(RESEARCH ARTICLE)

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Design of salinity tolerant in alkaline surfactant systems for high salinity reservoirs

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Abstract

Chemical oil recovery from offshore reservoirs which are usually characterised by harsh conditions such as high salinities have remained a source of concern. This study assesses chemical compatibilities of alkalis –surfactant systems under high salinity and divalent ions (Ca^{2+} and Mg^{2+}). It analysed the synergy between alkali-surfactant slugs and crude oil, leading to the design of an optimal low-cost alkaline- surfactant flooding. Three alkali systems: sodium hydroxide, sodium metaborate and ethylene-diamine-tetracetic acid-(EDTA/NaOH) were evaluated with two high salinity synthetic brines; one without divalent ions (soft brine) and the other containing divalent ions (hard brine). Compatibility of these alkali systems with the commercial-grade surfactant was evaluated based on fluid-fluid interaction. Phase behaviour experiments were conducted to determine the alkali–surfactant compatibility with brine. Solutions free of precipitation were used for the interfacial-tension (IFT) and phase separation analysis, obtained level readings were used to calculate optimal salinity. Results showed that all alkali systems were compatible with soft brine, while compatibility with hard brine was highly controlled by the pH. Alkali-crude oil failed to produce Type III micro-emulsion; however, the addition of surfactant achieved an ultra-low IFT. EDTA/NaOH effectively sequestered the divalent ions like sodium metaborate hence increasing the solubilisation of surfactant at higher salinity. Comparison of both alkalis with commercial surfactant, alcohol alkoxy sulphate at controlled pH exhibited a higher optimum salinity for EDTA/NaOH than for sodium metaborate. This study shows that at pH ≥ 11 and an increased salinity above optimal salinity, chemical precipitation occurs resulting in reduced oil recovery.

Keywords: Divalent ions; Alkaline-surfactant flooding; Optimal salinity; Microemulsions; Fluid compatibility

1. Introduction

Alkaline and surfactant flooding improves oil recovery through a synergistic reduction of oil-brine interfacial tension, wettability alteration, thus making it a highly effective oil recovery method (Hazarika and Gogoi, 2020) As early as 1917, the production of insitu surfactant was first proposed by F. Squires who recognised the efficiency of alkali-based chemicals in forming insitu surfactants via saponification process. The addition of alkaline chemicals during surfactant flooding generates an insitu surfactant (due to the reaction of alkali with the carboxylic acid present in the crude oil). Furthermore, the addition of alkali reduces the amount of surfactant loss by and improves their phase behaviour (Sheng, 2013). The high cost of surfactant chemicals has resulted in a decline in their application as recovery agents because a greater percentage of the surfactants are lost during flooding due to their high surfactant retention/ adsorption thus making the flooding process less profitable. However, when alkaline chemicals which are relatively low cost are added into the surfactants, due to their high pH, they assume the role of the 'sacrificial lamb' and are adsorbed onto the rock surface thereby reducing the amount of surfactant chemicals that will be lost. For example, sandstone rocks containing positively charged clay will react with negative surfactant solution at low pH to give rise to high adsorption. Injecting

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alkaline increases pH which reverses the positive charge of the rock via dissociation of surface hydroxyl as illustrated in Equation (1).

$$SiO_2 + H_2O \leftrightarrow Si(OH)_4 \dots\dots\dots\dots\dots\dots\dots\dots\dots\dots\dots\dots\dots [Eqn\ 1]$$
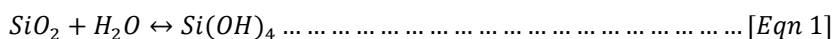
Similar charges will give rise to repulsive forces between the rock surface and the surfactant. This implies that adsorption of surfactant is low under high pH.

The improved phase behaviour of alkaline and surfactant systems emanates from the addition of alkali in a surfactant solution which lowers the optimum salinity, this implies that optimum salinity of the petroleum soap is lower than that of the synthetic surfactant, this is because the two surfactants have different hydrophilic properties with the synthetic surfactant being more hydrophilic. As the soap/surfactant ratio decreases, optimum salinity will increase. (Sheng, 2011). Liu et al. (2008) observed that injecting natural surfactant would not attain optimal conditions needed to attain low IFT; however, injection of small amount of synthetic surfactant with the alkali solution will achieve optimal reservoir conditions exhibiting a co-dependent mixing rule. In their experimental study, Pei et al. (2012) reported that the synergy between alkali and surfactant chemicals will be more significant in the recovery of heavy oil. Liu et al. (2006) also observed that heavy oil could not be emulsified in either alkaline or surfactant solution but when used together, emulsification was apparent. More so, the synergy in the alkaline-surfactant systems also results in an ultra-low IFT than with either alkaline or surfactant solution alone. Hazarika and Gogoi (2020) noted that the addition of alkali resulted in the lowest IFT value. They further reported on the role of salinity on IFT reduction, stating that an increase in the salinity of the chemical slug reduces the IFT value. Similarly, the study on the effect of increasing pH by Behrang et al. (2021) resulted in lower IFT. The acidic content of the crude oil has significant effect on the IFT reduction of alkaline-surfactant-oil system as stated by Arekhov et al. (2020). At medium to high acid concentrations, the addition of an alkali resulted in a more significant decline in IFT value compared to oil with low acid concentrations and produced an ultralow interfacial tension.

Despite the highlighted advantages of alkaline flooding, the level of alkali concentration has remained a concern especially when flooding in carbonate and sandstone reservoirs where divalent metals such as calcium and magnesium ions are found on the rock surfaces and in formation waters thereby causing chemical precipitation. Thus, designing the right alkaline concentration is vital for a successful alkaline flood.

This paper investigates the salinity tolerance of an alkaline surfactant slug for an enhanced oil recovery in high acidity heavy oil as well as the design of a suitable chemical slug using the theoretical model. This study will support the findings of solutions for high salinity and harsh conditions of oilfields, eliminating the need for brine softening processes with economic advantages of being able to use production water to prepare chemical slugs for EOR treatments.

2. Material and methods

Reagents such as sodium hydroxide, sodium metaborate, ethylenediaminetetraacetic acid (EDTA), distilled water, sodium chloride, calcium chloride and magnesium chloride were purchased from a Sigma Aldrich chemical supplier. Based on their high analytical grade, these reagents were not subjected to further processing. The apparatus used include water bath, thermometer, conductivity meter, filter paper, funnels, beakers, weighing balance, magnetic stirrer, borosilicate pipette, beakers, test tubes, pH indicator, pipettes stand, pendant drop, and syringe.

2.1. Methods

The methods adopted for this study include solubility equilibrium calculation, preparation of brine, aqueous stability test, salinity scan test, CMC determination, phase separation analysis and IFT determination.

2.1.1. Equilibrium solubility calculation

Alkaline concentration needed to prevent precipitation in brines containing divalent ions was calculated using Equations (2) and (3) which determines the aqueous solubility of a soluble compound under varying conditions.

$$M_aX_{b(s)} = aM^{n+}(aq) + bX^{n-}(aq) \dots\dots\dots\dots. (2)$$
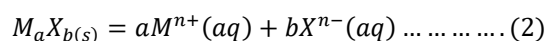
The relationship between solubility product and molar solubility is thus.

$$K_{sp} = [M^{n+}]^a \times [X^{n-}]^b \dots\dots\dots\dots\dots\dots (3)$$
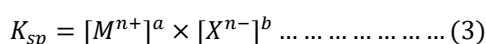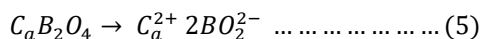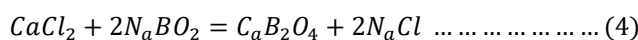
Where:

K_{sp} = solubility product constant, the equilibrium constant for a solid substance dissolving in an aqueous solution

M^{n+} = molar solubility, M of the cations produced in solution

X^{n-} = molar solubility, M of the anions produced in solution

To determine if 100ml of 0.1 M sodium metaborate will prevent precipitation of 0.046M of $CaCl_2$, the stoichiometric balancing is illustrated using Equations (4) and (5)

$$CaCl_2 + 2N_aBO_2 = C_aB_2O_4 + 2N_aCl \ \dots\dots\dots\dots\dots\dots\dots (4)$$

$$C_aB_2O_4 \rightarrow C_a^{2+} \ 2BO_2^{2-} \ \dots\dots\dots\dots\dots\dots (5)$$

Initial concentrations are determined using Equations (6) and (7):

$$Ca^{2+} = \frac{0.0464 \ mol \ CaCl_2}{1L} \times \frac{1 \ mol \ Ca^{2+}}{1 \ mol \ CaCl_2} = 0.0464M \dots\dots\dots\dots\dots\dots (6)$$

$$2BO_2^{2-} = \frac{0.1 \ mol \ NaBO_2}{1L} \times \frac{1 \ mol \ 2BO_2^{2-}}{1 \ mol \ NaBO_2} = 0.100M \ \dots\dots\dots\dots\dots\dots (7)$$

The new dilute concentration is given by Equations (8) and (9):

$$[Ca^{2+}] = \frac{0.1L \times 0.0464}{0.1 + 0.1} = 0.0232M \ \dots\dots\dots\dots\dots\dots (8)$$

$$[2BO_2^{2-}] = \frac{0.1L \times 0.1}{0.1 + 0.1} = 0.05M \dots\dots\dots\dots\dots\dots (9)$$

Substituting into Eqn. (2) to calculate solubility product quotient, Q, the value of Q is expressed by Equations (10) to (12)

$$Q = [Ca^2] \ \times \ [BO_2]^{2]} \dots\dots\dots\dots\dots\dots (10)$$

$$Q = [0.0232] \ \times \ [0.05]^2 \ \dots\dots\dots\dots\dots\dots (11)$$

$$Q = 5.8 \times 10^{-5} \ \dots\dots\dots\dots\dots\dots (12)$$

According to Butler (1991), the solubility product, K_{sp} of (CaB_2O_4) is given to be 6.5×10^{-4}.

If, $K_{sp} > Q$, no precipitation will occur but if $K_{sp} < Q$, solubility will be exceeded as such precipitation will formed. Thus, since $K_{sp} > Q$, no precipitation will occur, as such, 0.1M of sodium metaborate will prevent 0.046M of calcium from precipitating.

2.1.2. Preparation of brine samples

Synthetic brines (hard and soft brine) as shown in Table 1 were prepared in the laboratory to simulate actual formation brine. The soft brine contained varying concentrations of sodium chloride and potassium chloride with total dissolved solids of 57,340 g/L and a salinity of 5.7%. The hard brine contained salinity of 7.2% and a total dissolved solids of 66,290 g/L with 2,835g/L being concentrations of the divalent ions: Ca2+ and Mg2+. The presence of these ions is a major concern as its reaction with most alkali, such as sodium hydroxide results in calcium and magnesium hydroxide precipitation. This study intends to proffer a solution to this concern. The composition of the formulated brine is shown in Table 1.

Table 1 Composition of formulated brine samples

Components	Hard brine	Soft brine
NaCl (g/L)	56.77728024	56.77728024
KCl (g/L)	0.563147436	0.563147436
MgCl2 (g/L)	6.824487147	_
CaCl2 (g/L)	8.1575	_
T.D. S (g/L)	72.32241483 (7.23%)	57.34042768 (5.73%)

A series of phase behaviour test were conducted for the alkali- brine-oil system to ascertain the compatibility of the system under varying ionic strength, the phase behaviour between the aqueous and oleic phase, its optimal salinity and the effect of pH.

2.1.3. Aqueous Stability Test procedures

To analyse fluid-fluid interactions, a compatibility test on alkali and brine solution was performed to determine the presence of any non-homogeneity such as cloudiness or precipitation in the aqueous phase. This screening ensures an alkaline compatibility with the electrolyte concentrations. The concentrations were evaluated using the correlations of Equations (13) and (14).

$$\text{Molarity or concentration (mole/L)} = \text{moles of solute / litre of solution} \dots \dots \dots \dots \dots \dots (13)$$

$$\text{Mass (g)} = \text{no. of moles} \times \text{molar mass} \dots \dots \dots \dots \dots \dots (14)$$

Each selected alkali was mixed with brine (hard or soft) into test-tubes and sealed to avoid evaporation. These samples were visually inspected, cloudy samples containing solids such as precipitates was considered incompatible and failed the screening as only clear, cloudless fluids were selected. Anionic surfactant was later injected into alkaline –brine solutions to further ascertain compatibility.

2.1.4. Salinity scan procedures

Further tests were carried out to determine the salinity tolerance with selected alkali and surfactant at varying electrolyte concentration. Alkali concentration was kept constant, while brine salinity was varied. The experiment was conducted using glass test tube each containing a total volume of 10 ml. The solution was mixed based on calculations of molarity and total volume of the alkali –surfactant- brine using the expression in Equation (15).

$$C_1 V_1 = C_2 V_2 \dots \dots \dots \dots \dots \dots \dots (15)$$

Where,
C_1= Initial concentration (%);
C_2= End concentration (%);
V_1= Start Volume (ml);
V_2= Total Volume (ml)

2.2. Sample Calculation

With an initial concentration of 1.0 mole/lit NaOH, a final concentration of 0.5 moles/lit and a total volume of 10ml, the start volume of NaOH for the salinity scan was calculated:

$$C_1 V_1 = C_2 V_2 \dots \dots \dots \dots \dots \dots (16)$$

$$1.0 \times V_1 = 0.5 \times 10 \dots \dots \dots \dots \dots \dots (17)$$

$$V_1 = \frac{0.5 \times 10}{1.0} \dots \dots \dots \dots \dots \dots (18)$$

$$V_1 = 5ml \dots \dots \dots \dots \dots \dots (19)$$

Thus, 5 ml of NaOH was kept constant in each test tube, while brine and distilled water at varying salinities was used to make up total volume. A visual assessment for the presence of precipitates was done and the pH of the solution was determined. Similar procedures were carried out for the alkali-surfactant –brine system.

2.3. Critical Micelle Concentration

This is the lowest surfactant concentration above which monomers clusters to form micelles. It can be either determined experimentally or calculated. The CMC of the surfactant was determined from the point of inflection or discontinuity on a plot of the physical property (conductivity) of the solution as a function of surfactant concentration. The conductivity of the surfactant at varied concentration was determined using a conductivity meter.

2.3.1. Phase separation Test Procedures

Phase separation test was carried out to determine fluid-fluid (aqueous-oleic) interaction. Compatible alkali +brine and oil system were injected into an array of 5 ml borosilicate pipettes. Each pipette contained 2 ml of alkali- brine solution at varying salinities and an equal volume of oil. Samples were tightly sealed to avoid evaporation or inflow of oxygen and carefully inverted to allow a mix of the two phases.

Fluid interfaces were observed under atmospheric and reservoir temperature over an equilibration period of 28 days for presence of micro-emulsions. Similar test was carried out for the alkali-surfactant –brine + oil system. Only solutions containing Type III micro emulsions were selected because presence of emulsions causes increased surfactant adsorption. After visual assessment of the formed micro emulsion, level readings for aqueous, oleic and micro emulsion were recorded, their individual volumes as well as oil and water solubilization ratio versus salinity was calculated to obtain optimal salinity.

2.4. Interfacial Tension Test

Interfacial tension experiment between the brine-+alkali and oil and between the brine+ alkali+ surfactant and oil phases were conducted using pendant –drop method. Figure 1 shows a labelled diagram of the pendant drop apparatus. Heavy oil with API gravity of 20 and viscosity of 21.34 cP was used for the experiment. The oil was screened to eliminate contaminant such as rust inhibitors. The syringe was filled with oil whereas 5 ml alkali and brine solution was injected into the optical cell. The oil was pumped into the system to flow upwards and allowed to react with the aqueous solution in the optical cell while the images were obtained with the javelin video camera and transmitted to the computer. For system with high IFT a pendant drop- like- bubble will be formed, while low IFT will be seen as a flowing oil stream.
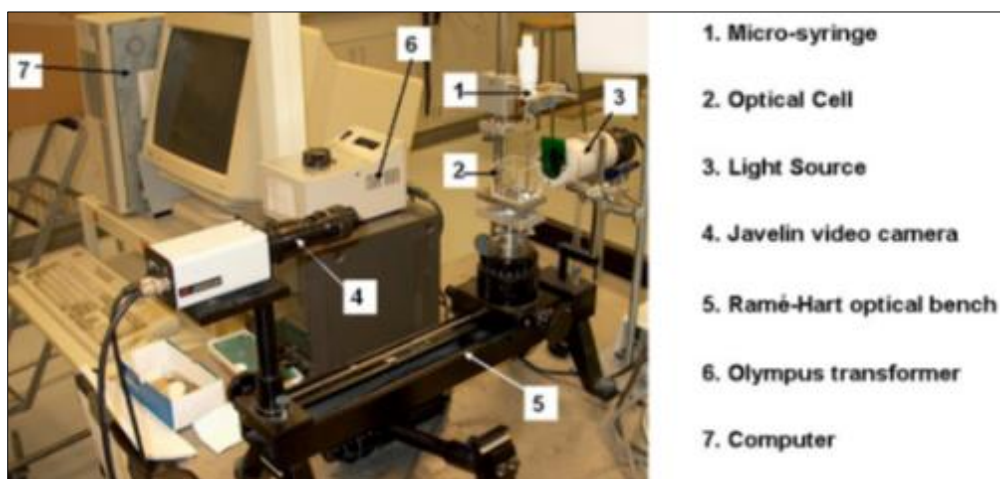

Figure 1 Pendant Drop apparatus

Interfacial tension was calculated using Equation (20):

$$\gamma = \frac{\Delta \rho g D^2}{H} \dots \dots \dots \dots \dots . (20)$$

Where,
γ = Interfacial tension

Δρ = density difference across the two phases (curved interface)
D^2 = Equatorial diameter
g = acceleration due to gravity
H = Shape dependent factor, which depends on the value of shape factor, (S =d/D)

3. Results and discussion

3.1. Alkaline-Soft Brine Phase Behaviour

Aqueous stability test conducted on varied concentration of sodium hydroxide, (0.004, 0.05, 0.5 mole/L) and soft brine produced clear compatible solution. Further compatible screening was carried out at varying salinities. Alkaline conc. (0.5 mole/L) added to soft brine at increasing salinity ranging from 0.5-5.7% produced a clear solution at both pH of 9, 11 and 13 (see Fig. 2) with pH increasing as salinity decreases as seen in Fig 3.
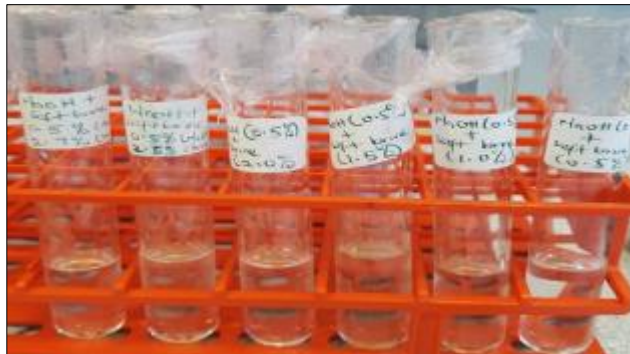

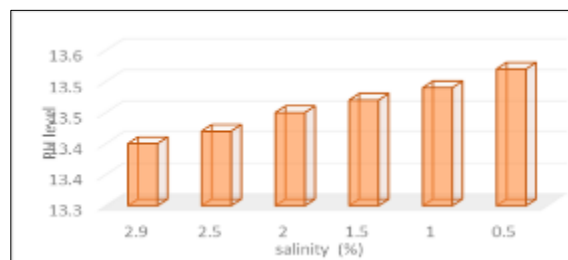**Figure 2** Diagram showing salinity scan of NaOH and Soft brine

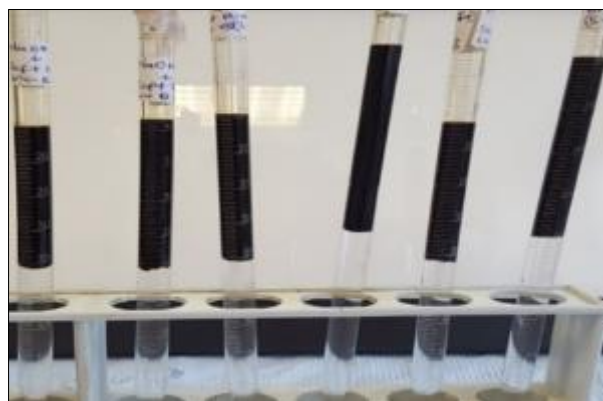**Figure 3** Plot of salinity versus pH level.

Figure 4 Pipette test on NaOH in soft brine and oil (upper phase micro-emulsions)

Phase separation test carried out on sodium hydroxide (conc.0.5mol/L) and soft brine at varying salinity with oil did not produce Type III micro emulsions as such could not achieve optimum salinity (Fig. 4). This is because saponification (which generates in-situ anionic surfactant) gives rise to increased salinity rendering the interface over-optimized, thus the surfactant partitions into the oil phase forming an upper phase, Type II micro emulsion as categorised by Windsor (1954).

3.1.1. Interfacial Tension Test

Results of IFT experiment showed no bubbles but flow of oil. It is pertinent to state that though the oil flow freely indicative of a low IFT, the absence of Type III micro-emulsions showed that IFT was not low enough to produce micro-emulsion, this is in line with Sheng (2011) report stating that an ultralow IFT is required for emulsification to occur.

3.1.2. Alkaline 2: Sodium Metaborate, (NaBO$_2$)

Aqueous stability conducted on varied concentration of sodium metaborate, (0.5, 0.2 mole/L) and 5.7 % soft brine at pH of 9 and 11 produced clear compatible solution with no precipitation. Further test on the salinity tolerance of the system was carried out on sodium metaborate 1.8% conc. with varying brine salinity (0.5% to 5.7 %). Alkali volume, 6.5ml was kept constant as the brine salinity changed. No precipitation occurred at both high and low salinities It was observed that alkalinity of the solution increased as salinity increased.

Phase separation test carried out on sodium metaborate, 1.8% conc. and soft brine at varying salinity with oil produced Type II micro emulsions as such could not achieve optimum salinity. This is because saponification (which generates in-situ anionic surfactant) gives rise to increased salinity rendering the interface over-optimized, thus in-situ surfactant (alkaline flooding) alone is unable to achieve optimum salinity. Similarly, IFT results showed free flowing stream of oil indicating low IFT but the absence of Type III micro-emulsions (which is an indicator of ultra-low IFT) indicated that ultra-low IFT could not be achieved in alkaline flooding (Sheng, 2011).

3.1.3. Alkaline 3: Ethylene-diamine-acetic Acid + Sodium Hydroxide, EDTA/NaOH

EDTA, a strong acid with pH of 3 was used because of its sequestering ability while NaOH, a strong alkaline was added to adjust the pH. Aqueous stability and salinity scan was conducted on EDTA/NaOH and soft brine. Alkaline concentration 0.1 mole/L was prepared in soft brine and the solution adjusted to pH of 9.5. A clear compatible solution with no precipitation at varying electrolyte concentration was observed. These results show that soft brine was highly compatible with all the selected alkalis.

Table 2 Salinity scan on EDTA and soft brine

EDTA/NaOH + Soft Brine							
EDTA/NaOH conc. @ 0.05%	Initial conc. (C$_1$)	Soft Brine volume (V$_1$)	End Conc. (C$_2$)	Total volume (V$_2$)	Distilled water (ΔV)	pH level	Observation
Volume (ml)	%	ml	%	ml	ml		
5	5.73	5.0	2.9	10	0.0	5.7	A constant alkali
5	5.73	4.4	2.5	10	0.6	5.9	conc. of 0.05% at
5	5.73	3.5	2.0	10	1.5	6.8	varied soft brine
5	5.73	2.6	1.5	10	2.4	7.2	conc. produced
5	5.73	1.7	1.0	10	3.3	7.7	clear solutions
5	5.73	0.9	0.5	10	4.1	8	with no precipitate

Pipette test carried out on EDTA/NaOH (conc. 0.5mol/L) and soft brine at varying salinities with oil produced Type II micro emulsions as such could not achieve optimum salinity as in earlier cases. This further stress the fact that alkaline (in-situ surfactant) flooding alone is unable to achieve optimum salinity.

IFT test carried out on this system produced bubbles at salinities greater than 1.5% while salinities between 0.5-1.5% resulted in flowing stream of oil. A critical study showed that the pH of solutions with salinities greater than 1.5% were acidic (< 7) as seen in Table 2, thus reaction between an acidic aqueous solution and the acid in oleic phase will not produce petroleum soap (in-situ surfactant) resulting in high IFT.

From the above results, it is evident that all three alkalis at different concentration have a high tolerance with soft brine at varying salinities in-terms of compatibility. Alkaline **(pH> 7)** reacts with naphthenic acid in the oil (neutralization process) to produced insitu surfactants causing a low interfacial tension between the two phases. Thus, IFT between alkaline and oil is largely dependent on salinity and pH The absence of micro-emulsions in pipette test indicates that alkaline flooding alone cannot achieve optimum salinity needed for an ultra-low IFT.

3.2. Hard Brine with Alkaline Chemicals

3.2.1. Alkaline 1: Sodium Hydroxide (NaOH)

Effects of strong inorganic sodium hydroxide with hard brine containing divalent ions; calcium and magnesium chloride were screened. Concentrated solutions of sodium hydroxide and soft brine were prepared by molecular weight percentage before mixing them together.

Aqueous stability conducted on sodium hydroxide at concentration (0.1, 0.05 mole/L), each prepared with hard brine produced cloudy solution with presence of precipitates (see Fig. 5). To affirm the incompatibility of the sodium hydroxide and hard brine system, salinity scan was performed on sodium hydroxide concentration 0.05mol /litre with varying brine salinity. NaOH volume, 2.5ml was kept constant as the brine salinity changed. A decrease in alkalinity was observed as the salinity of the brine increased. At pH of 13, precipitates of calcium and magnesium hydroxide formed in all salinities. A lower concentration of sodium hydroxide at pH 9 also produced precipitation. The insolubility of Ca^{2+} and Mg^{2+} in alkaline produced an incompatible system, resulting in divalent precipitation as seen in Equations (21) and (22)**.** This is in line with the findings of Sheng (2011) where he noted that to reduce the problem of scaling, moderate pH chemicals be used as opposed to strong alkali (NaOH). No further test was conducted on the system.
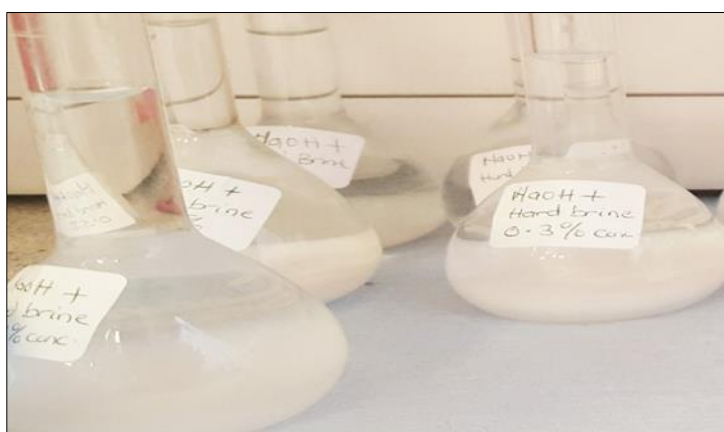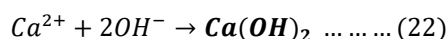
The ionic equation is:

$$CaCl_2 + 2NaOH \rightarrow \boldsymbol{CaOH_2} + 2NaCl \ldots \ldots \ldots \ldots (21)$$

$$Ca^{2+} + 2OH^- \rightarrow \boldsymbol{Ca(OH)_2} \ \ldots \ldots \ldots (22)$$

Figure 5 Compatibility test of sodium hydroxide in hard brine

3.2.2. Alkaline 2: Sodium Metaborate, (NaBO₂)

Aqueous stability was conducted on sodium metaborate in hard brine at varied concentrations, the following observations were made at different experiments:

- Alkaline concentration 0.5 mole/L at pH =10.6 produced cloudy solution with presence of precipitates.
- Alkaline concentration 0.2 mole/L at pH =10.4 produced cloudy solution with presence of precipitates. With pH adjusted to 12, precipitation still present.

- Alkaline concentration 0.05 mole/L at pH =9.9 produced clear compatible solution but at an increased pH of 12, precipitation occurred.
- Alkaline concentration 0.1 mole/L at pH =10.1 produced clear compatible solution but at an increased pH of 12, precipitation occurred.

Salinity test was carried out on the compatible system (0.05, 0.1mol/L) in hard brine at pH 9. Alkaline concentration was kept constant while the brine salinity varied. All brine salinities produced clear solution devoid of precipitation indicating that compatibility of a system depends on pH and ionic strength as reported by Liu (2007). Pipette test carried out on alkali conc. 0.05 mol/L and hard brine at varying salinity with oil produced Type II micro emulsions as such could not achieve optimum salinity. Similar test was conducted at a higher alkaline conc. of 0.1mol/L; this also produced similar results. This is because saponification (which generates in-situ surfactant) causes increased salinity, which renders the interface over-optimized and unable to produce Type III micro emulsions but rather produced Type II microemulsions.

IFT experiment on aqueous solution containing alkali conc. 0.05mol/L produced a stream of oil at low salinities but a more resistant flow at higher salinities (4.5 to 6.7%). This is because increased salinity reduces surfactant concentration, thus surfactants are partitioned into the oil phase reducing its amount at the oil-brine interface causing an increase in IFT values. At higher concentration (0.1mol/litre), flowing oil stream for all salinity range was observed.

3.2.3. Alkaline 3: Ethylene-diamine-acetic Acid + Sodium Hydroxide, EDTA/NaOH

Compatibility test was conducted on EDTA/NaOH and hard brine with varied concentration and adjusted pH values where the following observations were made:

- EDTA/NaOH (0.5mol/L) concentration between pH 6-7, produced a clear, cloudless solution.
- At 0.1mol/litre at pH 11-12 produced cloudy solution containing divalent ions precipitation. Same concentration at pH 9 produced a clear solution.
- Higher alkaline concentration 5% at pH 9 also resulted in a clear solution.

This further stressed the importance of pH to the solubility and compatibility of the aqueous solutions. Further test to ascertain the optimum salinity for the system was performed.

- 0.05 mol/L of EDTA/NaOH was kept constant while salinities from 0.5- 7.3% was varied with pH ranging from 9-9.6. Clear solution was observed.
- 0.03 mol/L of EDTA/NaOH was kept constant at pH 11-12 as salinity changes. Results showed cloudy solution at higher salinities and clearer fluids at lower salinities (see Fig. 6). As brine salinity increases, alkaline concentration reduces. This reduces the alkali concentration needed to sequester the divalent ions present. (Liu, 2007).
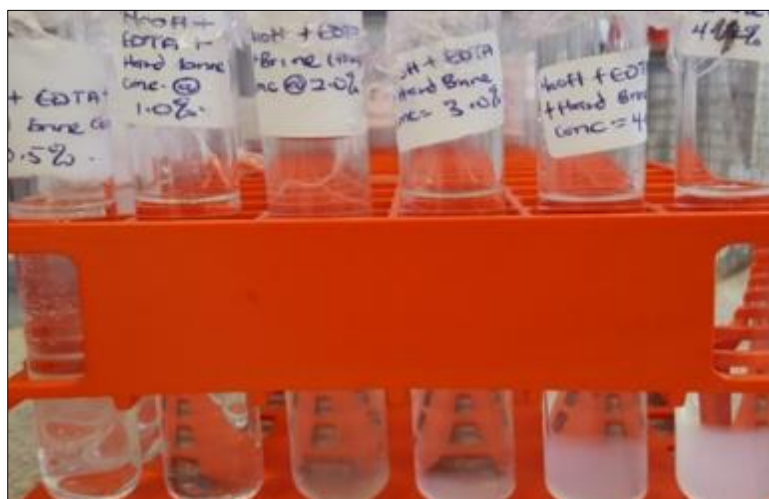

Figure 6 EDTA 0.3mol/lit in H. brine cloudy solution at pH >10

A lower alkaline conc. of 0.1mol/litre in hard brine at an adjusted constant pH of 9, produced clear solutions across all salinities (see Fig 7). This explains effect of pH on alkaline-brine compatibility. This is in line with the findings of Sheng (2011) who reported that alkaline flooding at pH> 9 would further increase IFT.
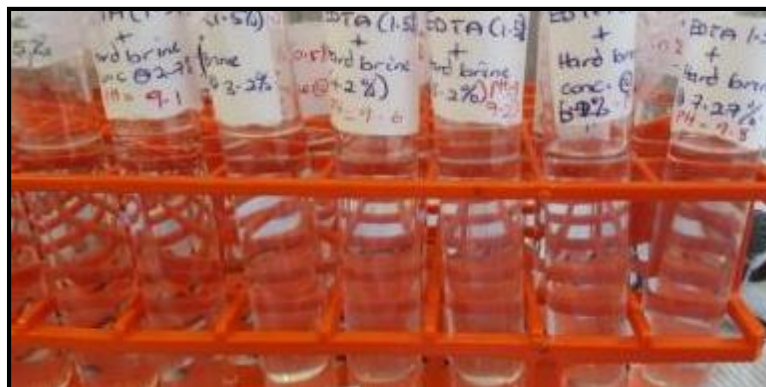

Figure 7 Clear solution of 0.1 mol/lit EDTA in H. brine at pH of 9

Phase separation analysis carried out on alkali conc. 0.05 and 0.1mol/L in varied hard brine salinities with oil produced Type II micro emulsions as seen with other alkali chemicals. IFT experiment conducted between aqueous solution containing alkali conc. 0.05mol/L and oil produced bubbles of oil in form of drops as seen in Fig.8. This was because the aqueous solution being acidic (pH 6) reacting with the acidic content of oil produced a high IFT due to the absence of an in-situ surfactant. *Recall, that in-situ surfactant is only formed when an alkaline reacts with acid in the oil*. Similar test was conducted with higher concentration of 0.1mol/L at pH 9, a stream of flowing oil was observed. From the results obtained, it is evident that at certain concentration and pH, sodium metaborate and EDTA could sequester Ca^{2+} and Mg^{2+} ions as such no precipitation occurred but sodium hydroxide formed precipitates of calcium and magnesium hydroxide. Secondly, in-situ surfactants formed by neutralization process, could not achieve optimum salinity on its own as observed by Liu *et al.* (2008), thus the need to add a synthetic surfactant. Conversely, the sole use of a synthetic surfactant is unable to achieve optimum salinity as reported by Obuebite and Okwonna (2022).
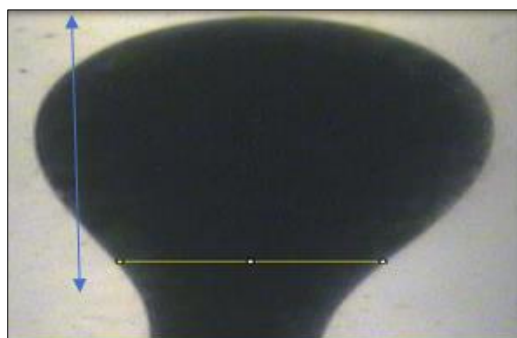

Figure 8 Bubble of oil resulting from high IFT

3.3. Alkaline-Brine-Surfactant Phase Behaviour

An anionic surfactant, Alcohol Alkoxyl Sulphates (S13c) with a molecular weight of 82.84g/mole was used in this study. The Critical Micelle Concentration (CMC) for the selected surfactant was determined to be 0.2% as shown in Fig. 9. This was obtained from the plot of the measured conductivity values versus surfactant concentration.
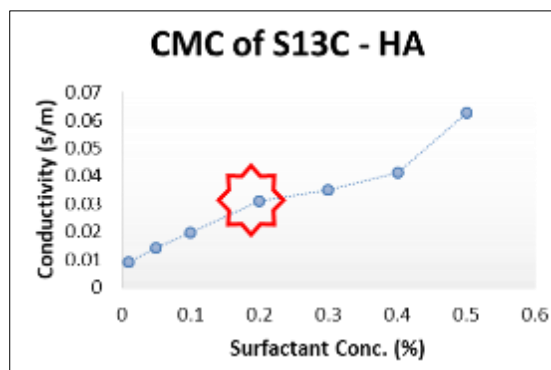
Figure 9 Critical Micelle Concentration of Surfactant- S13c

Soft brine with each of the alkaline chemical and surfactant was analysed and outlined below.

3.3.1. Alkaline 1: Sodium hydroxide (NaOH) and Alcohol Alkoxyl Sulphates (S13c)

A compatibility test was performed by injecting 0.2% surfactant, S13c into a stock solution of 0.005M sodium hydroxide in soft brine of varying salinities, alkaline and surfactant volume was kept constant while different salinities were analysed. A clear solution without precipitation was observed for all salinities. Using the clear solution at varying salinities obtained during the salinity scan, phase separation was analysed between aqueous and oleic phases. Equal volume of aqueous solution (alkali+ surfactant+ soft brine) and oil in a pipette produced type III micro-emulsions under room temperature. Optimal salinity was calculated to be **4.7%.** Samples were placed under temperature of 60°c for 21 days, Type III micro-emulsions were observed, and optimal salinity calculated to **be 4.7%.**

An IFT experiment conducted on (S13c 0.2% +alkaline concentration (0.0002%) at varying salinities ranging from (0.5 – 5.7%) and oil using the pendant drop produced a free-flowing stream of oil indicative of an ultra-low IFT. Similar result was observed when conducted on higher concentration of 0.02% with surfactant. This showed that addition of synthetic surfactant to in-situ surfactant generates ultra-low IFT.

3.3.2. Alkaline 2: Sodium Metaborate, (NaBO$_2$) + Alcohol Alkoxyl Sulphates (S13c)

Aqueous solution compatibility was performed on sodium metaborate (conc. 0.8%) + S13c (conc. 0.2%) and soft brine. Volume of alkali and surfactant was constant while brine salinity varied. Results showed highly compatible, clear solution in all salinity range. Pipette test between clear aqueous solution and oleic phases each having equal volume produced Type III micro-emulsions under room temperature. Optimal salinity was calculated to **be 1.2%.** Samples placed under increased temperature of 60°c for 21 days produce micro-emulsions and optimal salinity calculated to be **2.2%.** An IFT experiment conducted on aqueous solution with S13c 0.2% +alkaline concentration 0.8% at varying salinities ranging from (0.5 to 5.7%) and oil using the pendant drop produced a free-flowing stream of oil indicative of an ultra-low IFT.

3.3.3. Alkaline 3: Ethylene-diamine-acetic Acid + Sodium Hydroxide, EDTA/NaOH + Alcohol Alkoxyl Sulphates (S13c)

Aqueous solution compatibility was performed on EDTA/ NaOH (conc. 1.5%) + S13c (conc. 0.2%) and soft brine at pH 9. With constant volume of alkali and surfactant, a highly compatible, clear solution in all salinity range was observed. Using the clear solution at varying salinities obtained during the salinity scan, phase separation was analysed between aqueous and oleic phases at equal volume producing type III micro-emulsions under room temperature. Optimal salinity was calculated to **be 2.1%.** At an increased temperature of 60°c, micro-emulsions were observed, and optimal salinity calculated to be **3.0%.** An IFT experiment conducted on aqueous solution (S13c 0.2% + EDTA concentration 1.5%) at varying salinities and oil produced a flowing stream of oil indicative of an ultra-low IFT. Results showed that alkaline and surfactant system at varying concentration worked well with soft brine. An increase in temperature further increased optimal salinity. The injection of synthetic surfactant alongside an alkali chemical as reported by Obuebite *et al.* (2019) achieves optimum phase behaviour.

3.4. Hard Brine with Alkaline + Surfactant

Effect of the different alkaline chemicals with surfactant, alcohol alkoxyl sulphates in hard brine was analysed based on their compatibility and tolerance with divalent ions.

3.4.1. Alkaline 1: Sodium Hydroxide (NaOH) + Alcohol Alkoxyl Sulphates (S13c)

Earlier test carried out on sodium hydroxide and hard brine (without surfactant) in different concentrations resulted in precipitates of calcium and magnesium oxide as earlier shown in Fig 5. A compatibility test of the system with the addition of 0.2% surfactant, S13c also resulted in precipitates of calcium and magnesium oxide. Thus, no further test was conducted.

3.4.2. Alkaline 2: Sodium Metaborate, (NaBO$_2$) + Alcohol Alkoxyl Sulphates (S13c)

Aqueous solution compatibility was performed on sodium metaborate (conc. 0.2%) + S13c (conc. 0.2%) and hard brine. Volume of alkali and surfactant was constant while salinity was varied resulting in a highly compatible, clear solution (see Fig. 10). Surfactant dissolved completely in the solution at pH= 9.8 due to the presence of PO groups in S13c. Compatibility test on a higher alkaline concentration of 0.8% also produced clear solution (see Fig. 11).
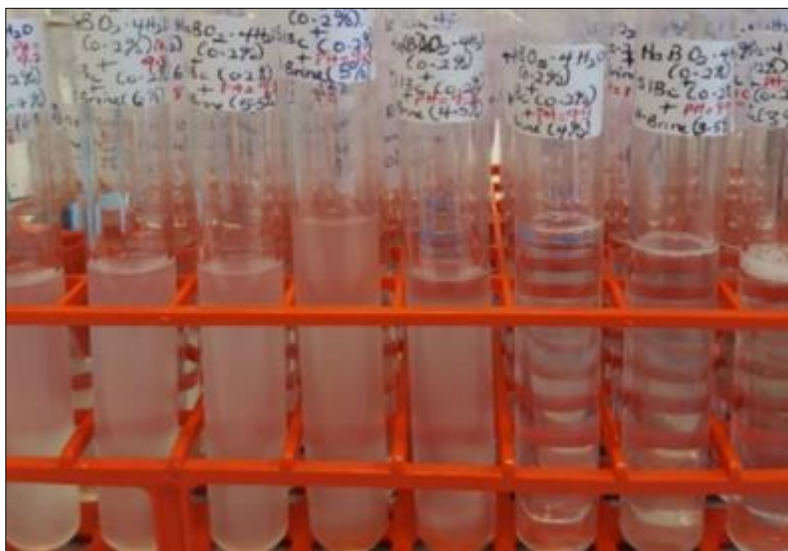

Figure 10 Salinity Scan on sodium metaborate 0.2% +S13c+ hard brine

Figure 11 Salinity Scan on Sodium metaborate 0.8% + S13c+ hard brine

With the aqueous solutions used for the salinity scan, a pipette test carried out between the oleic and aqueous (alkaline (0.2%) + surfactant (0.2%)) phase at room temperature produced Type III micro-emulsions with optimal salinity calculated to be **2.3%.** After 21 days, at an increased temperature of 60 °C, it increased to **2.6%.**

Similar test conducted at higher alkaline concentration (0.8%) at room temperature also produced type III micro-emulsions with optimal salinity calculated to be **1.7%.** and an increased optimal salinity of **2.5%.** under increased temperature of 60 °C. This indicates that extremely high alkali concentration reduces optimal salinity.

IFT conducted on the system at 0.2% and 0.8% alkaline concentration at varying salinity showed a free-flowing stream of oil as shown in Fig. 12 which is indicative of an ultra-low interfacial tension at the interface. IFT was mathematically determined using Equation (20) for 0.2% sodium metaborate + 0.2% S13c in hard brine and 0.8% sodium metaborate + 0.2% S13c in hard brine, resulting in an IFT value of **2.3 mN/m and 3.7 mN/m respectively.**

To achieve an ultra-low IFT, reaction between alkali and oil must be within a certain concentration. At extremely high alkali concentration, the low IFT will increase again resulting in reduced displacement efficiency. Lowest IFT occurs at a low alkali concentration.

Figure 12 Flowing stream of oil resulting from ultra-low IFT

3.4.3. Alkaline 3: Ethylene-diamine-acetic Acid + sodium hydroxide, EDTA/NaOH + Alcohol Alkoxyl Sulphate

Compatibility test on 1.5% EDTA/NaOH and 0.2% S13c in hard brine at pH 9 was conducted. Brine salinity varied while alkali/surfactant concentration remained constant resulting in clear solution in all salinities at ambient and reservoir temperature of 60 °C (see Fig. 13).
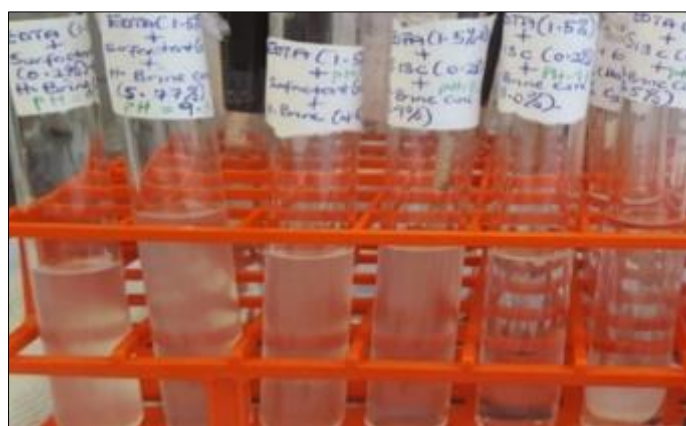

Figure 13 Salinity scan on EDTA (1.5%) + S13c (0.2%) in Hard brine

Pipette test containing equal volume of oil and alkali+ surfactant solution was performed using solutions prepared during salinity scan. Results showed Type III micro-emulsions under room temperature. Solubilisation ratio and optimal salinity calculations performed at room temperature equals **3.9%** as shown in Fig. 14**.** At increased temperature of 60 °C, type III micro-emulsions were observed, and optimal salinity calculated to be **5.1%** (see Fig. 15).
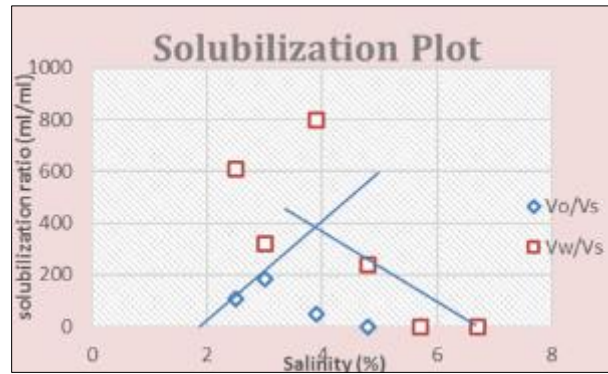
Figure 14 Solubilization plot of EDTA+ S13c+ Brine (under room temperature)
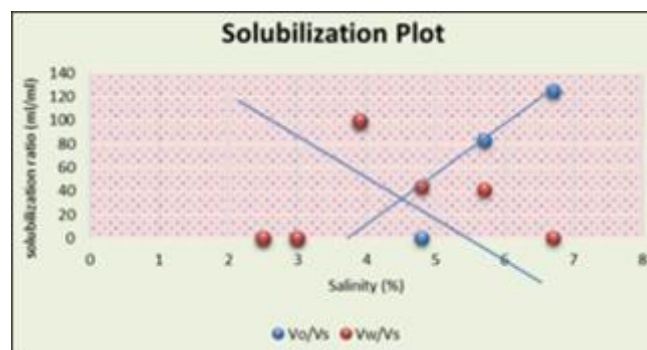

Figure 15 Solubilization plot of EDTA + S13c+brine (temp @ 60°)

The interfacial tension between aqueous solution (1.5% EDTA/NaOH + S13c) at varying salinities and the oil phase showed a free-flowing stream of oil indicative of an ultra-low interfacial tension as seen in Fig. 16. IFT measurement was mathematically determined using Equation (20) for aqueous solution of 1.5% EDTA/NaOH + 0.2% S13c in hard brine resulting in an IFT value of **1.6 mN/m.**

Figure 16 Flowing oil indicative of low IFT

Results from phase behaviour and IFT analysis showed that compatibility of the system is hugely dependent on the salinity and pH. Alkali chemicals (EDTA/NaOH) and sodium metaborate at pH 9-10, produced highly compatible fluids at varying salinities while at pH > 11, precipitates of magnesium ions occurred as also observed by Sazali *et al.* (2015). Magnesium ions are less soluble than calcium ions and are highly pH dependent. Below pH 7, magnesium silicate precipitation does not take place because silica is present in a unionized form. As the solution pH increases above pH 9, magnesium precipitates are likely to form as earlier noted by Amjad and Zuhl (2008). Furthermore, EDTA concentration of (0.03% and 0.1%), produced precipitations in brine salinities greater than 3% but an increased concentration of 1.5% resulted in clear solutions at all salinities. This is due to the decrease in alkaline concentration because of increased salinity, thus, increasing EDTA concentration increases calcium dissolution and removes precipitation of calcium and magnesium ions.

Secondly, the addition of synthetic surfactant to the alkali solution produced Type III micro emulsions, thus optimum salinity was achieved. Furthermore, the effect of temperature was seen as (reservoir temperature at >50 °C) increased temperature, increased the optimal salinity of the alkali (EDTA/NaOH & sodium metaborate) and surfactant system which is in-line with the findings of Obuebite *et al.* (2019). Solutions containing hard brine obtained higher optimal salinity compared to soft brine.

4. Conclusion

Salinity tolerance in alkaline and surfactant flooding for heavy oil sandstone reservoirs was examined in this study considering its fluid-fluid and fluid-rock reactions. Based on the obtained results, alkaline chemicals reduce the absorption of synthetic surfactants by the rock thus reducing the cost as well as the quantity of surfactant needed. Furthermore, an increase in alkaline concentration increases pH value and reduces the salinity. Alcohol alkoxy sulphate showed high solubilization ratio with heavy oil due to the polyoxyethylene (PO) group contained in it, while varying concentrations of the different alkalis in soft brine salinities produced clear solution. Alkali-brine –oil phase separation did not produce micro emulsions both at room temperature and at increased temperature of 60 °C but with the injection of synthetic surfactant, Type III micro emulsion was produced, and optimal salinity achieved. Both sodium metaborate and chelating agent EDTA, which is an acid, combined with strong alkali, sodium hydroxide increased the solution pH and sequestered the divalent ions. Conventional alkali, sodium hydroxide concentration (0.5% -1.0%) reacting with hard brine produced precipitates of calcium and magnesium hydroxide in all electrolyte concentrations. This study showed that pH played an all-important role in fluid-fluid, fluid- rock interaction during alkaline flooding. Alkali (EDTA/NaOH) and hard brine solution at pH 5 passed aqueous stability test with no precipitates but resulted in high interfacial tension, because the acidic aqueous solution reacting with oil (acidic) at the interface creates more positively charged surface, absence of in-situ surfactant and high IFT. At high pH of 9, alkaline (sodium metaborate, EDTA& NaOH) + surfactant+ hard brine solution resulted in ultra-low IFT but at pH above 11, hard brine and alkali (sodium metaborate and EDTA/NaOH) solutions produced precipitation. Increased alkali/surfactant concentration as well as increased temperature resulted in higher optimum salinity for both systems of sodium metaborate and EDTA/NaOH with surfactant (Alcohol Alkoxy sulphate) and hard brine. Finally, this work has adequately highlighted the effect of pH, temperature and concentration on the process.

Compliance with ethical standards

Disclosure of conflict of interest

The authors declare that they have no competing interest.

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