Wettability alteration on Limestone cores as a Chemical Enhanced Oil Recovery application

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Abstract: The research work is carried on investigating for suitable concentration of SDS (sodium dodecyle sulphonate) to enhance the efficiency of oil recovery for limestone cores. The objective of this work is to alter wettability for carbonate reservoir by conducting core flooding operation through the application of SDS.
Carbonate reservoirs under-going water flooding, only limited amounts of oil can be recovered from oil-wet layers because the water tends to flow mainly through the water-wet layers. In fact, recovery factors can be less than 10%.
The work has carried by injecting water, oil and surfactant simultaneously for adsorption onto pores. Wettability was observed by constructing relative permeability graphs for all fluids applied. Successful alteration had been reported by SDS and recovery has been enhanced to 90%.

Keywords: wettability, EOR chemistry, Surfactant concentration, sodium dodecyle sulhonate.

Introduction

More than 60% of oil and 40% of gas reserves are carbonates worldwide. In Middle East out of 62% of oil conventional reserves, 70% is carbonate, and out of 40% gas reserves, 90% were carbonate reservoirs.
Most carbonate reservoirs are naturally fractured. The fractures exist at all scales, from microscopic fissures to kilometer sized structures called fracture swarms or corridors, creating complex flow networks in the reservoir. As a consequence, the movement of hydrocarbons and other fluids is often not as expected or predicted. Recently, research into EOR has returned to the top of the agenda for most large international oil and gas companies.
The average recoverable oil from carbonate produced per original oil in-place is 35-40% which was considerably less compared to sandstone reservoirs worldwide [4]

Application of EOR chemistry on carbonate reservoirs

Fractured oil-wet carbonate reservoirs tend to have a high percentage of original oil in place (OOIP) after forced displacement because, the injected fluids flow predominantly in the high permeability fractures, while most of the oil remains trapped in the low permeability matrix by capillary forces. Surfactants can reduce the brine-oil interfacial tension (IFT) to ultra-low values (<10-3 mN/m) and/or alter the wettability of the rock to being preferentially water-wet, thereby overcoming the capillary forces that trap the oil. That is anionic Alkyl Propoxy (PO) Sulfates (APS) and their blends with Internal Olefin Sulfonates (IOS), an Alkyl Benzene Sulfonate (ABS) and an Alkyl Xylene Sulfonate (AXS) with PO groups to increase lipophilicity of the surfactant by adding more Pos. the additional oil from dolomite reservoir have been recovered through achieving optimal salinity [5].
Anionic surfactants have been identified which can change the wettability of the calcite surface to intermediate/water-wet condition as well or better than the cationic surfactant DTAB with a West Texas crude oil in the presence of Na_2CO_3. All the carbonate surfaces (Lithographic Limestone, Marble, Dolomite and Calcite) show similar behavior with respect to wettability alteration with Anionic surfactants (Alfoterra-33 and Alfoterra-38 and Alfoterra-68), which lower the interfacial tension with a West Texas crude oil to very low values ($<10^{-2}$ nM/m), have also been identified. Dilute anionic surfactants have been successfully applied on oil wet calcite surface to alter wettability by R. Gupta K. K. Mohanty [6].

Wettability alteration of asmari carbonate formation have been studies. Cationic, anionic and nonionic surfactant as DTAB,SDBS and Triton X 100. At different temperatures from 27 to 80C. nonionic were successful in altering wettability. [7]

Methods

Sara Analysis

The effectiveness of some improved oil recovery schemes can depend on the composition of the target oil. Crude oils can be described compositionally by a number of methods. SARA analysis divides crude oil components according to their polarizability and polarity using a family of related analytical techniques. Problems arise because several of the analytical techniques in use do not produce identical results, although the users of the data rarely distinguish between them, assuming that SARA fraction values generated by any of the common techniques are essentially interchangeable. We examine this assumption for SARA analysis methods: Centrifuge and Distillation.

polar compounds	**non-polar compounds**
Resins	Saturate or paraffin
Asphaltene	Aromatics

Colors
Saturates - White
Aromatics - Colorless
Resin - Golden Yellow
Asphaltene - Black or Brown

Crude will be separated into polar and nonpolar compounds by addition of methanol. The mixed crude will be agitated at 4000ppm under centrifuge to separate. Asphaltenes can be separated from resins in polar compounds by n-pentane and paraffins from aromatics in non polar by toluene.

Core Flooding Apparatus

The apparatus consists of a $3^{11}\times5^{11}$ core holder which holds cores of diameter less than its inner diameter of 3 inch as shown in fig.1. Cores of $3^{11}\times3^{11}$ 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 have been mounted to bypass fluids from the core.

Cores can be flooded with low pressures based on column inside to extract fluids from core. Wettability of a core sample can be calculated by constructing Relative permeability curves through core flooding

Initially, cores were made oil wet by aging them three days in oil. After that water has been injected to displace oil. The left out oil after waterflooding has been recovered by surfactant injection. The saturations were recorded simultaneously to construct relative permeability curves for oil and water wet cores as shown in graph 1.

Critical Micelle Concentration (CMC) Test

The chemistry behind Micelle is to form a droplet at the interface of oil and water by addition of surfactants. The formation of droplet will increase by increasing surfactant concentration [15]. 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 analyzed by conductivity [16].

Figure 1. Core flooding apparatus

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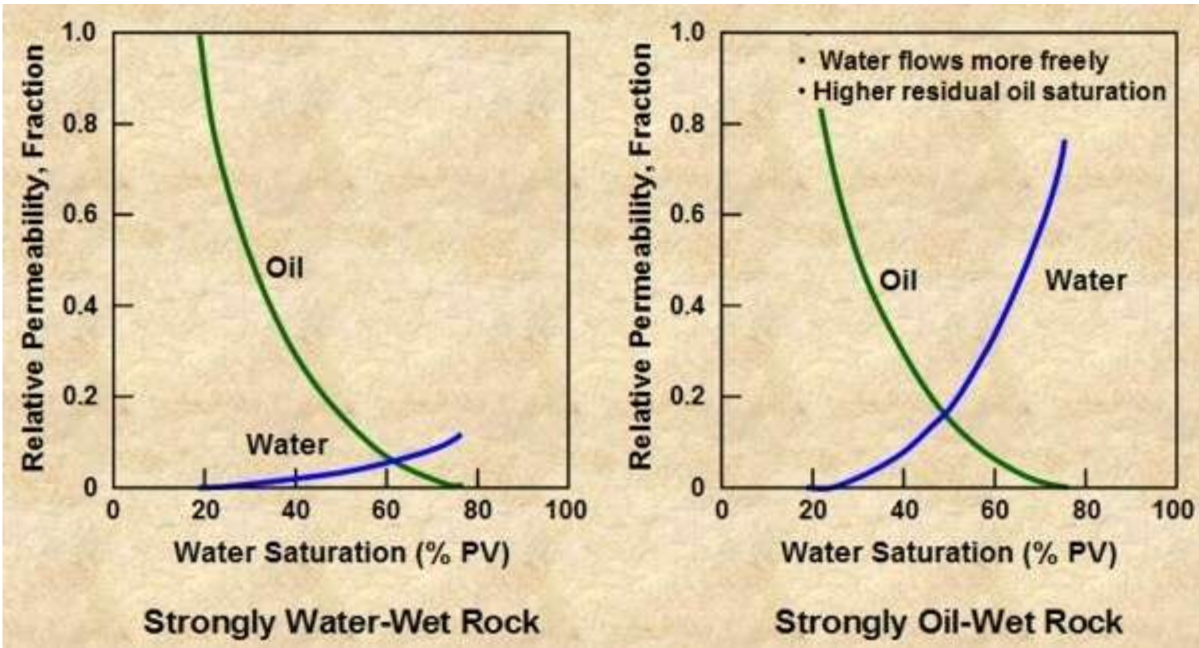
In this test conductivity rises with increasing concentration of surfactants until the formation of micelle is completed [17]. Beyond addition of surfactants will increase the number of micelles, which has no effect on conductivity [18]. CMC can be observed by a peak variation on a graph between conductivity and surfactant concentration shown in fig.3.



Graph1.: An Ideal Relative permeability curves for oil and water wet conditions.

Emulsion Tests

In this test, the concentration which has been chosen for core flooding operation should be suited for dissolution [18]. 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 with SDS (sodium dodecyle sulphonate). The three layer emulsion will be chosen for coreflooding.

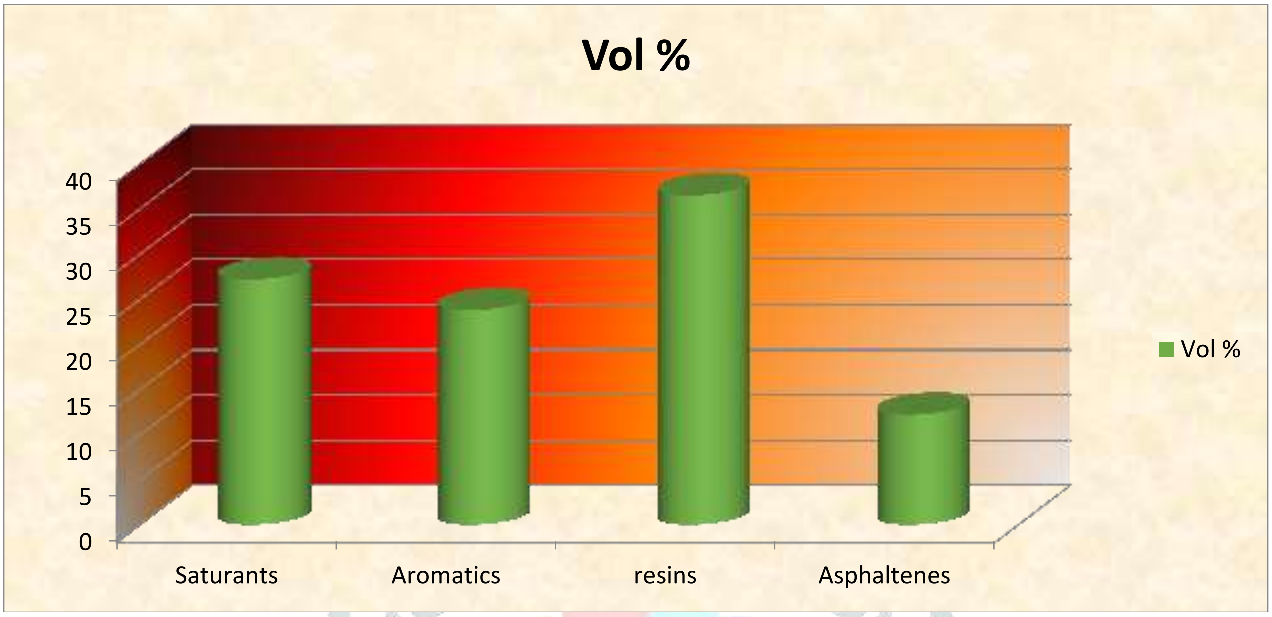
Results

From 5 ml of crude 3 ml of methanol has been added and centrifuged at 4000 RPM. 5.5 ml of polar has been settled at bottom. Toulene and n-pentane were mixed with non polar and polar solvents separately. Paraffins and asphaltenes were precipitated respectively. The composition of oil is shown in table 1. and graph 2.

Composition	Observation	Vol %
Saturants		**27.5**
Aromatics		**23.8**
Resins		**36.5**

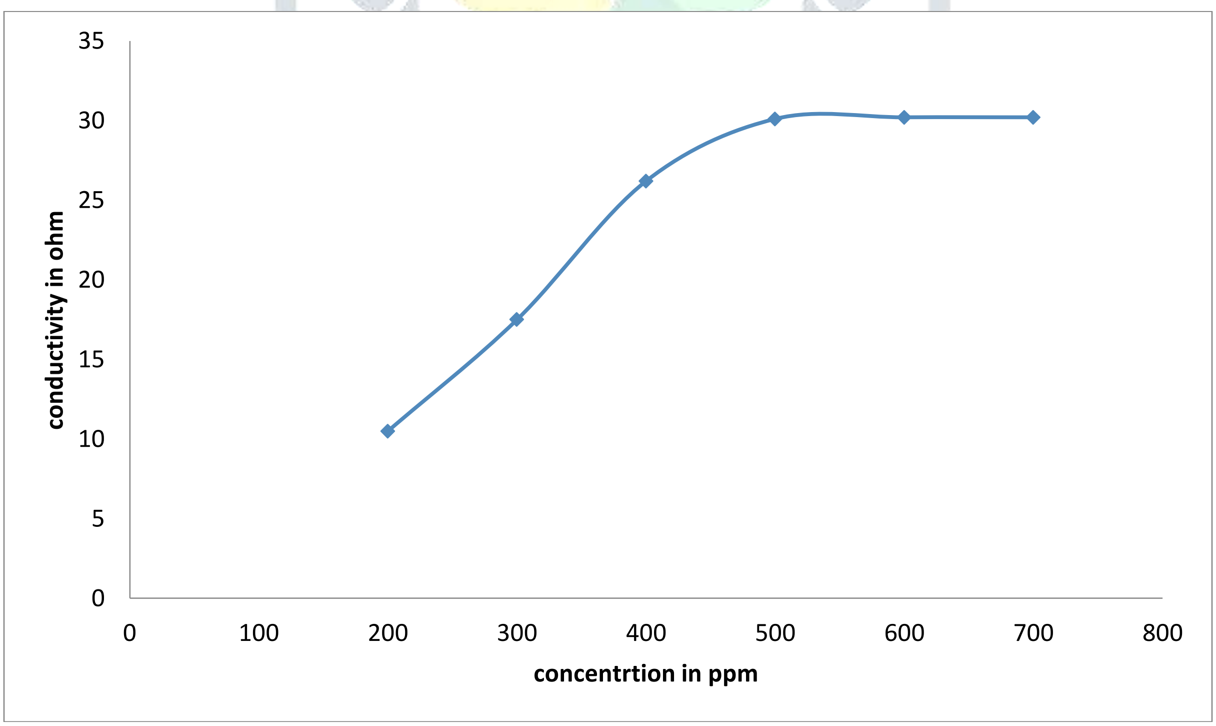
Asphaltenes		**12.2**

Table 1: Composition of SARA through centrifuge and Distillation



Graph 2.: Volume percentage of oil

CMC was estimated by preparing seven concentrations of Sodium dodecyle sulphonate (SDS) surfactants from 200ppm to 1000ppm as shown in graph 3. The CMC has been observed at 500ppm due to sharp deviation observed on graph between conductivity vs concentration.



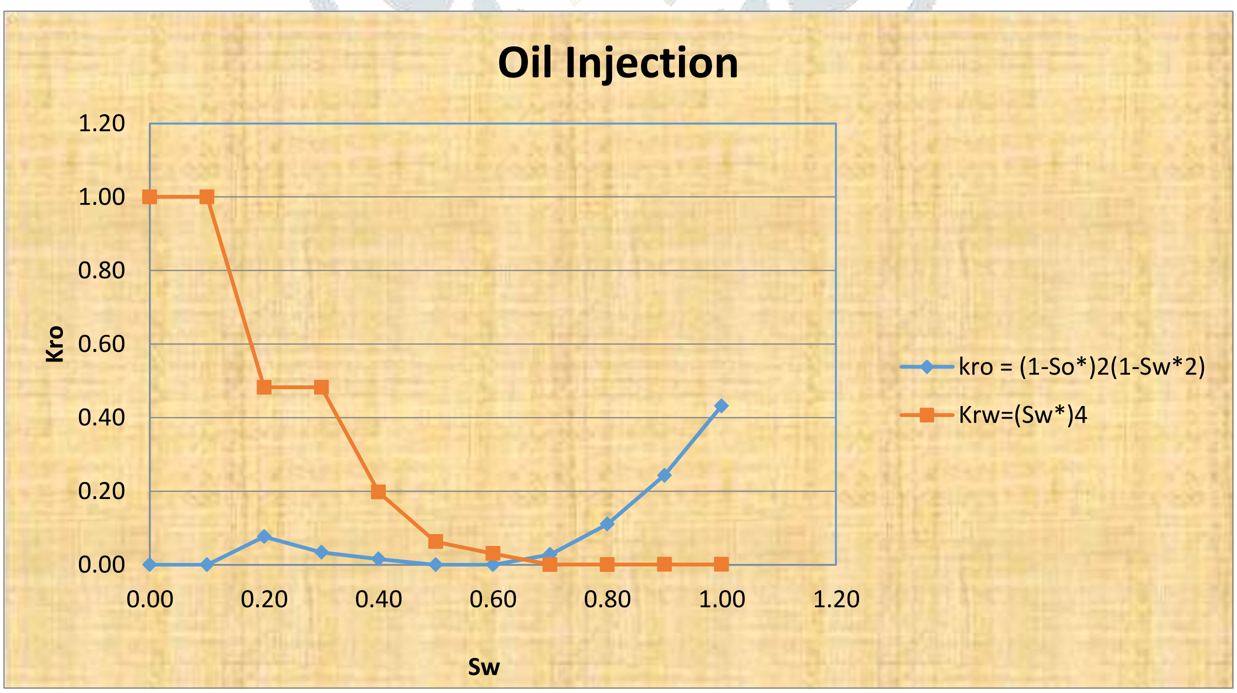
Graph 3.: CMC by conductivity test

Si No :	Surfactant In (Ppm)	Nacl(Sodium Chloride) Grams	Na_2co_3(Sodium Carbonate) Grams
1	7.5	-	-
2	7.5	0.5	-
3	7.5	-	0.5gm
4	7.5	0.5gm	0.5gm
5	7.5	1gm	0.5gm
6	7.5	0.5gm	1gm
7	7.5	1gm	1gm

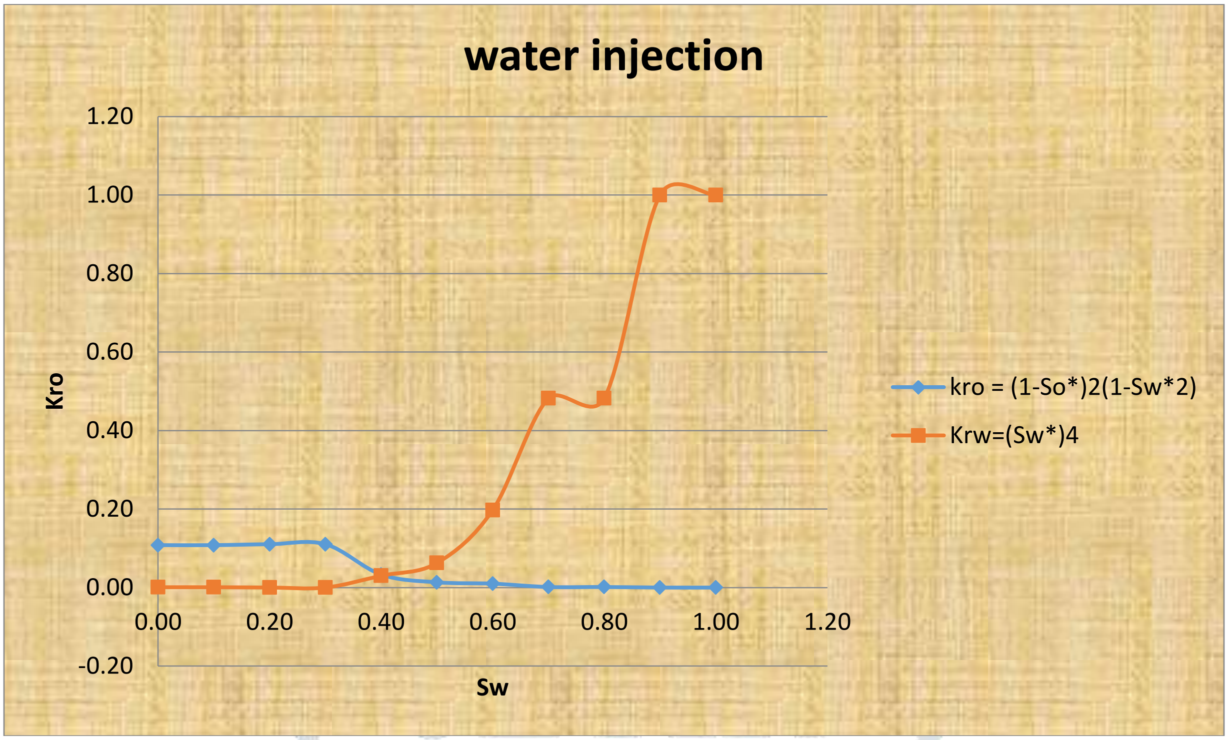
Table2: Concentration and combination of each of the chemical in composition is tabled.

After selecting 750 ppm of SDS as suitable concentration, Six emulsions were prepared with different proportions shown in table 2. The three layer emulsion was observed at 0.5 % M Na_2CO_3.
From emulsion test, three layer concentration was chosen for chemical flooding. During core flooding 3 pore volumes of water has been injected for 100% saturation. Then oil has been injected to displace water until connate water saturation and it was observed at 0.3 Sw. According, the saturation record during water displacement relative permeability curve has constructed and observed to be oil wet as shown in graph 4.
Then water has been injected to displace oil as water flooding until breakthrough. It was observed that 0.7 of So was recovered as shown in graph 5. SDS has been injected to recover remaining 0.3 of So. It was observed that 90% of 0.3 of So has been recovered by making core water wet as shown in figure 6.

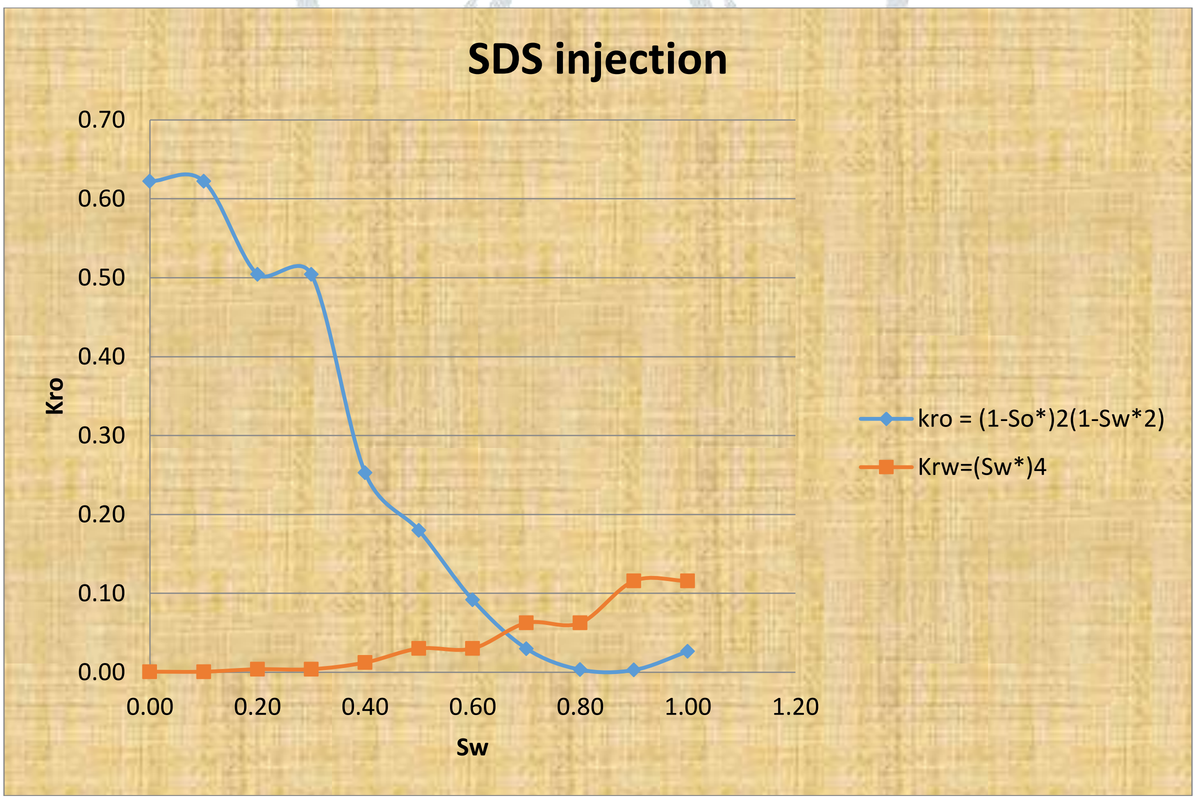
Discussion
During CMC test, the conductivity raised upto 700ppm of SDS and after that it was observed to be constant. The deviation in graph represents formation of micelle has completed. Beyond addition of SDS, conductivity would not rise due to accumulation of micelles. Three layers in emulsion represent the suitable proportion to extract water from oil and it was observed at 0.5%M Na_2CO_3 at 750ppm SDS. After water saturation, oil breakthrough was observed at early stage indicating water wet. For making core oil wet, hot oil has been injected and kept it for three days. Then water has been flooded to displace it. The relative permeability graph for oil displacement shows core has converted to oil wet as shown in graph 5. The residual oil left was observed to be 0.3 of So after water flooding. SDS was injected to alter wettability of core from oil wet to water wet. It was observed that with SDS injection out of 0.3 Sor, 0.25 of residual oil has been recovered. The improvement in recovery was due to wettability alteration and it was observed on graph 6 as water wet.



Graph 4.: oil wet Relative Permeability during water displacement by oil



Graph 5: oil wet Relative Permeability during oil displacement by water



Graph 6: water wet relative permeability curves by SDS injection

Conclusions

Wettability was concerned to be an important parameter for improving recovery after water flooding. Selection of proper surfactant and their combination is the key for effective recovery. SDS as an anionic surfactant was considered to alter limestone wettability.

CMC was observed at 750ppm of SDS through conductivity test. Recovery has been improved by altering oil wet to water wet through SDS up to 83%. The effectiveness of wettability was observed through relative permeability curves.

Chemical EOR has shown good potential in laboratories and pilot studies, than any other methods for recovering residual oil. With the laboratory results and theoretical assumptions, chemical EOR would be a great scope for oil Industry.

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