

Recovery Modification through Surfactant Adsorption by altering Hydrophilic to lipophilic balance on a chalky core

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Abstract: The research work is carried on investigating for suitable surfactants to enhance the efficiency of oil recovery for artificial limestone cores (chalks). This work carries by the application of surfactants like anionic and nonionics. The objective of this paper is to find the suitable surfactant concentration for chalky cores by conducting core flooding operation through adsorption, wettability and emulsification. The improvement in recovery has been observed by altering Hydrophilic to lipophilic balance (HLB) ratio successfully due to nonionic surfactant. The suitable concentrations of anionic and nonionic surfactants have been reported in this paper.

Keywords: Hydrophilic to lipophilic, adsorption, chalk, nonionic surfactants.

Introduction

The porosity of chalky core can be grouped into three types, namely connected porosity, existing between the carbonate grains and vugs. Which are unconnected pores resulting from the dissolution of calcite by water. Fracture porosity which is caused by stresses following deposition [1]. Fractures can be responsible for water breakthrough in oil industry. Together, these porosities create a very complex path for fluids and directly affect crude oil productivity [2].

In addition to the variations in porosity, wettability is a further heterogeneous characteristic in chalky cores. The surface of chalk containing water and oil turns initially water-wet rocks into mixed-wet or even oil-wet rocks [3]. Oil adherence to the surface of chalk and it is therefore harder to produce. Most chalky reservoirs are mixed wettability or to be oil-wet [4].

Chalk surfaces under-going water flooding, a limited amount of oil can be recovered from oil-wet layers because the water tends to flow mainly through the water-wet layers [5].

Methodology

Core flooding test

Core flooding as is a sophisticated equipment to simulate at reservoir conditions in laboratory. Any core can be cutted into 3-3 inch size which can be fitted and observed in high temperature and pressure [6]. Initially water will be injected to create naturally water wet. Then, oil will be injected as pore volumes. Then as per the requirement displacing fluids will be analyzed by injecting. The efficiency of recovery is measured. Properties like wettability and capillary pressures can be studied.

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. At specific concentration, the micelle will appear with its lowest size leads to lower IFT at optimum [7]. The concentration, where IFT is minimum is considered to be critical micelle concentration of that surfactant can analyzed by conductivity. In this test conductivity rises with increasing concentration of surfactants until the formation of micelle is completed. Beyond addition of surfactants will increase the number of micelles, which has no effect on conductivity.

Emulsion Tests

In this test, the concentration which has been chosen for core flooding operation should be suited for dissolution. The CMC concentration from conductivity test will be tested with different proportions of brine and alkali for complete de emulsification [8]. The suited proportion will be chosen by observing three clear layers in an emulsion after treatment with surfactants.

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

HLB calculation:

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

SDS mol.wt= 288.44g/mol,

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

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

$$0.23 \times 100 = 23$$

$$HLB = 23/5 = 4.6$$

Six different emulsions with EO has been prepared and treated separately in core flooding operation [12]. HLB increases water solubility by addition of EO and reduces adsorption on oil wet surface reservoirs.

Wettability Test

It 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 as shown in **Fig.1**. The core has been found to be oil wet by amott wettability index[9].

$I_w = S_{spw} - S_{cw} / (1 - S_{cw} - S_{or})$ and $I_o = S_{spo} - S_{or} / (1 - S_{cw} - S_{or})$. I_w is imbibition of water and I_o is imbibition of oil. The difference between imbibition of water and oil will lead to know either core is oil wet or water. If it is negative then core is Oil wet and water wet when positive. The core is intermediate when the difference is zero.

Results and Discussion

The core has been saturated in oil for seven days the temperature of 90°C to make it oil wet. After treatment with oil capillary pressure curves have been constructed based on **table 1** to observe the level of wettability. The breakthrough of oil had observed at connate water saturation as 0.05 of water at the end of **fig.2 (a)** as drainage of water.

During **fig.2 (b)** water has been imbibed by displacing oil spontaneously upto both pressures were equal. The saturation for water at this level is considered to be spontaneous saturation of water of 0.35 PV beyond where additional pressure has been applied. In the same way residual oil saturation of oil was observed at 0.35 and spontaneous saturation of water at 0.5 shown in **Fig .2 (c)**.

According to amott wettability Index, $I_w = 0.33$ and $I_o = 0.75$, and the differenc between I_o and I_w is -0.42 , which indicates oil wet .During conductivity test six concentrations of surfactants from 200ppm to 700ppm were prepared for critical micelle concentration. The CMC has been observed at 500ppm shown in **Fig. 3** chosen for emulsion tests. By this observation the core sample wettability was analyzed to be oil wet. After selecting suitable concentration six emulsions with seven different proportions were prepared shown in **table 3**.

From the emulsion test 500ppm SDS with 1% wt alkali was chosen appearance of clear layers by shown in Fig. 4. During core analysis the adsorption behavior of surfactants has been observed by injecting oil followed by water and surfactants to improve recover efficiency.

The pore volume (PV) of core sample has been calculated to be 30.5cc by Ruska porometer used for readings. During core analysis, core has been saturated by 2 PV of water for 2 days, where 1.35 PV was collected at outlet. Then 2 PV of oil has been sent into core by displacing water upto 0.6 PV. At outlet 0.85PV of oil has been collected. The core has been saturated by 0.05 PV of water considered to be connate water and 1.15 PV of Oil. The loss of 0.2 PV additional PV of oil shows the adsorption nature of core as oil wet. The core sample was treated by 5 PV of water leads to collect 0.55 PV of oil out of 1.15 PV at outlet until breakthrough. Then the surfactant flooding from CMC and Emulsion tests was initiated by stopping water flooding. 5 PV of Emulsions was 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 0.2PV.

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.

During dynamic adsorption, SDS of 1 PV was treated with core sample to enhance recovery after water flooding had resulted upto 0.5 PV additional to waterflood recovery of 0.4 PV. It has been observed that the adsorption of SDS was low upto 0.15 PV. This adsorption has been reduced by EO and resulted recovery is upto 0.91 PV.

For static adsorption SDS of 1 PV was treated with core for three days post water flooding. Both dynamic and static adsorptions was compared in **Fig.4**. The recovery of oil after water flooding is 0.4 PV out of 1 PV of oil, saturated in core sample that has been enhanced upto 0.84 by SDS by altering wettability. At this stage, surfactant loss has been observed upto 0.6PV due to limestone internal surface interaction with SDS. The adsorption of SDS have been reduced by application of EO at 3000ppm from **table 5** chosen by emulsion tests improved recovery upto 0.93 PV of oil.

Conclusions

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. Methods for reducing adsorption through surfactants have a great scope for enhancing recovery of crude addition to its flooding. HLB is being the key parameter.

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Tables

Capillary Curves		Pc	So	Sw	So	Sw
Curve 2	curve 3	-4	0.35	0.6	0.35(Sor)	0.6
		-3.5	0.45	0.55	0.35	0.6
		-3	0.45	0.55	0.35	0.6
		-2.5	0.45	0.55	0.35	0.6
		-2	0.4	0.5	0.4	0.55
		-1.5	0.4	0.5	0.5	0.45
		-1	0.4	0.5	0.5	0.45
		-0.5	0.4	0.5	0.5	0.45
		0	0.5(spo)	0.6	0.6	0.35
	0.5			0.6	0.35	
	Curve 1	1	0	1	0.6	0.35
		1.5	0.2	0.8	0.6	0.35
		2	0.6	0.4	0.65	0.3
		2.5	0.9	0.05(Scw)	0.65	0.3
		3			0.65	0.3
		3.5			0.75	0.2
		4			0.9	0.05

Table 1 Capillary pressures vs Saturations

Number of emulsions	SDS ppm in 15ml	NaCl wt%	Na ₂ CO 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

SIF.no.	SDS PV	oil recovered	dynamic adsorption	SDS PV	oil recovered	static adsorption
1	0.2	0.45	0	0.2	0.4	0.1
2	0.4	0.5	0.05	0.4	0.51	0.2
3	0.6	0.56	0.06	0.6	0.61	0.31
4	0.8	0.75	0.1	0.8	0.72	0.42
5	1	0.9	0.15	1	0.84	0.6
6	EO PV	0.9	0.15	EO PV	0.86	0.6
	0.2			0.2		
7	0.4	0.91	0.15	0.4	0.86	0.65
8	0.6	0.91	0.12	0.6	0.89	0.7
9	0.8	0.91	0.09	0.8	0.9	0.77
10	1	0.91	0.05	1	0.93	0.78

Table 4 Surfactant adsorption vs oil recovery

HLB by EO							
ppm	Brine %.	wt concentration in moles	SDS ppm	HLB	Oil recovery in PV	Surfactant recovery in 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 5 SDS concentration vs HLB

Figures

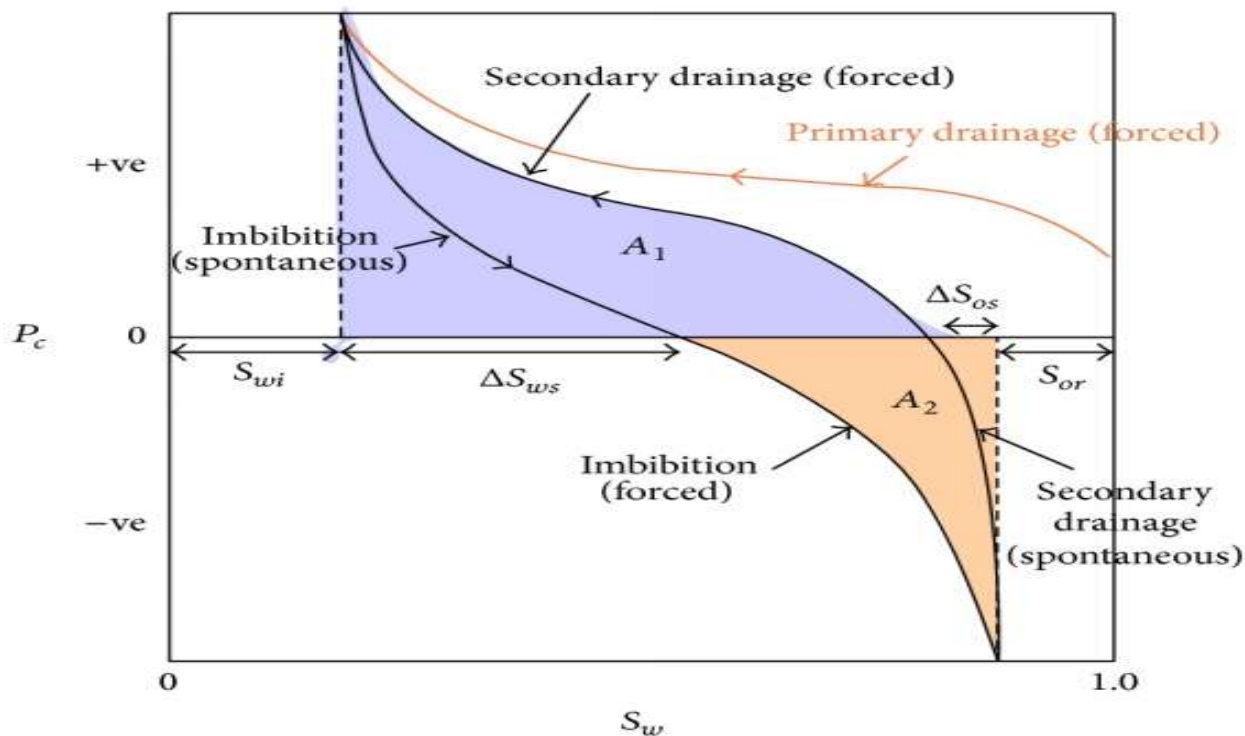
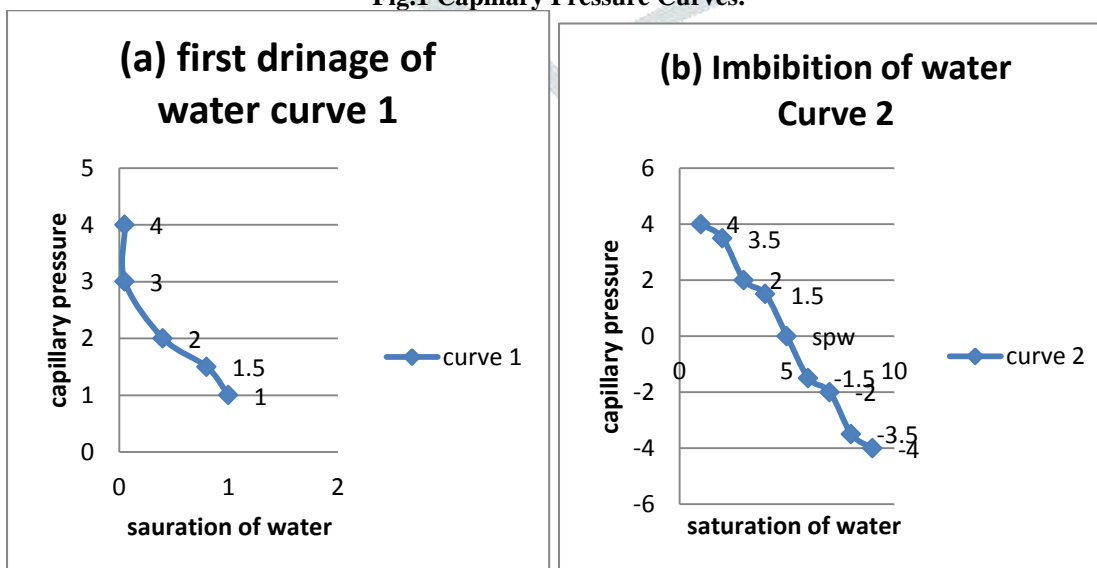


Fig.1 Capillary Pressure Curves.



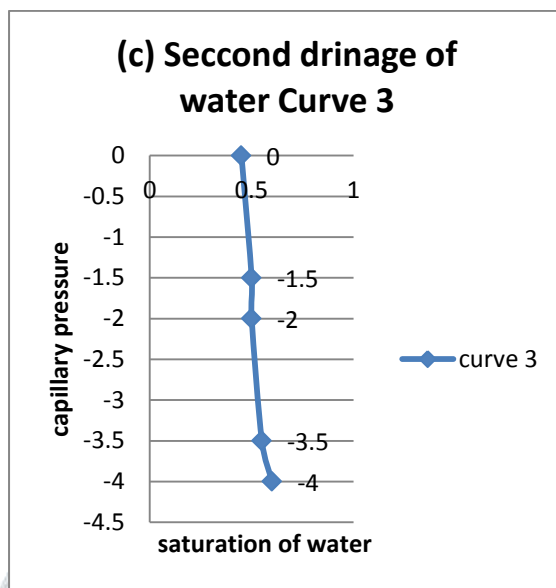


Figure 2. Capillary Pressure Curves during water injection under corflooding apparatus.

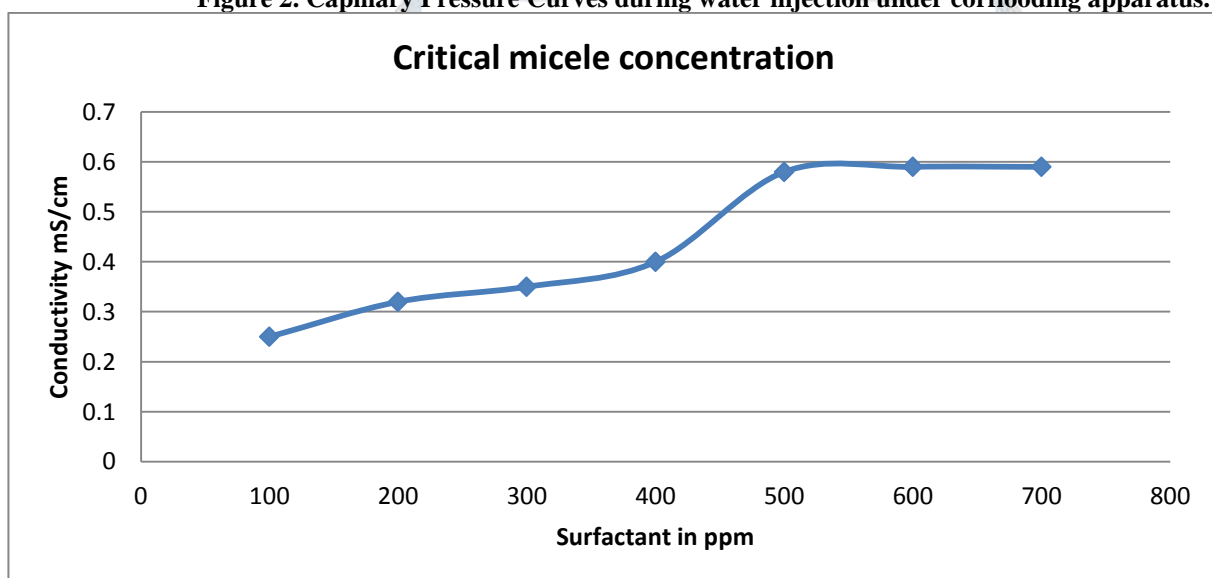


Figure 3. CMC

measurement by increasing conductivity with surfactant Concentration

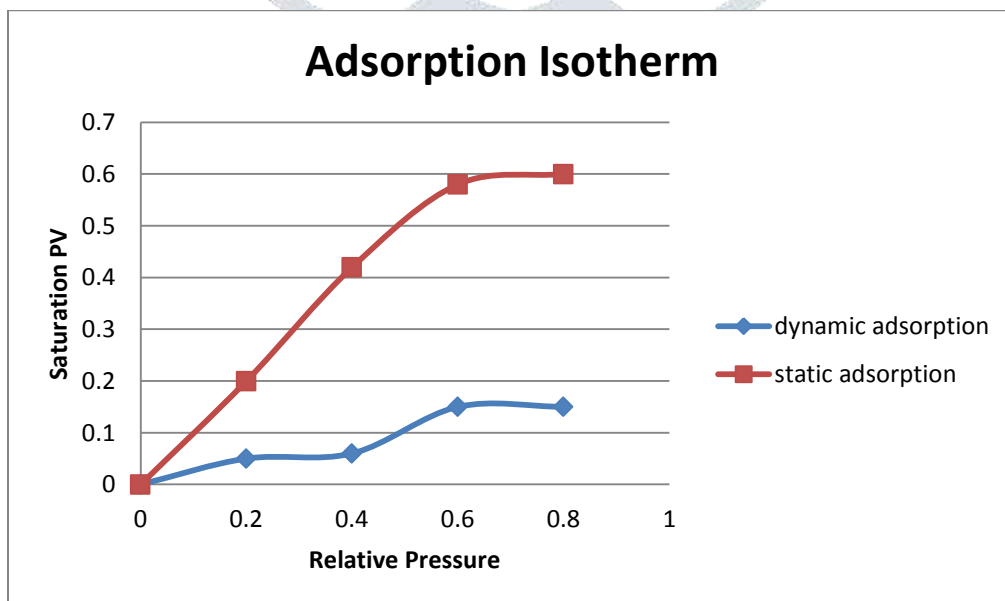


Figure 4. dynamic and static adsorption for SDS at ambient conditions

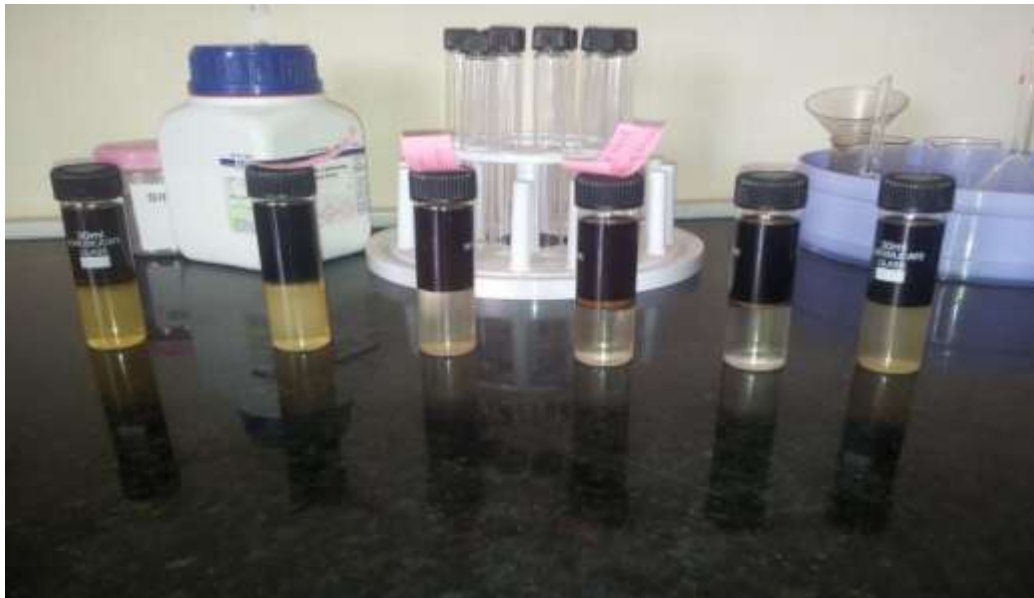


Fig.5 SDS Emulsion with Oil and Water

