International Journal of Latest Research in Engineering and Technology (IJLRET)
ISSN: 2454-5031
www.ijlret.com || Volume 02 - Issue 12 || December 2016 || PP. 06-11

Designing an optimal low saline surfactant co-injection fluid for enhanced recovery from clay laden hydrocarbon reservoir: an experimental approach

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Abstract: Enhanced oil recovery is a fruitful technique in exploiting remaining oil from the reservoir. However, there are a number of challenges in designing an injection fluid in order to recover more oil from the subsurface. The basic principle in working on designing of the injection fluid is to understand the subsurface heterogeneities, mechanisms involved in recovery of oil and dominating forces that leads to the recovery of oil. Paramount of research has been conducted on recovery of oil through low saline water (LSW) flooding. It is believed that destabilization of oil adhered to the surface of rock minerals is the dominant mechanism in exploiting oil through LSW flooding. Also, a considerate amount of research has been conducted on recovery through surfactant injection. It is been proved that surfactant acts on surface of the medium or in other words it reduces the interfacial tension between the oil and water and hence increases the capillary number. This allows the oil to move through the pore spaces and hence, helps in recovering the oil. This thesis is an effort to understand the combined effect of both the mechanisms. The combination of LS water at reduced capillarity can avoid re-trapping of destabilized oil and exceed recoveries of either of the techniques applied alone.

In this project an anionic surfactant, Sodium Dodecyl Sulphate (SDS) was used in order to reduce the interfacial tension between the crude (heavy paraffin oil) and water (Low Saline Water). The formulation of surfactant and low saline water combination was selected based on the previous researches as well as screening experiments performed at initial stages of the experimentation. The crude was soaked in bentonite clay and clay was aged for approximately for 6 weeks at 70 degrees Celsius. It was then washed initially using de-ionised (DI) water and further using the low saline surfactant solution of various concentrations. The washed filtrate was collected in sample bottles and was analysed using the UV-VIS and Fluorescence spectroscopy.

The untreated and oil-treated clay sample were also analysed using the XRD and FTIR spectroscopy. These tools helped in characterization of clay and also helped in determining the change in composition of clay from untreated to treated. FTIR data gives a range of information like the presence of alcohols and phenols, -CH3 and –CH2 in aliphatic compounds with symmetrical and anti symmetrical stretching, etc. Final design of the injection fluid is concluded by analysing the results from each set of data obtained from different instruments.

1. Introduction

This paper is an effort to understand one really successful technique in the field of EOR – Low Saline Surfactant Flooding (LSSF), which is a method of chemical flooding. Low saline flooding is widely used in North Sea, Clair Field by BP in order to produce approximately 100, 000 barrels of more oil as tertiary recovery. On the success of this technique, the researchers have put their interest in combining this technique with surfactant flooding, especially in the field where oil viscosity is high. With the help of LSSF both the interfacial tension between the oil and water as well as the adherence of surfactant on the surface of clay reduces.

Tremendous research has been conducted from past few decades on both LSW flooding and LSSF. Martin in 1959 compared freshwater and sea water injection in sandstone core samples and suggested that migration of clay particles leads to an increase in oil recovery in case of freshwater flooding rather than sea water injection [1]. Later, Bernard (1967) [2] and Jadhunandan [3] in 1990 presented results from laboratory experiments showing increase in recovery of oil by reduction of the salinity of the injected brine and stated that the wettability of rock is the key to recover oil through waterflooding, respectively. Extensive research on the effect of brine composition on oil recovery using aged Berea sandstone was carried out by Tang and Morrow [6-11] from 1996-2002. They observed significant increase in oil recovery by reducing the brine composition. Additionally it was observed a wettability alteration by spontaneous imbibition.

Surfactant flooding is now a common EOR method to obtain the residual oil from the reservoir. Alagic et al. [12-14] presented a hybrid EOR process combining the effect of LS water injection and surfactant flooding in a low salinity surfactant (LS-S) injection process. The idea is that a more efficient oil recovery process can be obtained by combining destabilisation of oil layers during a LSW with a low IFT environment that prevents re-trapping of these oil layers.

In this paper, the reservoir medium is considered to be sandstone. Hence, the work is accomplished by using Bentonite clay. The goal is to understand the oil-brine-surfactant-clay interaction, microemulsion formation and its influence on recovery of oil from the samples and hence designing an optimal injection solution to recover oil in tertiary phase. A combination of varied weight percentage of surfactant with different brine concentrations is used. The oil laden clay samples were kept at a constant temperature (70^{o}C) for approximately 45 days. Experiments were conducted on these clay samples and results were thoroughly analysed using various powerful tools like X-Ray diffractometer (XRD), Fourier Transform Infrared (FTIR) Spectroscopy, UV Visible and fluorescence spectroscopy, both for raw and oil laden clay samples.
Thus the objective of this paper is to understand the oil-brine-surfactant interaction and microemulsion formation and to design an optimal LS-S solution to exploit oil from oil-leaden, aged clay (montmorillonite) samples.

2. Materials and Methods

Test samples were prepared by adding 12 gm of raw clay with 10 gm molten crude and keeping it in dry air oven at a constant temperature (70 ^{0} C) for 45 days in order to give time for the oil to get soaked in the clay completely to mirror the reservoir conditions. Three different concentrations of Sodium Dodecyl Sulphate (SDS) surfactant of 0.5, 1.5, 3 wt% were used in combination with different saline concentrations- 500, 1500 and 3000 ppm of NaCl solution in order to design a co-injection solution. The clay sample used in experimentation was analysed by X-Ray diffraction and FTIR. The mineralogy of both raw and oil treated clay samples is given in table 1 including the 2ϴ and d-spacing values. Also, the crude was characterized using FTIR.

Sample Name	2ϴ values	d-spacing values	Assigned Minerals
Untrated Clay Sample	19.76	4.493	muscovite
	26.6977	3.339	Quartz, Muscovite, Albite
	29.443	3.0337	Muscovite
Oil Treated Clay Sample	5.67	15.567	Muscovite
	19.72	4.499	Muscovite
	30.8	2.902	Muscovite, Albite
	33.15	2.702	Muscovite, Albite

Table 1: Mineralogy, 2ϴ values and d-spacing values of the raw and oil-treated clay samples

3. Experimentation:

The oil treated clay sample was aged for 45 days in a dry-air oven. The sample was then cleaned thoroughly using de-ionised water to remove all the possible oil from it. The cleaning of sample was done by centrifugation of the sample-solution till a visibly clear filtrate is obtained on repeated centrifugation. The sample was then dried and measured. An equal amount of sample is then taken at nine different places in order to exploit remaining oil from the sample. The combination of surfactant wt % with different saline concentration solutions is given in table 2. This co-injection solution was then used by taking 20 ml of each solution in a 100 ml beaker containing 0.4 gm of oil-treated powdered clay sample in each beaker. This solution of oil + low saline water (varied salinity for each beaker) + surfactant (varied salinity for each beaker) + clay is kept overnight in order to give sufficient time to the solution to exploit remaining oil from the clay sample being cleaned previously using DI water.

SDS (wt. %)	NaCl (wt. %)	Brine Concentration (ppm)
0.5	0.25	500
	0.75	1500
	1.5	3000
1.5	0.25	500
	0.75	1500
	1.5	3000
	0.25	500

3	0.75	1500
	1.5	3000

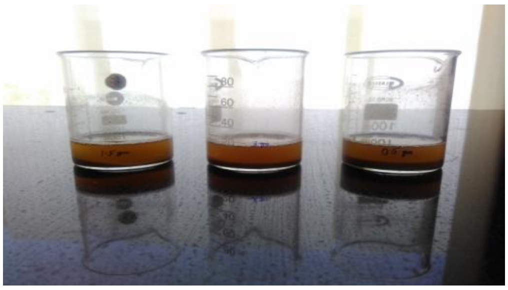
Table 2: Combination of different wt% of SDS with different saline solutions

The samples kept overnight were filtered and the filtrates were collected in 25ml bottles for UV Visible and Fluorescence analysis.

4. Results and Discussions

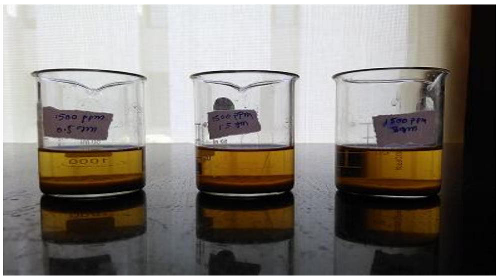
The prepared solutions were observed to have oil at the top of the solution changing it from opaque brown to translucent brown-colored solution (Shown in figure 1).

Figure 1: Change in transparency of the solution. The oil layer is ultimately visible at the top of the solution after keeping it undisturbed for 24 hours.



LSS solution used in order to exploit oil from the oil treated clay sample. The solution is opaque and muddy.

500 ppm surfactant solution after leaving it for exploiting oil overnight



1500 ppm surfactant solution after leaving it for exploiting oil overnight

3000 ppm surfactant solution after leaving it for exploiting oil overnight

Figure 1: Change in transparency of the solution. The oil layer is ultimately visible at the top of the solution after keeping it undisturbed for 24 hours.

The results were obtained by carrying UV-VIS and Fluorescence analysis on the obtained filtrate. It was clearly seen that the UV-VIS absorbance spectrum for 3000 ppm solution the absorption increases abruptly for higher concentrations of SDS (figure 2). From an embodied, it has been found that this type of increase in absorbance could be due to the presence of auxocromes (typically hydroxyl, alkoxyl or amino group). The presence of these substituents could lead to hyperchromic effect (an increase in absorption).

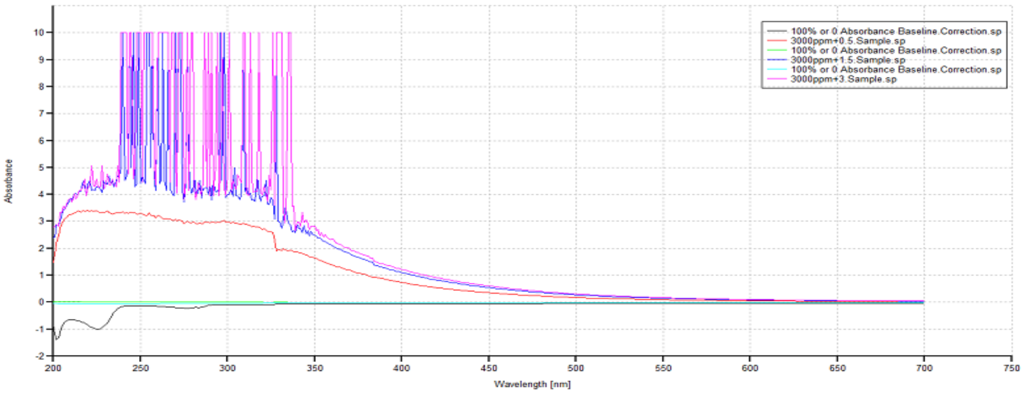


Figure:2 Showing abrupt increase in the absorption for 3000 ppm solution at higher saline concentration (1.5 and 3 wt%)

Further, from these plots we can conclude that the variation in wavelength from the hypsochromic to bathochromic region could be the result of conjugation when the surfactant molecules interacted with HC molecules. The maximum absorbance value for 500 ppm + 0.5 wt% SDS solution is 3.547 at 242 nm wavelength (Figure 3).

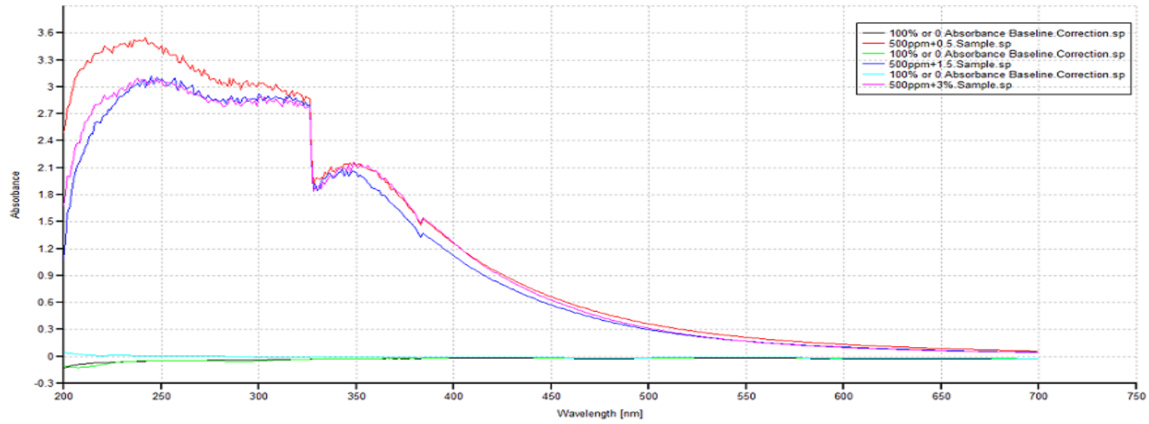
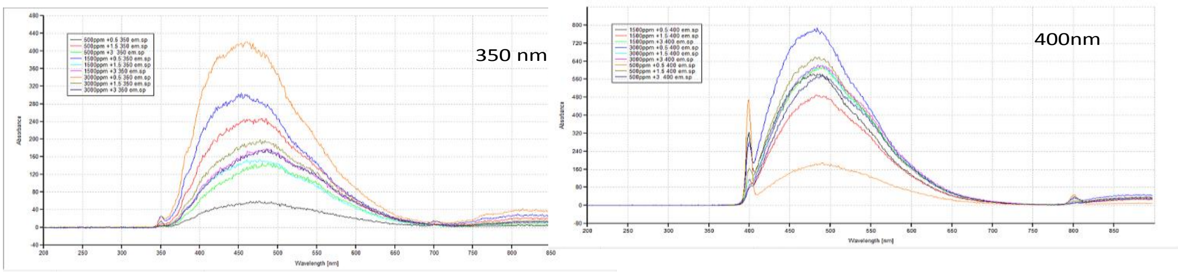


Figure: 3 The red line is showing 500 ppm + 0.5 wt% SDS solution

According to one of the studies, the maximum absorbance obtained at this particular wavelength is marked by the presence of unsaturated ketone. Also, from studies it has been found that in between the range of 240-260 nm wavelengths (UV-Region), simple benzene compound can be found. (Mainly at around 254 nm wavelength for non-conjugated derivatives).

Further, from the fluorescence studies it has been observed that at 350 nm and 400 nm excitation wavelengths, the maximum absorbance value is obtained for 3000 ppm + 0.5 wt % SDS solution whereas, at 450 nm excitation wavelength, the maximum absorption is obtained at 500 ppm + 0.5 wt % SDS solution (Figure 4).



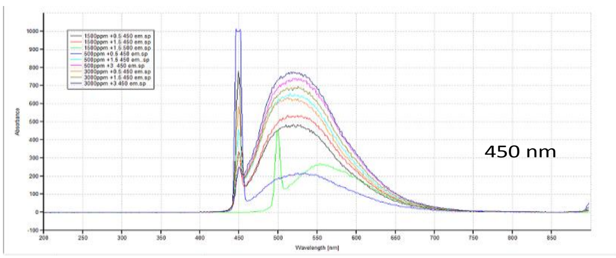


Figure 4 : Fluorescence data at 350, 400 and 450 nm excitation wavelength

5. Conclusion

From the conducted experiment, we concluded that all the three low saline NaCl concentrations taken for conducting the experiment i.e. from 500 ppm, 1500 ppm and 3000 ppm could be suitable for exploiting the oil in tertiary recovery phase. However, out of the three amounts of surfactants 0.5 wt %, 1.5 wt % and 3 wt % of SDS taken, the optimal surfactant would be 0.5 wt % as we get the maximum absorption values at this particular SDS concentration. Thus, we concluded that lower concentration of surfactants could yield more oil in tertiary phase which is also economically feasible due to high costs of surfactants.

From this study not just the successful approach of LSS flooding is proved but also, it is being shown that this method can be economically feasible for EOR projects. Least amount of surfactants could result in more recovery when combined to different salinities. Lower the amount required, lower will be the cost of application. Hence, the economics of the project could also be taken care of using this approach of EOR.

6. Future scope of the paper

In this project, three salinity ranges are taken – 500 ppm, 1500 ppm and 3000 ppm. This range could be altered in between 100 ppm to 5000 ppm which is a range of low saline solution. In the present thesis, only NaCl salt is taken in order to perform the experiment. However, future work could be carried out using combination of salts (MgCl, NaCl, $CaCl_2$) at different concentrations. Further the amount of surfactant taken could also be altered. In this project 0.5 wt % is considered to be the optimal surfactant amount whereas the experiments could be performed using even lower amounts of surfactant. Also, other surfactants like cationic or non-ionic surfactants could be used. The type of clay could also be altered in order to see the effect of the presence of different clay types on recovery of oil. Various other properties could be determined for crude, clay and LSS solution. The experiment is carried out at surface temperature and pressure however these parameters could also be altered in order to determine the change in recovery.

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