LA\phi(p_i + p_o)}$$
(3)

 $(Q_i)_{pv}$ = cumulative injected water expressed as pore volume

 $LA\phi$ = total pore volume of the sample

 Q_{ic} = cumulative water injected at pressure p_i

P_i and P_o previously defined.

A quantity known as $S_{w(av)}$ may be calculated simply by dividing the cumulative oil produced by the pore volume of the sample. Both the water injected and oil produced have been measured respect to the time and therefore can be cross plotted so that a plot of $S_{w(av)}$ as a function of the cumulative pore volume of water injected can be obtained. The slope of $S_{w(av)}$ - injected water curve represents the fraction of the total outflow from the sample that is oil at any given time, which defines the following equation:

$$f_o = \frac{d(S_w)_{av}}{d(Q_i)_{av}} \tag{4}$$

Where f_o represents the fraction of the total outflow that is oil. The relative permeability ratio of water to oil can be calculated from the following equation:

$$\frac{k_{m}}{K_{m}} = \frac{1 - f_{o}}{f_{o}(\mu_{w} / \mu_{o})}$$
(5)

 $\frac{k_{nv}}{K_{ro}}$ = relative permeability ratio of water to oil

 μ_{w} = viscosity of water

$$\mu_o$$
 = viscosity of oil

This particular value of the relative permeability ration applies at the water saturation at the outflow face. The water saturation at the outflow face is expressed by the following equation:

$$(S_w)_o = (S_w)_{av} - (Q_i)_{pv} f_o$$

(6)

Hence the relative permeability ratios are obtained as a function of saturation by solving the above series of equations. In order to determine the actual value of the relative permeability to water or oil, it is necessary that one or the other be independently determined.

3. DISCUSSION

C12TAB andC10TAB are most efficient in spontaneously displacing the oil from the oil-wet core material. In this study, most of the collected experimental data were related to C12TAB, and the concentration of monomers is governed by the CMC-value. The cationic monomers have interacted with adsorbed anionic materials from the crudeoil.In addition to electrostatic interactions, theion-pair is stabilized by hydrophobic interactions. Once the adsorbedorganic material has been released from the surface, the chalk becomes more water-wet and the imbibitionof water is in fact governed by capillary forces. In spite structural similaritybetween of the these surfactants, the imbibition rate of the C16TAB solution is much lower compared toC12TAB.The hydrophobic part of the cationic surfactantplays an important role in changing the wettability of the chalk because the imbibition rate of C12TAB and C10TAB isvery comparable, even though there is a factor of about 5 in the CMC-value in favor of C10TAB.Dissolution as ion-pair in the organic phase isalso enhanced by more hydrophobic surfactants.Negligibleamounts of oil were produced when using C8TABeven though the CMCs0.14 M, which is muchhigher compared to C12TAB. The hydrophobic interactionwith adsorbed organic material is lower forC8TAB, and

this may be an explanation for the lowoil production at 408C.The increase in the imbibition rate by increasingthe temperature from 408C to 708C for the C12TABsystem can be explained by the increase in the diffusion rate of the surface active material, bothmonomers and micelles. For the present surfactant system, it is also known that the interfacial tension,IFT, increases as the temperature is increased (Austadet al., 1997).

We detected that a gravity segregation of the oil has takenplace during the imbibition process. As the surfactant concentration decreases below the CMC, the IFT-valueand the capillary forces will increase, which shouldprevent gravity segregation.It is noticedthat the ethoxylated carboxylate, n-C₈- (EO)₈ -OCH₂ -COONa(Akypo), only displaced traces of oil, probably due to low hydrophobic interactionbetween the n-C₈ -group and the hydrophobic surface and complex formation with Ca²⁺. The other anionic surfactants tested did not imbibein any significant amounts of water into theoil-wet chalk, confirming that the EO-groups play avery important role regarding the imbibition mechanism.

Tabatabal et al. (1993)indicated that the adsorption of cationic surfactants onto calsite is very low in general, and they observed a negative surface excess of the surfactant in the presence of added multivalent co-ions like Ca²⁺. The loss of cationic surfactant during the wettability alteration process in chalk due to adsorption must be very low provided that the brine contains sufficient amounts of Ca²⁺.

Partitioning of cationic surfactants into the oilphase at natural pH-values is very much related tothe acid number, AN, of the crude oil. High values of the AN will cause high surfactant partitioning (Standnes and Austad, 2000). The surfactants are probably dissolved as 1:1 ion-pairs with organiccarboxylates from the crude oil.Similarly, the desorbed carboxylates will also form a 1:1 ion-pair complex with surfactants that will also dissolve in the oil phase or micelles. Surfactants dissolved in the oil phase as ion-pairs are probably not active in the wettability alteration process, and this must be taken into account in designing an actual field project.

CONCLUSION

In the present study, the influence of chemical cationic surfactant Hexadecyl-tri Methyl Ammonium Bromide and anionic new surfactant Hexadecyl-Amino-Benzene Sulfonic Acid on wettability alteration and oil recovery in carbonate rocks was investigated. Contact angle and relative permeability were measured to indicate the wettability alteration. The obtained result showed that HABSA surfactant is more effective than CTAB in wettability alteration from oil wet to water wet in carbonate rocks.

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