

## Improving Recovery Through Surfactant Desorption on An Oil Wet Limestone Reservoir

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### Abstract

The current paper investigates on reducing surfactant adsorption after its application onto limestone surface by Ethylene Oxide (EO) conjugated with Sodium Dodecyl Sulphonate (SDS) to improve oil recovery. SDS has been treated with EO as a nonionic surfactant with low critical micelle concentration to increase its hydrophilic nature that leads to desorb itself from oil wet surfaces like limestone reservoirs after altering wettability.

Although, surfactant has a great impact on Oil recovery, adsorption makes them ineffective. It's been a great concern for petroleum industry during enhanced oil recovery operations. This study focuses on finding a mechanism to reduce SDS adsorption on an oil wet limestone core sample and altering its wettability through EO at different concentrations.

Critical Micelle Concentration (CMC) of SDS was found at 500 ppm by conductivity test was chosen to reduce interfacial tension between oil and brine composition. Due to surface charge variation SDS was observed to adsorb onto limestone surface through core analysis. It has been flooded after water under core flooding operations, which shows near to field observations. For reducing this effect, EO was introduced with different concentrations to alter the hydrophilic properties of SDS. Being limestone oil wet surface, which leads SDS to adsorb onto its surface.

Since, SDS would adhere onto the inner layers of core lead to alter wettability by recovering crude. The recovery of crude from a limestone core has been carried in two ways. Firstly, SDS was treated to get adsorb onto the core surface and secondly desorption of SDS by enhancing its hydrophilic nature through EO. By its application, the recovery of oil has been improved by reduction in adsorption of SDS successfully have been reported.

**Keywords:** Wettability alteration; Surfactant adsorption; Core flooding; Critical micelle concentration

### Introduction

Globally, there is more than 50% of known oil reserves are in carbonate structures. The majority being oil wet primary and secondary recoveries are not sufficient to extract complete oil. Selection of a proper EOR method is required to alter the complex nature of carbonate reservoirs, lead more challenges in chemical flooding operations. Almost an average of 60% OOIP is left behind primary or secondary operations, majority at deep Oil wells. The concern area for surfactant application onto carbonate reservoirs has been limited to laboratories [1]. The unique structure and ability to alter surface properties makes surfactant more reliable for enhancing recovery [2].

Chemical flooding operations are less satisfied due to adsorption of surfactants on reservoir rocks and precipitation [3]. Adsorption and wettability depends on oil composition, structure of surfactants, blending mechanism and surface properties of rock. The mineral composition of rock plays a major role in adsorption and wettability alterations, which acts at solid liquid interface [4].

The application of surfactants on fields is limited because of fluctuations in oil prices. Even though some laboratory results are promising, the major concern is the large-scale availability of surfactants [5].

Adsorption of surfactant is the adherence of nonpolar molecules of surfactants which are organic in nature onto the carbonate surface by ion exchange and lipophilic bonding [6]. The adsorption depends on the availability of divalent ions, salinity and HLB ratio. Adsorption of surfactants means the loss in altering the surface properties which is uneconomical for chemical enhanced oil recovery [7].

Surfactant adsorption onto the surface depends on double layer at interface where there is polarity in charges [8]. At low concentrations, the adsorption is dependent on electric double layer. But at high concentrations near to CMC it depends on salinity, HLB and ionic strength. The adsorption of anionic surfactants has been observed to increase by increasing salt concentration (salinity), temperature and pH by addition of alkali [9].

In the current study, adsorption of surfactants has been reported at different temperatures with salt concentrations. SDS has been chosen to alter wettability for carbonate samples at CMC level. Due to high adsorption, the recovery of oil was observed to be low. The application of EO at different concentrations to reduce adsorption and enhancing oil recovery additional to the recovery obtained through SDS has been reported.

### Experimental Methodology

#### Core flooding apparatus

The apparatus consists of a  $3^{11} \times 5^{11}$  core holder which holds cores

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Figure 1: Capillary pressure curves.

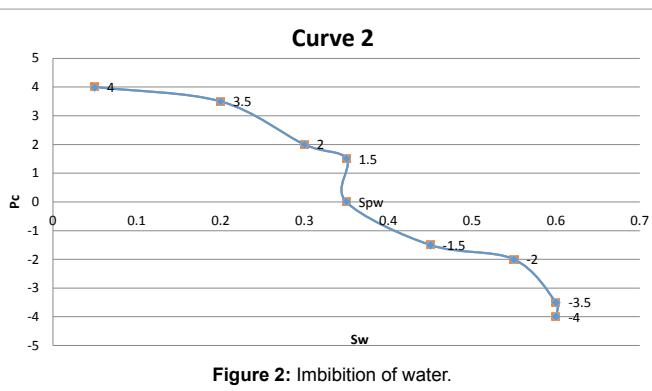


Figure 2: Imbibition of water.

of diameter less than its inner diameter of 3 inch as shown in Figure 1. Cores of  $3^{11} \times 3^{11}$  has been kept inside core holder and mounted by an inlet tube. To make the core static it has been cemented between the inner surface of core holder and inlet tube. At the end of core holder, a porous plate has been mounted to bypass fluids from the core.

Cores can be flooded with low pressures based on column height to extract fluids from core. Wettability of a core sample can be calculated by constructing capillary pressure curves through core flooding. Capillary pressures are measured as the pressure difference between nonwetting oil phase and wetting water phase.

### Curve 1: First drainage of water

Clean and dry limestone Cores have been placed inside core holder. Initially core has been flooded by water injected through inlet column. The pore volume of cores will be saturated by water has been displaced by oil injection. The pressure exerted by water inside core is wetting phase pressure (Pw) and the pressure by oil is non-wetting phase pressure (Po). Po has to reach higher than Pw will result in displacing water by oil. The resultant Pc will be positive and reaches maximum until the oil breakthrough at outlet. This indicates complete drainage of water by oil and the core is left with connate water saturation (Sw).

### Curve 2: First imbibition of oil

The core of complete oil saturation with Sw would be displaced by water injection. Water has to be injected slowly to displace oil until the curve reaches Zero. At Pc zero the water saturation will be recorded as Spontaneous water saturation (Spw) which indicated water have been

saturated by itself or spontaneously. From here a little more pressure has to be applied on water to displace remaining oil in place until it reached residual state recorded as (Sor). The Pc would move towards extreme negative.

### Curve 3: Second drainage of water

The process of oil injection will be repeated like curve 1. Slow injection of oil is preferable to displace water and to reach Pc at zero. At this level oil have been saturated in core spontaneously by itself and recorded as Spontaneous oil saturation(Spo) [10].

### Estimation of wettability

Wettability is the nature of a reservoir to have partial attraction towards a fluid. Limestone samples have been aged with oil at reservoir conditions in a core oven. Then it has been cleaned by soxhlet apparatus with the treatment of heptane. Through core analysis with water and oil simultaneous flooding saturation exponents can be observed by constructing capillary pressure curves. The core has been found to be oil wet by amott wettability index. According to Amott wettability Index

$I_w$  is imbibition of water and  $I_o$  is imbibition of oil

$$I_w = \frac{S_{spw} - S_{cw}}{1 - S_{cw} - S_{or}} \quad \text{and} \quad I_o = \frac{S_{spo} - S_{or}}{1 - S_{cw} - S_{or}}$$

If the difference between imbibition of water and oil is negative then core is Oil wet and positive for water wet. The core is intermediate wet at zero [11].

### Critical micelle concentration test

Micelle is a form of droplet appears at the interface of oil and water by addition of surfactants. The formation of droplet will increase by increasing surfactant concentration [12]. At specific concentration, the micelle will appear with its lowest size leads to lower IFT at optimum. The concentration, where IFT is minimum is considered to be critical micelle concentration of that surfactant can be analyzed by conductivity [13].

In this test conductivity rises with increasing concentration of surfactants until the formation of micelle is completed [14]. Beyond addition of surfactants will increase the number of micelles, which has no effect on conductivity[15]. CMC can be observed by a peak variation on a graph between conductivity and surfactant concentration shown in Figure 2.

### Emulsion tests

In this test, the concentration which has been chosen for core flooding operation should be suited for dissolution [16]. The CMC concentration from conductivity test will be tested with different proportions of brine and alkali for complete de emulsification. The suited proportion will be chosen by observing three clear layers in an emulsion after treatment with surfactants [17].

In the second stage, the selected proportion from first stage of three layers has been treated with EO at different concentration to increase hydrophilic nature by increasing HLB.

### HLB calculation

EO mol. wt = 44 g/mol hydrophilic nonionic surfactant,

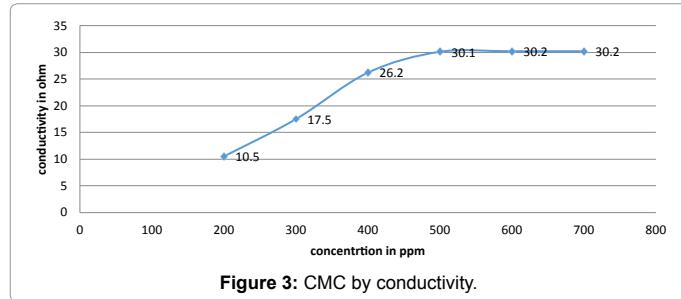
SDS mol. wt= 288.44 g/mol,

Curve 1			Curve 2			Curve 3		
Capillary Pressures (Po-Pw) psi	$S_o$	$S_w$	Capillary Pressures (Po-Pw) psi	$S_o$	$S_w$	Capillary Pressures (Po-Pw) psi	$S_o$	$S_w$
1	0	1	3.5	0.8	0.2	-4	0.4	0.6
1.5	0.2	0.8	2	0.7	0.3	-3.5	0.45	0.55
2	0.6	0.4	1.5	0.65	0.35	-2	0.5	0.5
3	0.95	0.05	0	0.65	0.35 <b>Spw</b>	-1.5	0.65	0.35
4	0.95	0.05 <b>Scw</b>	-1.5	0.55	0.45	0	0.75 <b>Spo</b>	0.25
4	0.95	0.05	-2	0.45	0.55	0	0.75	0.25
4	0.95	0.05	-3.5	0.4	0.6	0	0.75	0.25
4	0.95	0.05	-4	0.4 <b>Sor</b>	0.6	0	0.75	0.25

**Table 1:** Capillary pressures vs. saturations.

Number of emulsions	Brine Concentration in moles	SDS Concentration in ppm	Conductivity mS/cm
1	0.5	200	10.5
2	0.5	300	17.5
3	0.5	400	26.2
4	0.5	500	30.1
5	0.5	600	30.2
6	0.5	700	30.2

**Table 2:** SDS concentrations for conductivity.



**Figure 3:** CMC by conductivity.

Hlb calculation for mixture of 10mole SDS and 20 mole EO will be

$$HLB = (20*44) / ((20*44) + (10*288.44)) = 0.23$$

$$0.23*100 = 23$$

$$HLB = 23/5 = 4.6$$

Six different emulsions with EO has been prepared and treated separately in core flooding operation. The increase in HLB will raise water solubility by addition of EO and reduces adsorption on an oil wet surface reservoirs.

## Results

The limestone core has been saturated in oil for seven days to make it oil wet before core flooding. Then during core flooding capillary pressure curves were constructed to observe the level of wettability shown in Table 1.

According to amott wettability Index formulae  $I_w = 0.55$  and  $I_o = 0.64$

$$I_w - I_o = -0.09, \text{ which indicated oil wet.}$$

After wettability, CMC was estimated by preparing six concentrations of Sodium dodecyle sulphonate (SDS) surfactants from 200 ppm to 700 ppm as shown in Table 2. The CMC has been observed at 500 ppm due to sharp deviation observed on graph between conductivity vs. concentration shown in Figure 3. After selecting 500

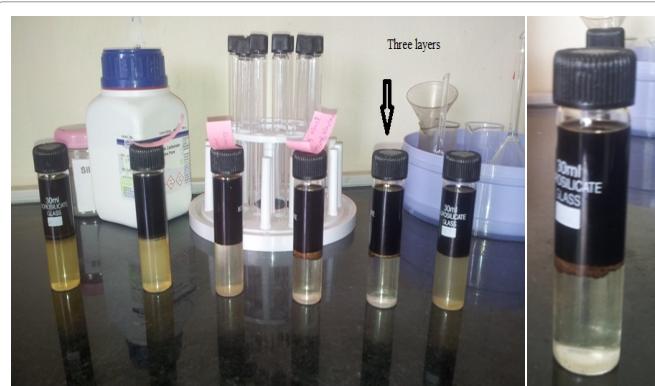
ppm of SDS as suitable concentration, six emulsions were prepared with different proportions shown in Table 3.

From the emulsion test 500 ppm of SDS with 1% wt alkali was observed to appear three clear layers as shown in Figure 4.

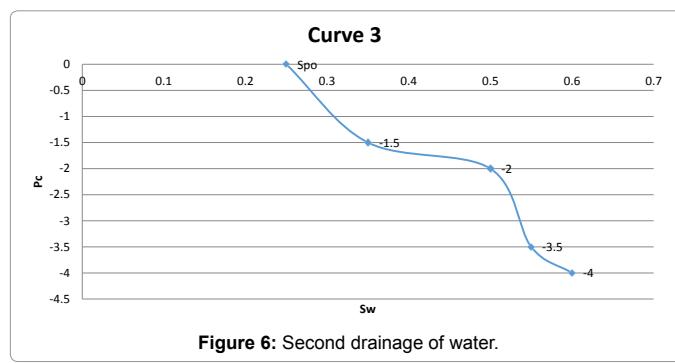
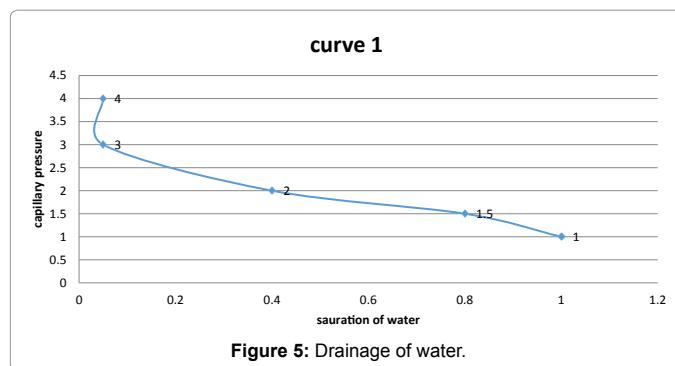
The pore volume ( PV) of core sample has been calculated to be 30.5cc by Ruska porometer. During core analysis, core has been injected by 2 PV of water for 2 days with  $P_c$  of 0.09psi, where 1.35 PV was collected at outlet. Then 2 PV of oil has been injected into core to displace water. Upto 0.6 PV out of 0.65 PV saturated water was collected at outlet. The remaining water was considered as connate water saturation  $Sc_w$  of 0.05 PV at  $P_c$  of 4 psi shown in Figure 5. At outlet, 0.85 PV out of 2 PV oil has been collected. It shows core have been saturated and adsorbed with 1.15 PV of oil and 0.05 PV of connate water. Since, the core has a space limit of 1 PV with consideration of 0.05 PV of  $Sc_w$  the total absorbed amount of oil was observed to be 0.2 PV apart from saturated 1 PV.

Number of emulsions	SDS ppm in 15ml	NaCl wt%	$Na_2CO_3$ wt%	Appearance in layers	Inference
1	500	0.0	0.0	1 phase	w/o emulsion
2	500	0.5	0.0	2 phases	slightly w/o emulsion
3	500	1.0	0.0	2 phases	Light w/o emulsion
4	500	0.0	0.5	2 phases	Light w/o emulsion
5	500	0.0	1.0	3 clear phases	De emulsification
6	500	0.5	0.5	2 phases	Light o/w emulsion

**Table 3:** SDS concentrations with NaCl and alkali.



**Figure 4:** Six emulsion were prepared indicating three-layer middle micro emulsion.



EO						
ppm	Brine wt %.	concentration in moles	SDS ppm	HLB	Oil recovery in PV	Surfactant recovery SDS PV
1000	0.5	10	500	2.6	0.05	0.33
2000	0.5	20	500	4.6	0.12	0.35
3000	0.5	30	500	6.2	0.13	0.44
4000	0.5	40	500	7.5	0.12	0.36
5000	0.5	50	500	8.6	0.11	0.36

Table 4: SDS concentration vs HLB.

The core sample was treated by injecting 5 PV of water to displace oil at  $P_c$  of 4 psi. It leads to collect 0.55 PV of oil out of 1.2 PV at outlet until breakthrough. Water has been imbibed by displacing oil spontaneously upto both pressures were equal. The saturation of water at this level is considered to be spontaneous saturation of water  $Sp_w$  of 0.35 PV beyond where additional pressure has been applied by injecting more water.  $Sp_w$  and  $Sp_o$  have been recorded at 0.35 PV and 0.4 PV respectively shown in Figure 3. In that 0.2 PV of oil is considered to be adsorbed. The left-out oil after water flooding is 0.4 PV as  $Sp_o$  in that 0.05 PV is connate water saturation. Water has been imbibed by displacing oil spontaneously upto both pressures were equal. The saturation of water at this level is considered to be spontaneous saturation of water of 0.35 PV beyond where additional pressure has been applied by injecting more water. The residual oil saturation of oil was observed at 0.4 PV, where the water saturation was maximum upto 0.6 PV as shown in Figure 3. The same process has been repeated by injecting oil to displace water until the capillary pressure becomes zero. Spontaneous oil saturation was recorded at this level to be 0.55 PV of oil as shown in Figure 6.

## Discussion

Surfactant flooding through CMC and Emulsion tests were initiated after water flooding. 5 PV of diluted Emulsions has sent and 0.35 PV out of 0.55 PV oil was collected until breakthrough. The surfactants

were collected by inlet of 4.4 PV and lost 0.6 PV was observed to be absorbed by core. Remaining connate water 0.05 PV and residual oil 0.2 PV were left behind.

In this test the loss of surfactant emulsion is the resultant of adsorption due to electrostatic charge polarity between carbonate minerals and SDS. This has been reduced by treating the same emulsion with EO has a HLB enhancer. EO leads to increase hydrophilic nature of surfactants contrary to core nature makes it desorbed and enhances recovery.

Before treating with EO, five different concentrations have been chosen for miscibility with the emulsions already sent into core by Table 4. These five concentrations have yield different recoveries of oil and surfactants. From the Table 4 it has been observed that 3000 ppm of EO at HLB 6.2 is the effective combination that could recover oil of 0.13 PV out of 2.0 PV of 65% and SDS of 0.44 PV of 0.6 PV upto 73%.

## Conclusion

The application of surfactants onto carbonate reservoirs has been effective under chemical EOR process. During core flooding analysis, the loss of surfactants was observed due to opposite ion interaction with the surface. Capillary pressure curves are considered to be one of the effective methods for estimating wettability of a core sample. While constructing capillary pressure curves second drainage of water has been stopped at spontaneous saturation of oil which can be extended up to the level of complete water saturation. The recovery of oil was found to be less after surfactant flooding due to adsorption. It has been improved by increasing HLB of SDS by EO.

Methods for reducing adsorption of surfactants have a great scope for enhancing recovery of crude addition to its flooding. HLB is one among the most parameters have been altered by the treatment of EO. There may be other parameters which can reduce adsorption of surfactants has to investigated. This process can be extended for reducing adsorption onto dolomite and sandstone reservoirs.

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