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Experimental Study of Chemical Reduction on Interfacial Tension by Using Dodecyl Trimethyl Ammonium Bromide

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Surfactant flooding has the potential to significantly increase recovery over that of conventional water flooding. The availability of a large number of surfactant structures makes it possible to conduct a systematic study of the relation between surfactant structure and its efficacy for oil recovery. Also, the addition of an alkali such as sodium carbonate makes possible in situ generation of surfactant and significant reduction of surfactant adsorption. In addition to reduction of interfacial tension to ultra-low values, surfactants can be designed to alter wettability to enhance oil recovery. Therefore, using surfactant increases water imbibition process into the matrix, which increases oil recovery. In this paper the effects of dodecyl trimethyl ammonium bromide (DTAB), on the reduction of interfacial tension (IFT) between water and oil. Oil sample obtained from fracture carbonate reservoir in southern of Iran, was studied at the reservoir temperature. The results show that the DTAB surfactant at 0.8 wt% concentration reduced interfacial tension between oil and water until 1.23 mN/m.

Keyword: Surfactant, Interfacial tension, Enhanced oil recovery, Fracture carbonate reservoir.

1. Introduction

Crude oil makes a major contribution to the world economy today. The provision of heat, light and transport depends on oil and there has not been a single energy source to replace crude oil so far that has broadly integrated. To meet the rising energy consumption in the world, there is a dire need to produce more crude oil. Stagnant oil production and unimpressive recovery by conventional methods have made the situation more precarious. Hence, attention is being paid to Enhanced Oil Recovery (EOR) techniques for recovering more oil from the existing oilfields.

On an average, only about a third of the original oil in place can be recovered by the primary and secondary recovery processes. The rest of oil is trapped in reservoir pores due to surface and interfacial forces. This trapped oil to secondary water floods can be recovered by reducing the capillary forces that prevent oil from flowing within the pores of reservoir rock and into the well bore. More and more advanced technologies are being implemented in the oil

industry today to recover this trapped oil under the banner called “Enhanced Oil Recovery Processes”.

Any process that involves the injection of a fluid or fluids into a reservoir to supplement the natural energy present in a reservoir, where the injected fluids interact with the reservoir rock/oil/brine system to create favorable conditions for maximum oil recovery is known as an EOR process [1]. These favorable interactions intended to maximize oil recovery may be oil swelling, lowering of IFT, rock wettability modification, oil viscosity reduction and favorable phase behavior [1]. The effect of capillary forces on trapping of oil with in the pores of reservoir rock is normally generalized by the use of a dimensionless number, called the capillary number.

The discovered original oil in place in the U.S is 536 Billion barrels, out of which 162 billion barrels of oil has been recovered by 1993. However, 23 billion barrels of oil can be recovered economically through the application of current proven technology.

Therefore, there still remains 351 billion barrels of oil trapped inside the producing reservoirs, which

amounts to nearly two thirds of original oil in place. The worldwide target for EOR is estimated to be two trillion barrels. Hence, EOR processes are essential to recover these huge amounts of trapped oil.

Oil productions from fractured reservoirs normally occur by spontaneous water imbibition and oil expulsion from the matrix into fracture network. Hence, spontaneous imbibition is considered to be the most important phenomenon in oil recovery from fractured reservoirs. In fractured systems, the rate of mass transfer between the rock matrix and fractures usually determines the oil production. Matrix contains most of the oil due to its much higher storage capacity compared to the fracture network. So, an effective matrix-fracture interaction is required to recover the matrix oil. For water-wet reservoirs, having sufficient supply of water in the fractures, the matrix oil is recovered mostly by capillary imbibition where simply the capillary suction draws the wetting liquid into the matrix. Thus, fractured reservoirs are amenable to water flooding only if the matrix blocks are water-wet. Further, injection of dilute surfactant in a water-wet reservoir can recover additional oil by lowering oil/water interfacial tension or wettability alteration. So, the emphasis here is transporting the surfactants through the fractures into the rock matrix where the residual oil to water flood resides.

However, if the reservoir is oil or intermediate-wet, then water flood recovers the oil only from the fractures and completely bypasses the matrix blocks. Injection of high pressure gases have been considered for oil recovery from such fractured reservoirs. These displacements are conducted at adverse viscosity ratio and non-zero density difference. In a fractured reservoir, oil will tend to be bypassed in the matrix blocks and in some fractures due to viscous fingering and gravity override. The recovery of this bypassed oil depends upon the level of mass transfer with the injectant. Generally, the mass transfer mechanisms that occur between the matrix and the fracture can be categorized into three types: transport within a single phase, transport across a partially immiscible phase along a single tie-line and transport across partially immiscible phases across many tie-lines (lines joining equilibrium liquid and vapor compositions of hydrocarbon components). Diffusion and dispersion mechanisms are important in all the cases. Equilibrium constants and phase behavior are important in the last two cases. Capillarity is important in the last two cases whereas insignificant

in the first case. Gas injection is considered to be the main mechanism for oil recovery in oil and intermediate-wet fractured reservoirs as it allows recovering substantial quantities of oil trapped in the matrix. The main mechanism involved in this recovery process is the gravity drainage. The density difference between the gas in the fracture and the oil in the matrix causes the oil production until gravitational forces are balanced by the capillary retaining forces.

Romm measured the two-phase flow behavior and oil-water relative permeabilities in a single fracture and obtained straight-line relative permeabilities for the phases as a function of wetting phase saturation for smooth fracture surface [2].

Tsang studied the effect of tortuosity on single-phase flow in a single fracture using statistical correlations. It was found that the more small apertures there are in the aperture distribution, the larger is the effect of tortuosity. When the fraction of the contact area between the fracture surfaces was raised to 30%, the aperture distributions were invariably large at small apertures and the effect of fracture roughness and flow path tortuosity depressed flow rate from the value predicted by the parallel plate representation of a fracture by three or more orders of magnitude [3].

Wang and Narasimhan conducted studies to characterize the fracture apertures and they created fracture surface roughness using fractal geometry correlations. They developed a fractal fracture model through the use of variograms to relate the aperture correlation structure with physically meaningful shear displacement and mathematically interesting fractal geometry to characterize rough fractures [4].

Pruess and Tsang experimentally measured the two-phase gas-water relative permeabilities for a single fracture [5]. They verified the results numerically by assigning log normally distributed apertures while neglecting the matrix contribution. *Mattx and Kyte* studied the effects of matrix block size on the recovery for reservoir scaling purposes. They showed that the imbibition time required to recover a given fraction of oil from a single matrix block is proportional to the square of the distance between fractures. They also observed that the recovery is sensitive to injection rate [6].

Iffly et al. studied both experimentally and numerically the effect of petrophysical and lithological characteristics on the imbibition behavior for a single matrix blocks with different imbibition

conditions. They also examined the effect of water composition on imbibition. The results showed that physico-chemical bondings between connate water, injected brine, oil and rock at any time during the imbibition can alter oil recovery. Organic molecules can influence oil recovery by changing $\sigma\cos\theta$ alone [7].

Graham et al studied the effect of fracture flow rate on the matrix imbibition. They found that imbibition is sensitive to injection rate and proportional to the square root of the matrix permeability, interfacial tension, a function of contact angle and depends on the fluid viscosities and characteristics of the rock [8].

Braester analytically modeled simultaneous flow of two immiscible fluids in a fractured reservoir and found saturation shock in the fractures, whereas in the blocks saturation varied gradually. In contrast to the Buckley-Leverett solution for a non-fissured porous medium, the front velocity and the saturation at the front decreased with time because of transfer of wetting fluid from fissures to the matrix blocks [9]. The results were found to be in agreement with laboratory experiments and field observations.

Kleppe and Morse conducted laboratory experiments involving flow of oil and water on matrix blocks surrounded by fractures and used a numerical model to simulate the experimental results. They found that the ultimate oil recovery from fracture reservoirs is greatly affected by the production rates at conductivity ratios higher than 1. For fracture flow capacities of the order of $1/10^{\text{th}}$ matrix flow capacities, the effect of production rate on oil recovery is negligible. At the production rates of the order of 0.05 times the gravity reference rate, fractured systems behave essentially as non-fractured reservoirs [10].

Kazemi et al. have demonstrated that the modeling approach taken by Swann [12] is more convenient and accurate than the frequently used dual porosity approach for simulation of flow through a fractured reservoir. *Swann and Kazemi et al.* neglected capillary pressure and used an analytical solution to test their finite difference numerical solution. A comparison of the numerical and analytical solutions revealed that the finite difference solution had numerical dispersion problems even if very small time and spatial increments are used [11, 12].

Civan [13, 14] extended the approach of *Swann* [12] to include compressibility, gravity and capillary pressure

and obtained an efficient numerical solution using differential quadrature.

Civan [15, 16] has shown that quadrature and cubature methods can alleviate numerical dispersion even for 10 times greater spatial increments and 3000 times larger time steps than the finite difference solution [12, 13, 14, 15, 16].

Gupta et al. [17] extended the double exponent model proposed by *Civan* to include the contribution of dead-end pore-space in the matrix to the oil recovery. Inclusion of contact angle term in the time scaling group of their model improved correlation of the imbibition recovery for samples with varying shapes and sizes, flow boundary conditions and fluid and rock properties. They used triple exponential functions to analyze their experimental data. These terms represent the transfer of oil from (1) dead-end pores to the primary network of interconnected pores (2) from the primary network to the matrix fracture interface and (3) from the interface to the fracture system. This model improved matches between experimental and predicted oil recovery during imbibition compared to the previous models [15, 16, 17].

Gupta et al. also investigated the effect of matrix-fracture transfer on oil displacement by water imbibition in naturally fractured porous media if wettability and process rate vary. They developed a mathematical model coupling the two-phase flow in the fracture network and in the porous matrix. An oil-water exchange function incorporates the rates of transfer of oil from the dead-end pores to the network of pores and then to the network of fractures. Parametric studies with this model indicated that the rate constants and matrix wettability play important roles in accurate description of oil recovery during water flooding in naturally fractured reservoirs.

Thus, by referring to the latest previously published literature on fracture-matrix mass transfer, it can be concluded that the wettability plays a vital role in accurately predicting the mass transfer flow behavior between the matrix and fracture in a fractured reservoir [17].

A surfactant is a polar compound, consisting of an amphiphilic molecule, with a hydrophilic part (anionic, cationic, amphoteric or nonionic) and a hydrophobic part. Addition of surfactant to oil-water mixtures reduces interfacial tension and/or alters wettability.

Depending upon the nature of the hydrophilic group, the surfactants are classified as:

1. Anionic - the surface-active portion of the molecule bears a negative charge.
2. Cationic - the surface-active portion bears a positive charge.
3. Amphoteric (or) zwitterionic - both positive and negative charges may be present in the surface-active portion and
4. Nonionic - the surface-active portion bears no apparent ionic charge.

When a surfactant is injected, it disperses into oil and water and lowers interfacial tension thereby increasing the capillary number. As a result, more of the otherwise immobile oil becomes mobile. At the same time, an oil-in-water emulsion may form, blocking the larger pores. This often leads to an improvement in the effective mobility ratio. The injected surfactant continues to mobilize oil and bank it up until the surfactant is diluted or otherwise lost due to adsorption by the rock until it is no longer available to lower the interfacial tension and mobilize oil. At that point, the process degenerates into a water flood.

The capillary pressure resistance to flow is proportional to oil/water interfacial tension divided by the diameter of the constriction. Viscous forces due to pressure gradients in the reservoir are much lower than the capillary forces. Oil mobilization is achieved if the capillary number is increased. Viscous forces cannot be increased greatly because of the limited pressure resistance of the reservoir. Hence, the reduction of the interfacial tension by the use of surfactants could produce the desired effect [18, 19].

However, for significant enhancements in oil recovery, several orders of magnitude reduction in interfacial tension is required. The surfactants capable of generating this reduction are expensive and are required in large quantities, rendering them uneconomical for field application. Hence, our emphasis is to study the wettability alteration rather than reduction in oil-water interfacial tension. Wettability alteration can be induced by low cost surfactants at moderate concentrations.

Factors that affect the interaction of surfactants with the solid surface of porous rock and consequently affect wettability are: surfactant structure, surfactant concentration, kinetics, pore surface composition, surfactant stability, co-surfactants, electrolytes, pH and temperature, pore structure/surface roughness and reservoir type and characteristics. Surfactant adsorption at the solid-liquid interface is a necessary but not sufficient condition for wettability alteration.

A number of studies have shown that wettability shifts from oil-wetting toward water-wetting due to surfactant adsorption [17, 20].

Surfactants are amphipole or amphiphathic molecules composed of a hydrophilic head and a hydrophobic tail. This dual nature of surfactant produces a strong affinity for interfaces between the immiscible fluids such as oil and water. The surfactant by adsorbing on a fluid/solid interface reduces the interfacial tension and thereby alters the wettability of the surface. A surfactant that orients itself on a surface in such a way that the surfactant molecules have the hydrophobic tail groups away from the surface or along the surface will decrease water-wetting and increase oil-wetting. Similarly, the orientation of a surfactant with the head group away from the surface can make the surface more water-wet [17, 20, 21, 22].

Surfactants have been considered for enhanced oil recovery by reduced oil-water interfacial tension. However, these surfactants may enhance oil recovery via wettability alteration as well. This study experimentally determines the influence of surfactant type and concentration on oil recovery, oil-water relative permeabilities and wettability in reservoir rocks [17, 20, 21, 22].

In this work, the effect of cationic surfactant dodecyl trimethyl ammonium bromide (DTAB) with salt materials, sodium hydroxide and sodium carbonate to reduce the interfacial tension between brine and oil sample taken from the Iranian reservoir at the reservoir temperature was studied.

2. Experimental

2.1. Materials

The cationic surfactants used in this study was dodecyl trimethyl ammonium bromide (DTAB) with the formula of $C_{12}N(CH_3)_3Br$, molecular weight 308.34 gr/mol, CMC of 0.418 wt% at 25 °C purchased from Sigma-Aldrich, and salts used in this study were NaCl and KCl obtain from Merck. The oil was obtained from a reservoir that was located in southern part of Iran. The oil properties and composition are given Table 1 and 2, and the structure of DTAB is shown in figure 1.

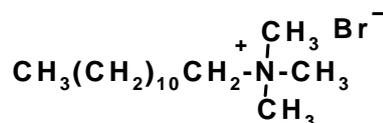


Fig 1: Chemical structure of DTAB

Table 1: Physical properties of Oil used for recombining

Viscosity (cp)	API	Compressibility (Psi ⁻¹)	Density at 25 °C (g/ml)	Asphaltene (wt %)	Oil volume Factor(RB/STB)	Acid number (mg KOH/g oil)
0.311	20	2.01×10 ⁻⁵	0.934	11.25	1.12	2.52

Table 2: Fluid composition used in experiments (mol %)

Component	Dead Oil	Separator Gas	Recombined Fluid	Reservoir Fluid
H ₂ S	0	0.08	0.04	0.03
N ₂	0	0.28	0.10	0.11
CO ₂	0	5.62	2.80	2.87
C ₁	0	45.79	19.50	16.96
C ₂	0.25	20.88	9.11	8.15
C ₃	0.73	15.25	8.01	6.79
i- C ₄	1.61	3.43	2.39	1.13
n- C ₄	3.30	4.43	5.24	4.26
i- C ₅	2.88	1.80	1.63	2.40
n- C ₅	3.60	1.74	2.11	2.55
C ₆	4.99	0.65	2.34	3.50
C ₇	4.95	0.05	2.66	3.15
C ₈	2.87	0.00	1.33	1.77
C ₉	1.50	0.00	1.22	1.01
C ₁₀	2.89	0.00	2.56	2.10
C ₁₁	4.34	0.00	3.45	3.12
C ₁₂₊	66.09	0.00	38.51	40.10

2.2. Interfacial tension (IFT) measurement

In all the experiments, the two salts NaCl and KCl the ratio of 1 to 1 was used as the salt. Surfactant and salt with designed ratios to a 40 ml value for each run of the experiments, solution was prepared. The IFT between the oil and water measured using tensiometer IFT700 model.

For experimental design in this investigation was used of Taguchi software. In this design of orthogonal arrays for design of experiments in order to study the lots of factors with small numbers of experiments, was used. After select of appropriate orthogonal arrays, two Factors, surfactant concentration and salt concentration, each with four levels were selected for cationic surfactant.

3. Results and Discussion

As seen in Table 3, for DTAB surfactant, Taguchi software was designed experiment to L 16 form. In these experiments, cationic surfactant concentration at levels of 0.2, 0.4, 0.6 and 0.8 wt% and salinity levels are 2, 4, 6 and 8 wt% was considered.

Table 3: Experimental design by Taguchi software for DTAB surfactant

Run	Surfactant Conc %wt	Salt Conc %wt		pH	IFT
		NaCl	KCl		
1	0.20	1	1	8.42	3.21
2	0.20	2	2	8.32	2.11
3	0.20	3	3	8.03	2.48
4	0.20	4	4	8.01	2.64
5	0.40	1	1	7.98	2.71
6	0.40	2	2	7.81	2.33
7	0.40	3	3	7.79	1.93
8	0.40	4	4	7.74	2.53
9	0.60	1	1	7.67	2.54
10	0.60	2	2	7.54	2.21
11	0.60	3	3	7.49	1.83
12	0.60	4	4	7.34	2.33
13	0.80	1	1	7.31	2.35
14	0.80	2	2	7.23	2.09
15	0.80	3	3	7.14	1.23
16	0.80	4	4	7.09	2.12

Table 3 and Figures 2 to 3, was shows the changes and effect of concentration of surfactant and salt on interfacial tension between oil and water. As shown in Table 3 and Figure 2 was observed with increasing surfactant concentration, interfacial tension decreases,

and the maximum reduction on the interfacial tension between oil and water in a concentration of 0.8 wt% is observed. Also increasing the salt concentration was caused the reduction of interfacial tension, but as was illustrated at figure 2, the salt concentration is not very effective and can be said that the DTAB cationic surfactant has good salt tolerance.

According to Table 3 amount of optimum pH for this surfactant, that on this pH was achieved the minimum interfacial tension, was 7.14. This indicates that the DTAB surfactant have a best activity at acidic and neutral pH.

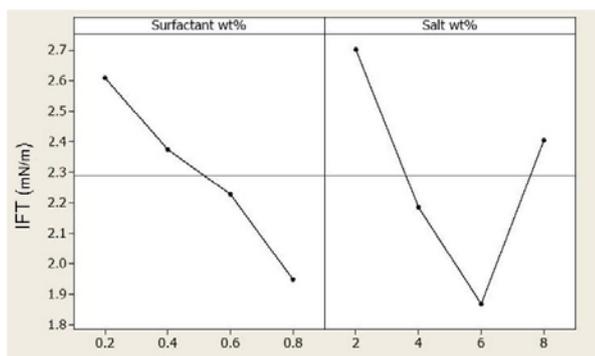


Fig 2: Effect of DTAB surfactant and salt on the interfacial tension between oil and water

Figure 2, the effect of concentrations of surfactant and salts to form a three-dimensional simultaneous on decrease interfacial tension between water and oil was show. The lowest interfacial tension in the concentration of 0.8 wt% of surfactant and 6 wt% of the salt was obtained.

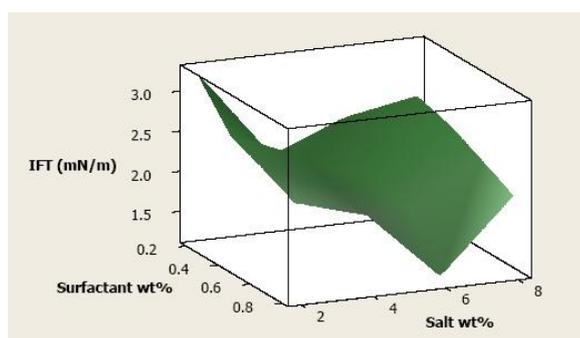


Fig 3: Effect of DTAB surfactant and salt concentration on the interfacial tension

4. Conclusion

1. The maximum reduction on the interfacial tension between oil and water in a concentration of 0.8 wt% is observed.

2. Cationic surfactant dodecyl trimethyl ammonium bromide has a high salt tolerance.
3. Lowest interfacial tension in the concentration of 0.8 wt% of DTAB surfactant and 6 wt% of the salts was obtained.
4. The optimum pH for activity this surfactant is 7.14.

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