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Enhancing Recovery by reducing Surfactant adsorption on oil wet carbonate reservoirs.

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Abstract : The objective of this investigation is to reduce surfactant adsorption from limestone surface by Ethelene Oxide (EO) to improve oil recovery. EO as a nonionic surfactant with low critical micelle concentration has been injected along with SDS (sodium dodecyl sulphonate), to increase hydrphilicity. That led to desorb SDS from oil wet surfaces like saturated limestone reservoirs.

Critical Micelle Concentration (CMC) of SDS was found to be 500ppm by conductivity test, which was chosen to reduce interfacial tension between oil and brine. Three layer emulsion with SDS was observed wettability of limestone from emulsion tests. It has been flooded after water injection under core flooding. SDS was observed to adsorb onto limestone surface through core analysis. For reducing this effect, EO was introduced with different concentrations to alter the hydrophilic properties of SDS. The recovery of crude from core has improved upto 65% of porevolume by desorbing SDS.

Introduction

More than 50% reserves globally are carbonates. Being organic wet, primary and secondary recoveries are not sufficient commercially. Due to its complex nature, predicting a relevant Enhanced oil recovery method (EOR) is becoming a major concern to oil industry.

Chemicals in EOR are considered to be one of the best potential recovery sources. Due to oil price fluctuations, chemical applications on carbonates were limited to academics than field [1]. Though results were promising, field analysis and case studies were few.

Applications of chemicals like surfactants and its components were promising to alter major properties like wettability [2]. Which is the key to enhance additional recovery after water flooding. But, results were not satisfied enough due to adsorption onto reservoir surfaces [3]. It has been a one of the major challenges faced today in oil industry.

Adsorption is a function of oil and mineral composition, structure of surfactants, blending mechanism and surface properties of rock [4]. It is the attraction of surfactant’s organic moiety onto the carbonate by ion exchange and lipophillic bonding[5,6]. The adsorption favors with the availability of divalent ions, salinity and HLB (hydrophilic to lipophillic balance). It depends on the concentration accumulated at double layer interface.

Present study, reports on surfactant adsorption and its effects on oil recovery at different concentrations. The adsorption of anionic surfactants SDS (Sodium do decyl Sulphonate) has been observed to increase by increasing salt concentration (salinity), temperature and pH by addition of alkali. These are the combinations applied during chemical flooding which results in adsorption[7]. The adsorbed surfactants and recovery has been improved by altering HLB through the treatment of EO (ethelene oxide).

Experimental Methodology

Critical Micelle Concentration Test

Micelles form as droplet concentrations at oil water interface during oil wet or water wet conditions[8]. The number of micelles rise with surfactant concentration. The concentration at which the micelle appears to be low exhibits ultralow IFT(interfacial tension)[9]. And considered as critical micelle concentration (CMC).

During conductivity test, CMC can be analysed by a sharp change observed in conductivity, at a particular surfactant concentration shown in fig.3.

Emulsion Tests

After selecting CMC from conductivity test different emulsions were prepared with different components. The components like brine and alkali with different concentrations were mixed with CMC of SDS and oil[10]. The chosen emulsion should consist with three different phases oil, microemulsion and water. It indicates the interface has converted to microemulsion leaving oil and water[11].

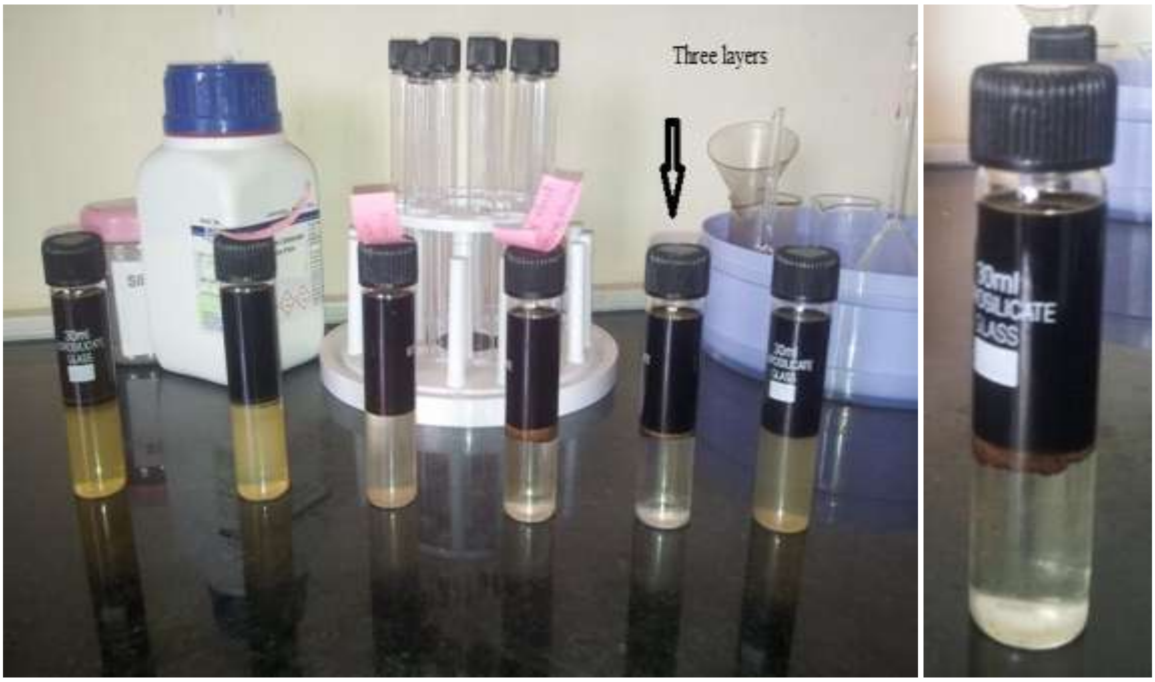

Fig 6. Six emulsion were prepared indicating three layer middle micro emulsion.

Six different emulsions with SDS has been prepared for three layer concentration and treated separately in core flooding operation as shown in table 3.

Table.3SDS concentrations with Nacl and alkali

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	0.5	1.0	3 clear phases	De emulsification
6	500	0.5	0.5	2 phases	Light o/w emulsion

In the next stage, the selected proportion of three layers has been treated with EO for hydrophilicity[12]. The rise in HLB increases water solubility by addition of EO and reduces adsorption on oil wet surface reservoirs[13].

Core Flooding apparatus.

The apparatus consists of a $3^{11}\times5^{11}$(inch) core holder which holds cores of diameter less than its inner diameter. The core flooding equipment can hold upto $3^{11}\times3^{11}$ (inch) core plug as shown in Fig.1. Cores will be treated with hot water and aged by oil simultaneously in an oven for atleast seven days to get complete saturation[14]. After aging core plugs will be flooded with water to get secondary recovery and with chemicals for EOR[15]. The injected pressure is recorded simultaneously with respect to outlet saturations. Then based on pressures capillary pressure curves can be constructed. Capillary pressure is the difference pressure for oil and water phase[16].

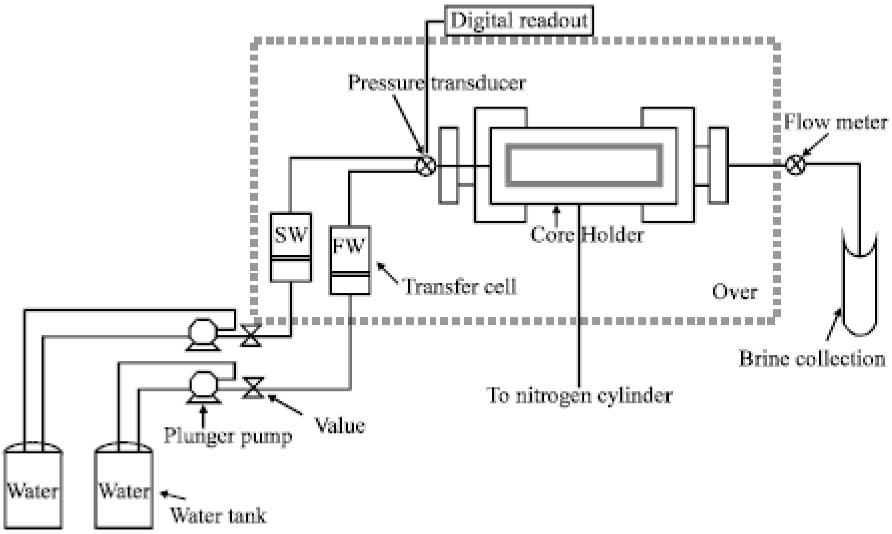

Fig.1 core flooding apparatus

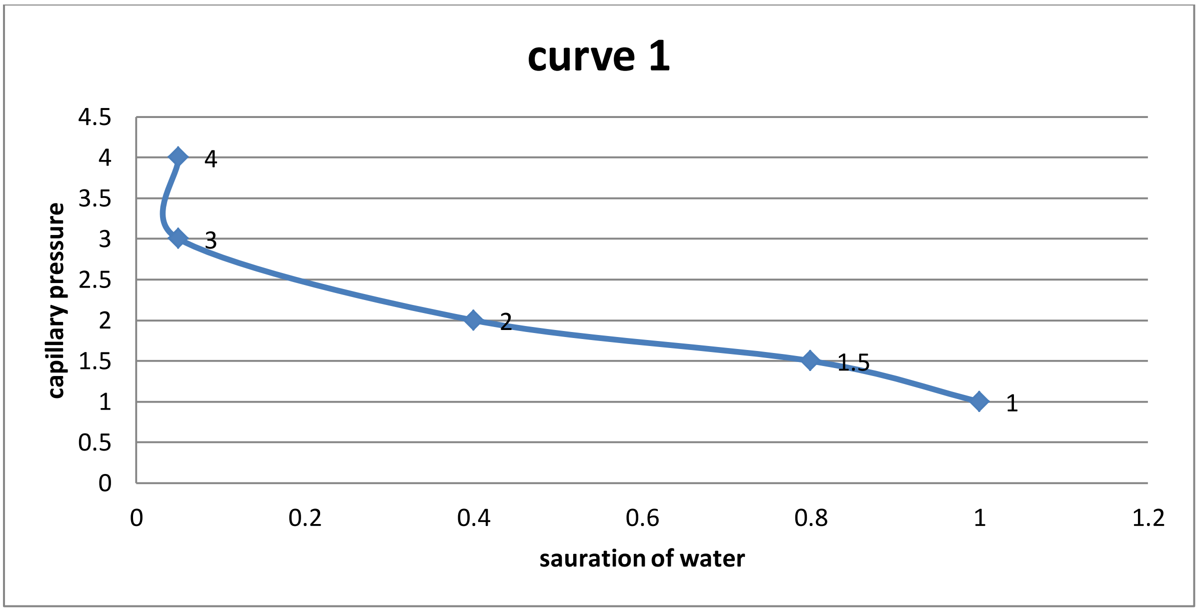

Fig.2 Drainage of water

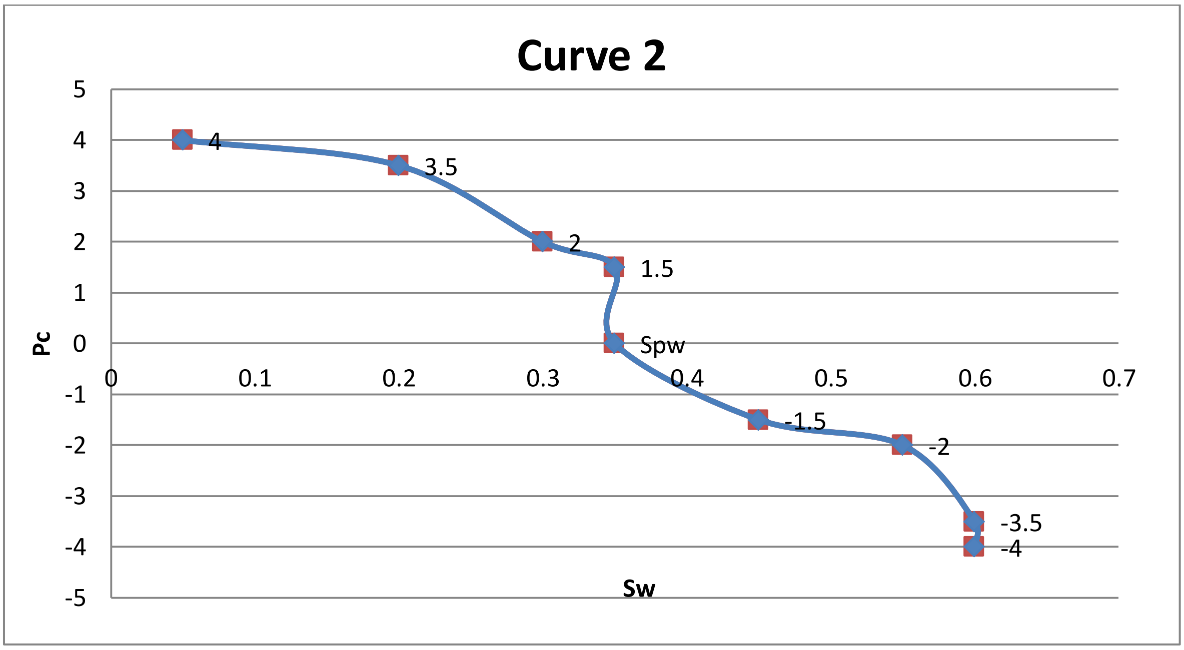

Fig.3 Imbibition of water

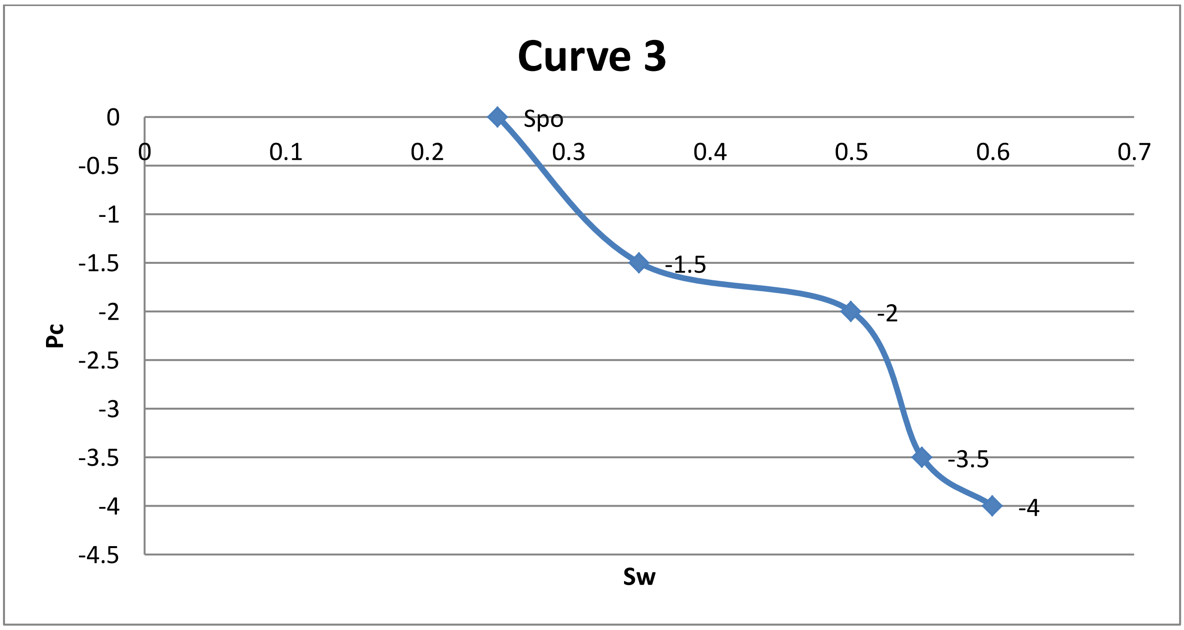

Fig.4 Second drainage of water

Table.1Capillary pressures vs Saturations

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 **Spw**	-1.5	0.65	0.35
4	0.95	0.05	-1.5	0.55	0.45	0	0.75 **Spo**	0.25

		Scw						
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 **Sor**	0.6	0	0.75	0.25

Capillary Curves

On a water wet core, oil as a nonwetting phase, water is saturated before oil injection. Oil displaces water with positive capillary pressure upto connate water saturation. The same process will be repeated for water imbibition and drainage. Curves were generated by recording capillary pressures at every stage.

The core plug has been kept at the center of the core holder. It was cemented around to make it static. A porous plate was below mounted to bypass fluids. Wettability is the nature of a reservoir to have partial attraction towards a fluid. I_w is imbibation of water and I_o is imbibation 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 imbibation of water to oil is negative, then core is Oil wet. If positive, then it is water wet. Intermediate wet at zero[17].

Results

CMC of SDS was observed from conductivity test to be 500ppm at 30.2ohms from the graph fig.5. Beyond that conductivity readings were observed to be constant. From emulsion test, three layer region has been observed for the combination of 0.1%M Alkali, 500ppm SDS and 0.5%Brine.

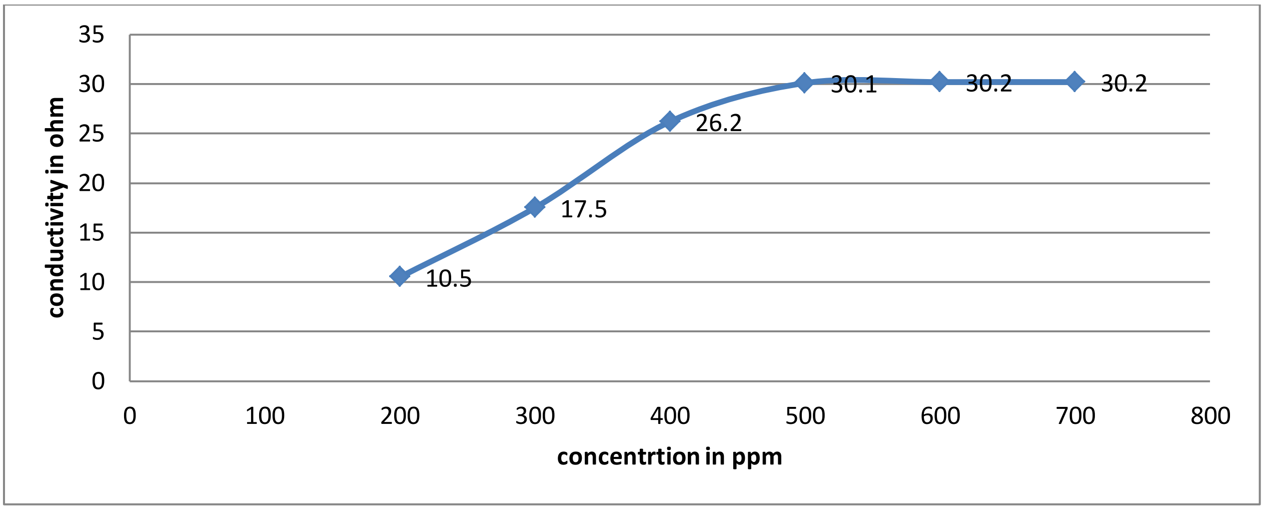

Fig. 5 CMC by conductivity

The pore volume (PV) of core sample has been calculated to be 30.5cc by Ruska porometer. Under core flooding , 2 PV of water has been injected for 2 days with an inlet pressure of 0.09psi. 1.35 PV was collected at outlet remaining 0.65PV saturated. Then 2 PV of oil has been injected into core to displace water. 0.6 PV of Sw was collected out of 0.65PV saturated water . The remaining water was considered as connate water saturation Scw of 0.05PV at Pc of 4 psi shown in table 2. At outlet, 0.85PV out of 2PVoil has been collected. It shows core have been satuarated and adsorbed with 1.15PV of oil and 0.05PV of connate water. Since, the core has a space limit of 1 PV with consideration of 0.05PV of Scw the total absorbed amount of oil was observed to be 0.2PV.

Table.2Connate water saturation (Scw) was estimated by displacing water through oil injection to be 0.05 of Sw. After finding Scw, oil have been displace by water injection until residual oil (Sor) at 0.4 of So was left out. Spontaneous water and oil saturations were observed at 0.35 of Sw and 0.75 of So.

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

The core sample was treated by injecting 5 PV of water to displace oil at Pc of 4 psi. It lead to collect 0.55 PV of oil out of 1.2 PV at outlet.

Water has been imbibed by displacing oil spontaneously until the pressures were equal. The saturation of water at this level is considered to be spontaneous saturation of water Spw of 0.35 PV, beyond where additional pressure has been applied by injecting more water to displace oil. Spw and Sor have been recorded at 0.35PV and 0.4PV respectively. In that 0.2PV of oil was considered to be adsorbed. The left out oil after water flooding is 0.4PV of So as Sor. Spo was estimated to be 0.75PV of So.

According to amott wettability Index Iw = 0.55 and Io = 0.64

Iw-Io = -0.09which indicated oil wet

After making core oil wet, 2PV of water was injected to reach Sor upto 0.4PV of So. Then 2PV of 500ppm SDS has been injected to recover oil. It was observed 1.6PV of SDS was collected at outlet by recovering 0.2PV of So out of 0.4 PV. It was recorded, that 0.4PV of SDS was absorbed by leaving 0.2PV oil. EO has been introduced at different moles with the combination of three layer emulsion as shown in table 4. At 3000ppm of EO , it was observed that the oil recovery was maximum upto 0.13PV of So Out of 0.2PV and SDS to be 0.36PV out of 0.4PV.

Table.4 SDS concentration vs HLB

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

Discussion

During conductivity test, rise in conductivity was observed by increasing surfactant concentration from 200ppm to 500ppm. The rise in conductivity indicates formation of a micelle was not completed. Once, the micelle has completely formed then the remaining concentration will lead to aggregate micelles. Conductivity beyond this concentration would by constant. The concentration where micelle formed has been chosen for emulsion studies.

Emulsions were generated with different combinations of alkali and brine with SDS. Three layer indicates that oil and water has been completely separated from interface. The micro emulsion was observed to be smaller and sharper at 1%alkali with 500ppm SDS.

Capillary pressure curves were constructed by injecting water initially to make core completely saturated. Then oil has been injected to displace water until connate water saturation achieved. During oil injection 0.15PV of oil was observed to be lost due to impurity charge variations. After oil saturation, water has been injected to displace oil until residual oil saturation reached. The residual oil was observed to be 0.4 of So. From capillary pressure saturations wettability was estimated to be oil wet.

The core was kept at residual oil condition by injecting water to reach 0.4PV of So.

SDS of 2PV with CMC of 500ppm, chosen from conductivity and emulsion tests was injected. With 0.4PV of SDS adsorption 0.2PV of residual oil recovered from 0.4PV of Sor.

The residual oil have been recovered by SDS is by reducing IFT, which is not enough for complete recovery. And, 0.4PV of SDS was observed to adsorb due to opposite charge interaction between SDS and carbonate mineral.

EO leads to increase hydrophilic nature of surfactants contrary to core nature makes it desorbed and enhances recovery. EO doesn’t possess any charge makes it neutral for adsorption onto any surface. The recovery of oil and surfactants were observed by injecting EO with SDS emulsions as shown in Table 4. It has been observed that 3000ppm of EO at HLB 6.2 is the effective combination that could recover oil of 0.13PV out of 2.0PV upto 65%, and SDS of 0.44PV of 0.6PV desorbed upto 73%.

Conclusions

Applicability of surfactants onto carbonate reservoirs is promising. The loss of surfactants during core analysis was observed. For estimating core wettability, capillary pressure curves were effective. Capillary pressure curves were constructed upto second drainage of water. It can be extended upto connate water saturation. The recovery of oil was observed to be less after surfactant flooding due to adsorption. EO as a HLB enhancer led to improve recovery by desorbing surfactants.

Methods for reducing surfactant adsorption have a great scope in enhancing recovery of crude during chemical flooding. HLB is one among the most parameters that has 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 shales, dolomite and sandstone reservoirs.

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