Sudan University of Science & Technology

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Research title:

Selecting Optimum Formulation of Surfactant-Alkaline System for a Sudanese Crude Oil Experimentally

اختيار الصيغة المثلى لنظام المخفضات السطحية و القلويات لخام نفط سوداني معملياً

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Project submitted to the college of petroleum engineering and technology-Sudan University of science and technology in partial fulfillment of the requirements for degree of B.Sc. in petroleum engineering

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<div align="right">Date: /   /2014</div>

قال تعالى:

بِسْمِ اللَّهِ الرَّحْمَنِ الرَّحِيمِ

(يَعْلَمُ مَا بَيْنَ أَيْدِيهِمْ وَمَا خَلْفَهُمْ وَلَا يُحِيطُونَ بِهِ عِلْمًا)

سورة طه الأية (110)

DEDICATION

This work is dedicated

To the people who helped and supported us in all aspects of life;

Our parents

To those who stand by our side during the whole journey;

Our brothers & sisters

To those who gave us a lot of lessons to learn, and inspired us to get involved in a beautiful world of science,

Our teachers

To those who have a hand in this success

Our friends

ACKNOWLEGEMENTS

Abstract

The primary objective of this research is to obtain an optimum concentration of alkali, surfactant and salt that can achieve the ultra-low interfacial tension, previous studies have shown that high performing surfactant formulations that achieve the ultra-low interfacial tension can be identified by conducting the micro-emulsion phase behavior tests. Similarly, in this research, a sample of a Sudanese crude oil from South Annajma field was mixed at specific water oil ratio with several combinations of chemical components that include surfactant (Benzalkonium chloride (BAC)), alkali (sodium hydroxide(NaOH), sodium carbonates(Na_2CO_3)), as well as sodium chloride(NaCl) to carry out phase behavior experiments. Oven was used to heat up and maintain the mixture at the reservoir temperature that is 50° C for equilibration period of two hours and the test was conducted under 1 atm. Observations and recording of phase behavior experiment results show that the optimum concentrations of the chemicals are 5%wt surfactant, 5%wt Na_2CO_3, and 2%wt NaCl, as the best formulation based on this research. This values have achieved a reasonable ultra-low of the interfacial tension.

التجريد

الهدف من هذا البحث هو اختيار الصيغة المثلى للمواد الكيميائية التي تعطي اقل توتر بين سطحي، و قد اظهرت دراسات سابقة انه يمكن الحصول على الصيغة المثلى لهذه المواد عن طريق دراسة سلوك الطور. بناءً على ذلك تم استخدام عينة من خام سوداني من حقل جنوب النجمة و تم خلطه مع محلول ماء بنسبة معينة حيث يحتوى محلول الماء على مواد كيميائية تتضمن المخفضات السطحية (Benzalkonium chloride (BAC))، والقلويات ($NaOH, Na_2CO_3$) اضافةً الي الملح؛ لدراسة سلوك الطور لهذه العينة. وتم استخدام الفرن لتسخين العينة والحفاظ عليها عند درجة حرارة المكمن (50° C) لفترة زمنية قدرها ساعتين تحت الضغط الجوي .ووجد ان الصيغة المثلى للمواد الكيميائية عبارة عن 5% كربونات الصوديوم، 5% مخفضات سطحية، و 2% كلوريد الصوديوم.

Nomenclature

EOR   Enhanced Oil Recovery

AS   Alkaline Surfactant

SPE   Society of Petroleum Engineering

OOIP   Original Oil In Place

IFT   Interfacial Tension

IFT_{om} Interfacial Tension between oil & microemulsion

IFT_{wm} Interfacial Tension between water & microemulsion

API   American Petroleum Institute

LPG   Liquefied Petroleum Gases

ASP   Alkaline Surfactant Polymer

OIIP   Oil Initially In Place

GNPOC Greater Nile Petroleum Operating Company

PDOC   Petro Dar Operating Company

WNPOC White Nile Petroleum Operating Company

NMR   Nuclear Magnetic Resistance

SAR   Surfactant Alcohol Ratio

WOR   Water Oil Ratio

CMC   Critical Micelles Concentration

CEOR   Chemical Enhanced Oil Recovery

O   Oil

W   Water

ME   Micro-Emulsion

HLB   Hydrophile - Lipophile Balance

MW_h Molecular Weight of hydrophilic

MW   Molecular Weight

W/O   Water in Oil

Oil/W   Oil in Water

SDS   Sodium Dodecyl Sulphates

SDBS   Sodium Dodecyl Benzene Sulfonates

BOPD   Barrel Oil per Day

TEACL   tetraethyl Ammonium Chloride

TBAB   tetrabutyl Ammonium Bromide

BAC   Benzalkonium chloride

DI   Deionized

V_o Oil Volume

V_w Water volume

V_{em} Emulsion Volume

σ   Interfacial tension

Nc   Capillary Number

μ   Viscosity

v Darcy's velocity

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Chapter One

Introduction

Chapter 1   Introduction

In the near future, there is no economical, abundant substitute for crude oil in the economies of the world. Maintaining the supply to propel these economies requires both developing additional crude oil reserves and improving oil recovery from the present reservoirs. The oil recovery methods that are commonly used include pressure depletion and waterflooding. Oil production by means of pure pressure depletion may result in an oil recovery less than 20% of original oil in place (OOIP), depending on the initial pressure and the compressibility of the fluids. And on average, water flooding whose purpose, in part, is to maintain reservoir pressure to recover more oil, leaves approximately two thirds of the OOIP as unswept and residual oil in reservoir for further recovery. This is due to both poor sweep efficiency and trapping droplets by capillary forces due to high interfacial tension between water and oil(Liu, 2008)

1.1. Problem Statement

Chemical EOR potential was identified for a Sudanese oil field. According to(Q.Wang.*et al*, 2013), 4-18% of a Sudan's oil field recovery factor is being improved by using Chemical EOR process, they provided the above mentioned recovery factor by using Eclipse EOR black oil simulator with chemical input lab data which crude oil properties are similar to that of a Sudanese oil field. Applying Chemical EOR technology is still challenging due to extensive expertise and preparation required to ensure successful application. Real lab data are needed for more evaluation studies of Chemical EOR potential for Sudan crude oil, So that this study is directed toward the laboratory phase behavior studies which are required to select and optimize chemical components for Sudan crude oil. Phase behavior evaluation using different types of alkaline and surfactant under reservoir conditions will achieve ultra-low interfacial tension and emulsion perform, that cause greatly reduces capillary forces that trap oil which lead to improve oil recovery.

1.2. Objectives & Scope of the Study

The objective of the big picture of this study is to find the optimum factors using chemicals (surfactant-alkaline) which increase the oil recovery after primary and water flooding. And the clear cut objectives are:

1. Select the optimum salinity.
2. Select the best suitable type of alkaline (sodium hydroxide, sodium carbonate) for Sudanese crude oil.
3. Select the optimum concentration of the candidate alkaline.
4. Select the optimum concentration of surfactant (Benzalkonium chloride (BAC).
5. Determine the effect of time on the emulsions formed.

The study attempts to give a review of published experimental works done by previous researchers in chemical EOR for oil reservoir. Since chemical EOR is a very vast topic, it will be narrowed down to some specific area. Therefore, this study only focus on phase behavior experiments which will be started for prediction of oil recovery in Sudanese oil reservoirs using alkaline, surfactant (AS) processes.

1.3. Proposed deliverable

Once the problem statement and objectives identified, researches would be made through book, SPE papers and internet about enhanced oil recovery, chemical EOR, EOR in Sudan and phase behavior study. Since chemical EOR is a very vast topic, it will be narrowed down to some specific area. This area is phase behavior study. Literature review of chemical EOR and phase behavior will be given. Samples of oil are given from companies in the Sudanese field and Data will be collected from that company. Experiment works will be done on chemical EOR on light oil samples. Finally, conclusion and recommendations will be withdrawn from experiment works. The overall work flow of study is given in the following gaunt chart represented by table (1-1).

Table 1-1: Time table

N.O	Detail	Oct 1	Nov 2	Dec 3	Jan 4	Mar 5	Apr 6	May 7	Jun 8	Jul 9	Aug 10	Sep 11
1	Project title selection& Introduction	■										
2	Laboratory Preparation		■	■								
3	Preliminary experiment				■	■						
4	Background & Literature review		■	■	■	■	■	■	■			
5	Methodology				■	■	■	■	■			
6	Main experiment									■		
7	Result & discussion									■	■	
8	Conclusion & Final Discussion											■

Chapter Two

Background

&Literature Review

Chapter 2　　Background & Literature Review

2.1.　Background

The general mechanism of oil recovery is movement of hydrocarbons to production wells due to a pressure difference between the reservoir and the production wells. The recovery of oil may be subdivided into three major categories those are primary, secondary and tertiary recovery which known as Enhanced oil Recovery.

Primary methods that use natural reservoir energy (gas cap drive, solution gas drive, water drive, liquid and rock expansion drive and combination drive) and secondary pressure maintenance methods (water, gas and combination of water and gas injection) leave behind more than half of the original oil in place. Enhanced Oil Recovery techniques must ultimately be employed in order to recover this massive amount of energy resource.

2.2.　Recovery stages

The following section will describe the recovery stages presented throughout a reservoir life time

2.2.1. Primary recovery

Primary recovery refers to the volume of hydrocarbon produced by the natural energy prevailing in the reservoir and/or artificial lift through a single wellbore. The efficiency of oil displacement in primary oil recovery process depends mainly on existing natural pressure in the petroleum reservoir. This pressure originated in the reservoir from various forces:

- Expanding force of natural gas.
- Gravitational force.
- Buoyancy force of encroaching water.
- An expulsion force due to the compaction of poorly consolidated reservoir rocks.

Among these forces, expanding force of high-pressure natural gas contributes mainly to oil production. These forces in the reservoir either can act simultaneously or sequentially, depending on the composition and properties of the reservoir.

The gravitational force is more effective in steeply inclined reservoir where it facilities the drainage of oil. This force alone may not be effective in moving large amount of oil into a production well. Another, more effective, force for displacement oil is encroachment of water from the side or bottom of a reservoir. In some fields, edge water encroachment from a side appears to be stationary.

The ability of the edge water to encroach depends upon the pressure distribution in the reservoir and the permeability. Compaction of the reservoir as fluids are withdrawn also is a mechanism for movement of oil to production wells. Part of the oil will be expelled to decrease in the reservoir volume (P.Sultan. and *etal*).

2.2.2. Secondary recovery

Secondary hydrocarbon recovery refers to the volume of hydrocarbon produced as a result of the addition of energy into the reservoir, such as fluid injection, to complement or increase the original energy within the reservoir. When oil production declines because of hydrocarbon production from the formation, the secondary oil recovery process is employed to increase the pressure required to drive the oil to production wells. The purposes of a secondary recovery technique are:

- pressure restoration
- pressure maintenance

The mechanism of secondary oil recovery is similar to that of primary oil recovery except that more than one well bore is involved, and the pressure of the reservoir is augmented or maintained artificially to force oil to the production wells. The process includes the application of a vacuum to a well, the injection of gas or water(P.Sultan. and *etal*, 2010).

2.2.3. Tertiary or Enhance oil Recovery (EOR)

Tertiary or enhance oil recovery refers to processes in the porous medium that recover not produced oil by the conventional primary the sweep efficiency in the reservoir by use of injectants that can reduce the remaining oil saturation below the level achieved by conventional injection methods. Included in the remaining oil defined here are both the oil trapped in the flooded area by capillary forces (residual oil), and the oil in areas not flooded by injected fluid (bypassed oil) (P.Sultan. and *etal*, 2010).

The main objective of all methods of EOR is to increase the volumetric sweep efficiency and to enhance the displacement efficiency, as compared to an ordinary water flooding. One mechanism is aimed towards the increase in volumetric sweep by reducing the mobility ratio and the other mechanism is targeted to the reduction of the amount of oil trapped due to the capillary forces (diva-portal, 2014).

The oil recovered by both primary and secondary processes ranges from 20 to 50% depending upon oil and reservoir properties. The goal of EOR processes is to recover at least a part of the remaining oil-in-place. These methods change the reservoir fluid properties. The objective of EOR is increase the pressure difference between the reservoir and production wells, or to increase the mobility of the oil by reduction of the oil viscosity or decrease of the interfacial tension between the displacing fluids and oil(P.Sultan. and *etal*, 2010).

Enhanced oil recovery (EOR) is any method that increases oil production by using techniques or materials that are not part of normal pressure maintenance or water flooding Operations. There are a number of different EOR mechanisms but they can be broadly categorized in to thermal methods, chemical methods, miscible methods, microbial methods and others. The application of each technique depends on the reservoir heterogeneity, interfacial forces and oil viscosity, which are main factors that lead to high oil saturation after the primary and secondary processes.

There are several EOR processes that are considered to be promising:

1. **Thermal Processes**

When petroleum reservoirs contains a low- gravity (less than 20 deg. API), high- viscosity oil and have a high porosity, secondary recovery methods are not effective for displacement of oil. For such reservoirs, thermal processes are most effective. The injection of steam reduces the oil viscosity which causes an increase in the oil mobility. Depending on the way in which the heat is generated in the reservoir, the thermal process can be divided into two categories:

- Steam injection
- In-situ combustion(P.Sultan. and *etal*, 2010).

2. Miscible process

The primary mechanism in a miscible process is to displace oil with a fluid that is miscible with the oil (i.e., CO_2) at the condition existing at the interface between the injected fluid and the oil bank being displaced. The primary slug (i.e. LPG) is displaced by a larger volume of a less expensive gas that is high methane concentration (dry gas).

The process is effective primarily because of miscibility between the primary slug and the oil phase.

The objective of miscible displacement is to increase the oil recovery by reducing the residual oil saturation to lowest possible value. Since residual oil saturation depends on the capillary number Nc, and the residual oil saturation decreases when capillary number increases, the interfacial tension should be reduced to its lowest value by injecting a slug of miscible solvent driven by natural gas until miscibility is achieved. Then, only one phase will result from the mixture of miscible fluids, with no interfaces and consequently no IFT between the fluids (C. Aurel, 1992).

3. Chemical process

The chemical processes is refer to those processes in which additional non-natural components are added to the fluid in order to stimulate the mobility between both the displacing and displaced fluid(P.Sultan. and *etal*, 2010).

Chemical EOR involves the injection of liquids that effectively displace oil because of their phase behavior properties which reduces the capillary pressure or the

interfacial tension between the displacing fluid (For example, water) and the oil. Injection of polymer, surfactant, alkali, or combination of polymer/surfactant/alkali can be categorized under chemical methods. Polymer injection increases the viscosity of the displacing fluid to about that of oil, as a result reduces the mobility ratio and improves the sweep efficiency. Surfactant injection will mobilize the remaining oil by enhancing the sweep efficiency through favorable alteration of oil-water interfacial tension, reservoir wettability and oil-water relative permeability. Alkali can be used to neutralize the heavy oil acidic content to form in-situ surfactants. With the assistance of these in-situ surfactants, O/W emulsion with much lower viscosity than heavy oil can be generated. In this way, the heavy oil is dispersed in the water and produced out of the reservoir.

2.3. Chemical flooding

Chemical flooding relies on the addition of one or more chemical compounds to an injected fluid either to reduce the interfacial tension between the reservoir oil and the injected fluid or to improve the sweep efficiency of the injected fluid. There are three general methods in chemical flooding technology. The first is polymer flooding, in which a large macromolecule is used to increase the displacing fluid viscosity. This leads to improved sweep efficiency in the reservoir. The second and third methods; micellar polymer and alkaline flooding, make use of chemicals that reduce the interfacial tension between oil and displacing fluid (Terry, 2001).

2.3.1. Polymers flooding

Polymers are used to achieve favorable mobility ratios during water or surfactant flooding. It is therefore essential that the viscosity of the polymer solution is not reduced during the flooding period.

Polymer flooding will be favorable in reservoir where oil viscosity is high, or in reservoirs that are heterogeneous, with the oil bearing layers at different permeability's. Polymers have been extensively used in field applications in order to reach the following goals:

➢ To improve mobility ratio and thus, to reach more favorable condition for oil displacement.

➢ To reduce the effective permeability to the displacing fluid in highly permeable zones or to plug those zones.

➢ To improve the affectivity profile of the injecting wells and to improve the production performance of producers by plugging off high conductivity vicinity of a well(P.Sultan. and *etal*, 2010).

Limitations of using polymer according to (Fall, 2001) are:

• High oil viscosities require a higher polymer concentration.

• Results are normally better if the polymer flood is started before the water-oil ratio becomes excessively high.

• Clays increase polymer adsorption.

2.3.2. Surfactant flooding

Surfactant Assisted Water Floods are employed in low permeability reservoirs (0.1 - 100 mD) where it is difficult to inject water. This process can also be employed as a tertiary recovery method where conditions are such that polymer and/or alkali cannot be introduced into the reservoir. This could be the case where the permeability is too low, the temperature is too high, or the salinity is too high to include polymer. A Surfactant Assisted Water Flood increases oil recovery by increasing injectivity and lowering interfacial surface tension(chem, 2014).

The main aim of the surfactant flooding is to recover the capillary-trapped residual oil after water flooding. By means of surfactant solutions, the residual oil can be mobilized through a strong reduction in the interfacial tensions between oil and water.

After the surfactant solution has been injected, the trapped oil droplets or ganglions are mobilized due to a reduction in interfacial tension between oil and water. The coalescence of these drops leads to a local increase in oil saturation. Behind the oil bank, the surfactant now prevents the mobilized oil from being

retrapped. The ultimate residual oil saturation will therefore be determined by the interfacial tension between oil and surfactant solution behind the oil bank.

The interfacial tension is generally in range of 20-30 dynes/cm, and by designing and selecting a series of specialty surfactants to lower the interfacial tension to the range of 10^{-3} dynes/cm, a recovery of 10-20% of the original oil in place, when not producible by another technologies, is technically and economically feasible by surfactant-flooding EOR.

The increased concentration of the surfactant at interface results in dramatic reduction of IFT between the phases. For EOR always prefer to use low salinity water for injection, because increasing salinity causes reduction in electrical double layer, so reduction in IFT will be low and hence more difficult to recover oil.

The magnitude and nature of interfacial charge and surface charge on minerals and clays present in the reservoir rocks in the oil displacement can contribute significantly to the design of surfactant formulations for optimum performance under given reservoir conditions. The sign and magnitude of the charge will influence the adsorption of the surfactant on minerals and clays of the reservoir (P.Sultan. and *etal*, 2010).

The challenges associated with surfactant flooding according to (Fall, 2001) are:
1. Complex and expensive system.
2. Possibility of chromatographic separation of chemicals.
3. High adsorption of surfactant.
4. Interactions between surfactant and polymer.
5. Degradation of chemicals at high temperature.

The success of the surfactant flooding EOR depends on different factors:
- Formulations
- Costs of surfactant
- Availability of chemicals
- Environmental impact
- Oil price

All these factors are critical due to the high volumes usually required to flood one field. Therefore, in order to minimize the transportation costs, it is critical to have

plants, big enough to accommodate the capacity needed to satisfy the demand in close to proximity to the field being flooded and that the cost of the chemicals be low enough to make the sizeable initial investment in chemicals profitable in the long terms.

Types of Surfactants

The term surfactant is a blend of surface acting agents. Surfactants are usually organic compounds that are amphiphilic, meaning they are composed of a hydrocarbon chain (hydrophobic group, the "tail") and a polar hydrophilic group (the "head"). Therefore, they are soluble in both organic solvents and water. They adsorb on or concentrate at a surface or fluid/fluid interface to alter the surface properties significantly; in particular, they reduce surface tension or interfacial tension (IFT).

Surfactants may be classified according to the ionic nature of the head group as anionic, cationic, nonionic, and zwitterionic. **Anionic** surfactants are most widely used in chemical EOR processes because they exhibit relatively low adsorption on sandstone rocks whose surface charge is negative. **Nonionic** surfactants primarily serve as cosurfactants to improve system phase behavior. Although they are more tolerant of high salinity, their function to reduce IFT is not as good as anionic surfactants. Quite often, a mixture of anionic and nonionic is used to increase the tolerance to salinity. **Cationic** surfactants can strongly adsorb in sandstone rocks; therefore, they are generally not used in sandstone reservoirs, but they can be used in carbonate rocks to change wettability from oil-wet to water-wet. **Zwitterionic** surfactants contain two active groups. The types of zwitterionic surfactants can be nonionic-anionic, nonionic-cationic, or anionic-cationic. Such surfactants are temperature- and salinity-tolerant, but they are expensive. A term amphoteric is also used elsewhere for such surfactants. Sometimes surfactants are grouped into low-molecular and high-molecular according to their weight.(Sheng, 2011)

2.3.3. Alkaline flooding

Alkaline flooding is an enhanced oil recovery process where the PH of the injected water is increased by the addition of relatively inexpensive alkaline agents such as sodium carbonate, sodium silicate, sodium hydroxide and potassium hydroxide in an effort towards improving oil recovery.

In the alkaline flooding process, the alkali reacts with the acidic constituents in the crude leading to lower water-oil interfacial tension, emulsification of oil and water, and solubilization of rigid, interfacial films. Also alkali may react with the reservoir rock, leading to wettability alteration. All of these mechanisms will potentially increase oil recovery.

The alkaline recovery process is a relatively simple process as compared to other chemical floods, but still sufficiently complex to warrant careful laboratory investigation and field trials before application.

The factors which determine the entrapment and release of oil from a rock matrix are:

1. The geometry of the pore network and microscopic heterogeneities of the porous medium.
2. Fluid-fluid properties such as interfacial tension, phase behavior, and (bulk) viscosities.
3. Fluid-rock properties, such as wettability, adsorption ion-exchange, and dissolution reactions.
4. Applied pressure gradients and gravity.

Alkaline flooding enhances the recovery of the acidic oils by two stages processes. The first stage involves the mobilization of the residual oil by configurational changes like emulsification and wettability alteration.

Surface-active salts are formed in situ by the acid-base reaction between alkali and organic acids in the residual oil. The surfactant thus generated may:

1. Adsorb at the oil-water interface to lower the interfacial, and in some cases cause spontaneous emulsification and phase swelling.
2. React with or adsorb at the rock surface, changing the wettability characteristics of the rock and hence the configuration of the residual ganglia of the crude oil.

The second stage involves the modification of the macroscopic production characteristics of the mobilized oil phase. The overall recovery efficiency may be increased in this stage by improvements in the displacement efficiency through mobility control, i.e., by reduction in the floodwater mobility(Erle C. Donaldson .and *et al*, 1989).

The most common associated constrains for alkaline flooding are represent in limited range of applicable salinity, high chemical consumption and brine incompatibility – precipitation.

2.3.4. Alkaline surfactant polymer flooding (ASP)

ASP scheme is a chemical EOR method which uses a combination alkaline, surfactant and polymer as injection fluid. ASP scheme involves injecting a predetermined pore volume of ASP in to the reservoir. Often the ASP process is followed by an additional injection of polymer. Upon the completion of the ASP and polymer injection, regular water flooding behind the ASP wall resumes again. The combination of the three chemicals is synergetic. Together they are more effective than as components alone.

In the Alkaline Surfactant Polymer (ASP) process, a very low concentration of the surfactant is used to achieve ultra-low interfacial tension between the trapped oil and the injection fluid/formation water. The ultra-low interfacial tension also allows the alkali present in the injection fluid to penetrate deeply into the formation and contact the trapped oil globules. The alkali then reacts with the acidic components in the crude oil to form additional surfactant in-situ, thus, continuously providing ultra-low interfacial tension and freeing the trapped oil. In the ASP Process, polymer is used to increase the viscosity of the injection fluid, to minimize channeling, and provide mobility control(chem, 2014).

Types of Microemulsions

Microemulsion phase behavior is described as Winsor type I, type II, and type III. A transition in phase behavior can be caused by changing a variable such as salinity, temperature, surfactant structure. At low salinity, type I or oil-in-water microemulsions occur, and are characterized by coexistence with an excess brine phase. At very high salinity, type II or water-in-oil microemulsions are formed, which are characterized by coexistence with an excess oil phase. A narrow intermediate range exists between the type I and type II regions in which oil and water microemulsions are formed as a middle phase and coexist with both excess oil and excess water phases. These are referred to as type III microemulsions. The salinities at which the transition occurs between types I and III behavior is referred to as the lower critical salinity, and the salinity of the transition between type III and type II is referred to as the upper critical salinity, as illustrated in figure (2-1).
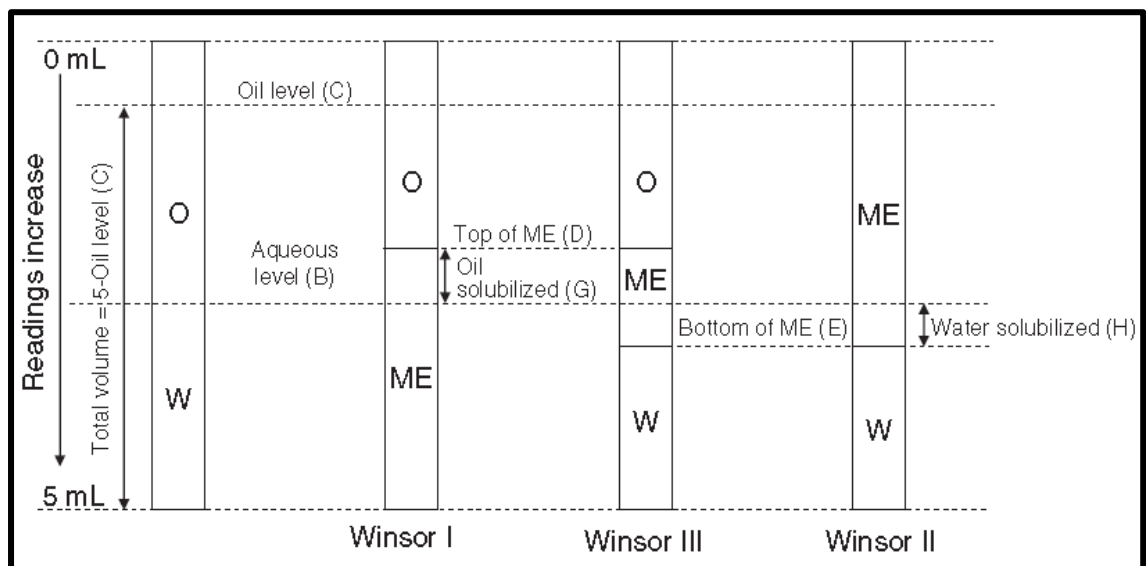

Figure 2-1: types of microemusion

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2.4. Basic concepts

- **Surface/interfacial tension**

The surface tension is defined as the force exerted on the boundary layer between a liquid phase and a vapor phase per unit length. This force is caused by differences between the molecular forces in the vapor phase and those in the liquid phase, and also by the imbalance of these forces at the interface. When the interface is between two liquids, the acting forces are called interfacial tension.

An ultralow interfacial tension between crude oil and brine phases should be required for easy flow of trapped oil droplets. It has been reported that in the presence of a suitable surfactant, an ultra-low interfacial tension can be achieved at an oil-brine interface.

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- **Mobility ratio**

Mobility ratio (*M*) is defined as the mobility of displacing phase to mobility of displaced phase, and can be given by:

$$M = \frac{\lambda \text{displacing}}{\lambda \text{displaced}} \qquad (2\text{-}1)$$

$$M = \frac{Krw}{Kro} * \frac{\mu o}{\mu w} \qquad (2\text{-}2)$$

Where:

Kro, krw = relative permeability to oil and water, respectively.

$\mu o, \mu w$ = viscosity of oil and water, respectively.

If a mobility ratio greater than unity, it is called an unfavorable ratio because the invading fluid will tend to bypass the displaced fluid. It is called favorable if less than unity and called unit mobility ratio when equal to unity.

- **Wettability**

Wettability is defined as the tendency of one fluid to spread on or adhere to a solid surface in the presence of other immiscible fluids.

The wettability of a crude oil- brine-rock system can have a significant impact on flow during oil recovery, and upon the volume and distribution of the residual oil. Wettability depends on the mineral components of the rock, the composition of the oil and water, the initial water saturation, and the temperature. Wettability can be quantified by measuring the contact angle of oil and water on silica or calcite surface or by measuring the characteristics of core plugs. Contact angle tests for wettability are widely used.

- **Phase behavior**

The phase behavior of surfactant/oil/water mixtures is the single most critical factor determining the success of a chemical flood. The desired ultralow IFT in surfactant systems is usually measured by examining the phase behavior of the microemulsion system, where the regions with high solubilization are located. The phase behavior is dependent on the type and concentration of surfactant, and brine. Other important parameters are the effect of high temperature and pressure on the microemulsion properties (at typical reservoir conditions). Predictive models, such as equations of state, cannot describe the phase behavior of surfactant systems adequately, due to the presence of both surfactants and salts, which are not, included in the available prediction tools. Therefore phase behavior of a particular system has to be measured experimentally.

- **Hydrophile–Lipophile Balance**

The hydrophile–lipophile balance (HLB) has been used to characterize surfactants. This number indicates relatively the tendency to solubilize in oil or water and thus the tendency to form water-in-oil or oil-in-water emulsions. Low HLB numbers are assigned to surfactants that tend to be more soluble in oil and to form water-in-oil emulsions. When the formation salinity is low, a low HLB surfactant should be selected. Such a surfactant can make middle-phase microemulsion at low salinity. When the formation salinity is high, a high HLB surfactant should be

selected. Such a surfactant is more hydrophilic and can make middle-phase microemulsion at high salinity. HLB is determined by calculating values for the different regions of the molecule, Griffin's equation is used to calculate HLB for nonionic surfactants is

$$HLB = 20MWh\ /\ MW \qquad (2\text{-}3)$$

Where MWh is the molecular mass of the hydrophilic portion of the molecule, and MW is the molecular mass of the whole molecule, giving a result on an arbitrary scale of 0 to 20. An HLB value of 0 corresponds to a completely hydrophobic molecule, and a value of 20 corresponds to a molecule made up completely of hydrophilic components. The HLB value can be used to predict the following surfactant properties:

- A value from 0 to 3 indicates an antifoaming agent.
- A value from 4 to 6 indicates a W/O emulsifier.
- A value from 7 to 9 indicates a wetting agent
- A value from 8 to 18 indicates an O/W emulsifier.
- A value from 13 to 15 is typical of detergents.
- A value of 10 to 18 indicates a solubilizer (Sheng, 2011).

- **Critical Micelle Concentration**

Another important characteristic of a surfactant is critical micelle concentration (CMC). CMC is defined as the concentration of surfactants above which micelles are spontaneously formed. Upon introduction of surfactants (or any surface active materials) into the system, they will initially partition into the interface, reducing the system free energy by (a) lowering the energy of the interface (calculated as area times surface tension) and (b) removing the hydrophobic parts of the surfactant from contact with water. Subsequently, when the surface coverage by the surfactants increases and the surface free energy (surface tension) decreases, the surfactants start aggregating into micelles, thus again decreasing the system free energy by decreasing the contact area of hydrophobic parts of the surfactant with water.

Upon reaching CMC, any further addition of surfactants will just increase the number of micelles (in the ideal case), In other words, before reaching the CMC, the surface tension decreases sharply with the concentration of the surfactant. After reaching the CMC, the surface tension stays more or less constant. For a given system, micellization occurs over a narrow concentration range(Sheng, 2011)

- **Solubilization ratio**

Solubilization ratio for oil (water) is defined as the ratio of the solubilized oil (water) volume to the surfactant volume in the microemulsion phase. Solubilization ratio is closely related to IFT, as formulated by Huh (1979). When the solubilization ratio for oil is equal to that for water, the IFT reaches its minimum(Sheng, 2011).

- **Surfactant Adsorption**

Adsorption is defined as the adhesion of a chemical species onto the surface of particles. In the surfactant flooding process, as the surfactant slug comes into contact with the reservoir rock and brine, there would be a loss of surfactant due to adsorption at solid-liquid interface.

The adsorption of sulfonates on oil-wet cores was found greater than on the water-wet cores. The adsorption of petroleum sulfonates increased with increasing salt concentration.

- **Capillary pressure**

Capillary pressure is defined as the pressure of the non-wetting fluid minus the pressure of the wetting fluid. For oil/water systems, water is regarded as a wetting phase and expressed by the equation:

$$\boldsymbol{P_c = P_o - P_w = P_{nw} - P_w} \qquad (2\text{-}4)$$

Where:

Pc is the capillary pressure, P_{nw} is the Pressure of non-wetting phase at interface (oil) and P_w is the pressure of wetting phase at interface (water).

- **Capillary number**

Capillary Number (Nc) is a dimensionless ratio between the viscous forces and the capillary forces, it is given by:

$$N_c = \frac{\mu v}{\sigma} \qquad (2\text{-}5)$$

And

$$N_c = \frac{K\Delta P}{\sigma L} \qquad (2\text{-}6)$$

Where v is the Darcy's velocity, μ is the viscosity of the displacing fluid while σ is the interfacial tension between the displaced and the displacing fluid; k is the effective permeability to the displaced fluid and $\Delta P/L$ is the pressure gradient. By reducing the interfacial tension between the displacing and displaced fluids the effect of capillary forces is lowered, yielding a lower residual oil saturation and hence higher ultimate oil recovery.

As the capillary number increases, the oil displacement efficiency also increases. Capillary number can be increased either by increasing the aqueous phase viscosity (μw) and flow rate or by decreasing the interfacial tension between crude oil and water.

- **Volumetric sweep efficiency**

The volumetric sweep efficiency *Evo* is the fraction of the volume swept by the displacing agent to total volume in the reservoir. It depends on the selected injection pattern, character and locations of the wells, fractures in the reservoir, position of gas-oil and oil-water contacts, reservoir thickness, heterogeneity, mobility ratio, density difference between the displacing and the displaced fluid, and flow rate etc. (Liu, 2008).

2.5. EOR Screening

The world petroleum industry has extensive experience in the application of EOR methods. A variety of conditions, both geological and geographical, require systematic analysis of the applicability of EOR processes under varying reservoir conditions.

Screening EOR techniques has various applications:

- Identifying EOR methods that are technically feasible for given reservoir conditions. This implies defining ranges for some critical reservoir/fluid parameters.
- Predicting EOR reserve potential for a given field. Combined with the result of a simple economic calculation it enables determining if there exists a realistic possibility for any field application.
- Predicting EOR reserve potential for a number of fields.
- Evaluating the economy of various EOR techniques.
- Uncertainty analysis by relating the uncertainty in EOR production to that of the critical reservoir/fluid parameters.

A feasibility study for screening potential EOR methods should be done at early stage of a project design. It improves the timing of important planning decisions(diva-portal, 2014).

2.6. Literature Review

This section provides a highlight and general over view of previous works related to enhanced oil recovery that have been conducted by some researchers on chemical EOR especially Alkaline-surfactant (AS) flood.

(Clark et al, 1988) considered four enhanced recovery methods four enhanced oil recovery methods: Conventional water flooding (40% OIIP), Polymer flooding (40% OIIP), alkaline-polymer flooding (40%), and alkaline-surfactant-polymer flooding (56%) for West Kiehl field. The polymer flood is expected to deplete the field faster than a conventional water flood without an increase in ultimate recovery, while the ASP technology is expected to extend the field life and increase ultimate recovery dramatically. They found out laboratory core-floods using ASP solutions recovered 23% OIIP additional oil beyond water-flood recovery. (Mohammadi *et al*, 2008) modeled ASP process using the University of Texas Chemical Composition Simulator, UTCHEM. Their results indicated that ASP core flood gave a high oil recovery of 98% for small chemical slugs of 0.3 PV with 0.2 wt% surfactant. Qiao Qi *et al* tested ASP combination flooding in Karamay oil field. They achieved 24% OIIP incremental oil recovery for pilot area and 25% OIIP incremental oil for the central production well(Qiao Qi et al, 2000).

Limited studies have been reported on enhanced heavy oil recovery by chemical flooding. The paper by Nelson et al. (1984) is the first that describes the benefits of combining alkali with surfactants and demonstrates the effect of in situ generated surfactant referred to as soap on phase behavior. Nelson et al. pointed out that the in situ generated surfactants are a distribution of relatively high molecular weight carboxylic structures which result in a very low optimal salinity. The desired salinity level could be raised by adding a more water soluble surfactant (Nelson. et al, 1984).

(Bryan.J, 2008) described a suite of Alkali –Surfactant (AS) floods that were performed in systems containing viscous heavy oil. Their study investigated how AS injection can be used to generate oil and water emulsions, which can in turn lead to improvement of sweep efficiencies and oil recovery. The data used in the study were obtained from core flooding experiments, with in-situ saturation measurements made using low field NMR (Nuclear Magnetic Resistance) The core flood in this study indicated that emulsification is most efficient when used to block pre-formed water

channels and improve sweep efficiency of the flood. They observed Both O/W and W/O emulsions may form in the same system, even under least partially salinity conditions. Their work demonstrated that low flow rate chemical flooding, which utilize the mechanism of emulsification and entrapment, can be successful in heavy oil. Under high rate AS injection, the emulsions were only prevalent at the inlet of the core, but under brine AS injection W/O emulsion formed everywhere. Under low rate emulsion flooding, where significantly more time was provided for surfactant adsorption to occur, water in the rock was converted to emulsified water all along the length of the core. Core wettability was altered an oil wet state during the course of water flood.

A recent study by (Q.Wang.*et al*, 2013) was conducted for chemical EOR potential in both Greater Nile Petroleum Operation Company (GNPOC) and Petro Dar Operation Company (PDOC) fields in Sudan. And they found from the initial EOR screening, the most amenable EOR processes identified for both GNPOC and PDOC are mainly chemical and thermal EOR. Chemical EOR is the more dominant process in GNPOC. They used Eclipse EOR black oil stimulator to perform chemical EOR evaluation. The chemical input data was referenced mainly from Qing Hai oil field lab data which oil properties are similar to that of Sudan's. The chemical EOR evaluation encompasses polymer flooding, surfactant-polymer (SP) flooding, and alkaline-surfactant -polymer (ASP) flooding. ASP flooding process is the highest potential with increment oil recovery over water flood ranging between 12%-18% followed by SP flooding and polymer flooding(Qiao Qi et al, 2000).

A more detailed studies were carried out by other researchers including in 2012 Sara investigated the phase behavior of surfactant system in relation to enhanced oil recovery. A high pressure experiments has been carried out on surfactant system consists of a mixture of (heptane, Sodium, dodecyl sulphate (SDS) /1-bentanol / NaCl / water) at constant salinity (6.56%) and constant surfactant alcohol ratio (SAR) with varying water oil ratio (WOR). The experiments were performed on Latin American and middle-east crude oil. It was reported that the effect of increased pressure became more significant when combining with increasing temperature. The Latin crude oil showed a decrease in oil viscosity with an increase in sulphate concentration in brine solution after contacted in PVT cell (sara B, 2012).

As well as, surfactants have been applied to different types of crude oils However, it is important to select the best surfactant formulation according to the

crude type based on phase behavior In 2006 David *et al* carried out an experimental study to select the best surfactants for different crude oils. They used phase behavior screening to reach the best formulations, meanwhile salinity scans (the process of changing the concentration of the salt and maintaining the concentration of the other components in the solution in the hope of obtaining the optimum salinity) were conducted to observe equilibration time, microemulsion viscosity, oil/water solubilization ratio and interfacial tension (IFT). Co-surfactants and co-solvents were used to minimized gels, liquid crystals, and macroemulsions as well as to boost rapid equilibration to low-viscosity microemulsion. They conclude that Branched alcohol propoxy sulfates and internal olefin sulfonates are the best surfactants for EOR. One of the best formulations was tested in both sandstone and dolomite reservoirs cores and found to give excellent oil recovery and low surfactant retention (Surfactant retention by adsorption and phase trapping determines the amount of surfactant required for a surfactant enhanced oil recovery process) (David B. Levitt, 2006).

 When alkaline is used, it is of great significance to study the phase behavior and factors that will effect on it.(F.D.Martin and J.C. Oxley, 1985, F.D.Martin. and J.C. Oxley, 1985) specifically were investigated the effect of alkaline chemicals (sodium carbonate, sodium hydroxide, potassium hydroxide, ammonium hydroxide, and sodium silicate) on the optimal salinity of a synthetic petroleum sulfonate system. Their work considered the addition of surfactants to midcontinent type crude oils that alone do not produce low IFTs against high pH aqueous phases. Their study concluded that the type of alkaline cation added has sensitive effect in phase behavior of system, hence potassium had a greatest effect, and alkaline anion has no effect on the phase behavior of surfactant system studied. ASP(Alkaline, Surfactant, and Polymer.) flooding process the highest potential with incremental oil recovery over water flood ranging between 12%_ 18%(Q.Wang.*et al*, 2013).

Intensives studies were obtained an optimized condition where different concentrations of Alkali, Surfactant, and Polymer that they can produce desirable rheological properties and interfacial tension to be used for enhanced oil recovery. In this study the aqueous solutions of polyacrylamide ($CH_2CHCONH_2$, type of alkaline) where used to improve the mobility ratio by increasing the viscosity of the solution. The experiments were also conducted to measure the reduction of surface tension of aqueous solutions of Surfactants and Alkali at different concentration, in presence and absence of polymer. The experimental data on viscosity and surface tension were

analyzed by studying the effect of (salts, alkali, and surfactant.) on polymer viscosity. The simultaneous effect of surfactants and alkalis on polymer viscosity and an optimum formulation of the alkali, surfactant, and polymer were designed, where provide optimum properties with respect to both mobility and interfacial tension between oil and water. While the solution temperature was increasing the solvent viscosity decreases, polymer viscosity decreases with sodium hydroxide concentration and surface tension decreases while alkali concentration increasing. Alkali with 0.7wt% concentration has given the most significant decreasing surface tension for the combined system. Finally an optimum formulation were designed as follows Alkali with 0.7wt%, polymer with 2000 PPM, and surfactant with 0.1wt% for SDS (Sodium Dodecyl Sulphate $C_{12}H_{24}SO_4Na$), and 0.075wt% for SDBS (Sodium Dodecyl benzene Sulfonate $C_{18}H_{29}NaO_3S$) concentration have given the most significant decreasing surface tension(M.Ajay and O.Keka, 2008).

In 2013 Aparna *et a*l identified surfactants for enhanced oil recovery by brine-oil interfacial tension reduction for a carbonate reservoir at ~ 25ºC and salinity of ~11,000ppm TDS; thus, Alkyl Propoxy Sulfates and their blends with sulfonates were evaluated to determine optimal salinity and solubilization parameters with dead crude. Imbibition experiments were performed in reservoir and dolomite outcrop cores to determine the oil recovery efficiency of surfactant systems, selected from their phase behavior test results, with potential to recover oil. Tridecyl alcohol 13 propoxy sulfate (TDS-13A) with an oil solubilization parameter of ~8 at reservoir salinity was found to recover greater than 75% oil in imbibition experiments, at a concentration as low as 0.5wt%.(Sagi.A.R. et al, 2013).

Since 1999 production of Sudanese petroleum resources started at block 1/2/4, the operator Greater Nile Petroleum Operation Company (GNPOC) was the owner of this fulfillment, but soon after this the peak of production was reached due to problems of water cut and that was in 2006, Other operators also such as Petro-Energy, Petro Dar Operation Company (PDOC), and White Nile Petroleum Operation Company WNPOC started their oil production in 2006, and the current total production is 522 KBOPD.

Total Sudan oil in place was estimated in the 1th Jun 2009 as 15.9 billion barrel, of which 39% (6.2 billion barrel) is in block 3/7 operated by PDOC this contributes about 37% of the total Sudan estimated ultimate oil recovery. GNPOC comes after with 5.5 billion barrel oil in place, but it has the highest recoverable oil of 1.6 barrel

contributing about 45% of the national reserve. The rest of the reserves are in WNPOC and Petro-Energy.

The average recovery factor for Sudan is estimated at 23% which is relatively low based on international standard. GNPOC's average recovery factor is the highest at 26% followed by PDOC, Petro-Energy, and WNPOC at 23%, 21.5%, and 11.9% respectively. This low recovery factor is due to quality of the oil and also a non-favorable reservoir properties.

GNPOC'S API is the highest at 33 degrees API followed by PDOC, WNPOC, and Petro-Energy at 25, 21, and 18 degrees API.
Total cumulative oil production at the end of 2008 is 1.05 billion barrel.

Today most oil fields production is on natural depletion assisted by artificial lift pumps, only Unity/Talih fields in GNPOC is on water injection to provide pressure maintenance, while a pilot is being implemented in PDOC. Water injection usually is not favorable for application in low API oil due to poor mobility ratio which is susceptible to water fingering, early high water cut, and low oil production rate are expected in heavy oil production, so a suitable and cost effective EOR technique should be implemented. In the view of the heavy oil nature of WNPOC crude (21° API) and unconsolidated reservoirs, WNPOC has initiated an EOR feasibility study which is divided into three phases:

- building representative static model
- evaluating optimum primary recovery
- assessing the potentiality of secondary recovery

The main focus is the second phase which is to identify feasible EOR technique and pilot test design for pilot implementation.

A more related work to this research was carried out by (K. Kanan et al, 2012) on Phase behavior of systems containing sodium dodecyl sulfate (SDS) as anionic surfactant and each of tetraethyl ammonium chloride (TEACl) and tetrabutyl ammonium bromide (TBAB) as cationic hydrotropes (a compound that solubilizes hydrophobic compounds in the aqueous solutions) in the presence of water and heptane oil. Ultralow interfacial tension for microemulsion was calculated theoretically using Chun Huh equation. And the optimal salinity was found to be 4% NaCl for 8% SDS/TBAB (1:1 M ratio).

Chapter Three

Methodology

Chapter 3   Methodology

The phase behavior of surfactant/oil/water mixtures is the single most critical factor determining the success of a chemical flood. The desired ultra-low IFT in surfactant systems is usually measured by examining the phase behavior of the micro-emulsion system, where the regions with high solubilization are located. The phase behavior is dependent on the type and concentration of surfactant, and brine. Other important parameters are the effect of high temperature and pressure on the micro-emulsion properties (at typical reservoir conditions). Predictive models, such as equations of state, cannot describe the phase behavior of surfactant systems adequately, due to the presence of both surfactants and salts, which are not, included in the available prediction tools. Therefore phase behavior of a particular system has to be measured experimentally.

3.1.   Phase Behavior Description

Phase behavior experiments are a fast and efficient method to identify surfactant formulation given a crude oil compared to core flooding. Generally there are four criteria for a successful surfactant formulation that may then be used in core flooding to validate its efficiency.

1.   Surfactant solution must be clear and in one single phase at reservoir temperature. In order to achieve this, optimal salinity of the surfactant solution with specific crude oil must be below the aqueous phase stability limit, which will be described below. This criterion is critical and should never be compromised.

2.   Solubilization ratio should be higher than 10. Surfactant formulation with high solubilization ratio corresponds to low interfacial tension between microemulsion and water/oil. Surfactant formulations with a solubilization ratio lower than 10 could also achieve high oil recovery. It is better to have the solubilization ratio as high as possible if that's possible while still meeting the other criteria, however, a solubilization ratio of higher than 10 is used to select certain formulations for further tests.

3. The surfactant solution should be free of gel, liquid crystal and other viscous phases at any possible salinity the surfactant slug may encounter in core flood or reservoir condition. Viscous phases in microemulsion tend to retain surfactant in porous media and therefore deteriorate surfactant performance.

4. Equilibration time is the time when the volume of microemulsion phase at optimal salinity ceases changing. Phase behavior samples should have fast equilibration time, usually less than 7 days. The equilibration of microemulsion phase will decrease as the salinity deviates from optimal salinity. Fast equilibration of microemulsion is a good indicator of fluid interfaces and low microemulsion viscosity. The equilibration of microemulsion when surfactant slug meets crude oil at core flood or reservoir is understood to be faster than at lab because of more contacting area due to porous structure. Long equilibration time will reduce surfactant oil recovery efficiency and therefore is not recommended in chemical flooding design (Ahmed, 2012).

3.2. Phase Behavior Measurements

Phase Behavior Measurements were conducted on selected chemical systems to evaluate the effects of several experimental factors such as: total surfactant concentration, salinity, crude oil type, and proportion different surfactant type on phase behavior of the overall chemical/hydrocarbon system. These tests were typically conducted using solution that were made up at a fixed water-to-oil ratio (volume water: volume oil =1), unless otherwise specified. These solutions were prepared in 10-mL glass pipets that were sealed end equilibrated in ovens at desired temperature condition. The relative volumes of different phases were read and recorded at set time intervals until constant reading were obtained. This constant phase volume readings were then used to calculate the solubilization parameters of the oil and the brine in the microemulsion phase(Feliciano et al, 1992).

3.3. Materials used for experiments

1. Surfactant

The type of surfactant used in this research called Benzalkonium Chloride Solutions, which can be tailored to specific industrial requirements. Benzalkonium chloride (BAC 50 & BAC 80) is used in oil and gas industry to control the activities of sulphate-reducing bacteria (SRB) in sulphate rich waters and cause deposition of ferrous sulphides which causes pitting of steel equipment and pipelines. SRB are also implicated in oil well souring, and responsible for the liberation of toxic H2S gas. Additional applications of Benzalkonium chloride include enhanced oil extraction through de-emulsification and sludge breaking.

2. Crude Oil

Crude oil from Sudanese field with the following descriptions:

Field name	South Annajma
Well name	South Annajma 1
API	38°
Reservoir temperature	$(49\text{-}50)^o$ C
Viscosity at 50° C	8 *cp*
Viscosity at 40° C	16 *cp*
Pour point	33° C

3. Deionized (DI) water

Ions in tap water will interfere with phase behavior results in phase behavior screening; therefore it is important to use deionized water.

4. Alkaline

Sodium carbonate (Na_2CO_3) and Sodium hydroxide (NaOH) were used as the main alkali in this study.

5. salt

Because sodium chloride (NaCl) is the main salt in saline water, we commonly use the mass of sodium chloride as the salinity. The common units are ppm or wt.%. (Sheng, 2011).

3.4. Equipment & tools Description

The experiments were conducted in Oil properties lab in college of petroleum Engineering & Technology in Sudan University of Science & Technology, at which all of the tools to be used are exist. There are many tools used in these experiments in order to prepare the solutions and to provide the required conditions for testing. The equipment consisting of:

1. Mass balance

Digital mass balance model JM-B as shown in figure (3-1) was used in this research; Which has a capacity of 500 grams, an accuracy 0.1 grams and power supply AC/DC, and it was used for accurate measurements of the chemicals such as surfactant, alkali and NaCl during the preparation of their stock solutions.

Figure 3-1: Mass Balance

2. Oven

Oven is used to provide the temperature that is critical in phase behavior studies. Phase behavior pipettes are housed in a Scott Science Laboratory convection oven as shown in the figure (3-2), to be allowed to equilibrate at reservoir temperature for

crude oil. A calibrated digital thermometer and an oven temperature gauge ensure a constant temperature in the oven.

Scott Science LDO-series Natural Convection Ovens are ideal for general laboratory drying application in temperature ranging from ambient to 250 ^{o} C with accuracy $\pm 1.0\,^{o}$ C.

LDO series oven are equipped with membrane type touch keypad. A digital PID controller provides precision temperature control. The main controller displays time, current and user set temperature.

Figure 3-2: oven

3. Digital Camera

The phase behavior pipettes were inspected periodically. A picture of the pipettes helped to record the physical appearance of microemulsion and the interfaces could be read later from the pictures of pipette.

Taking a picture was also faster than reading the pipettes individually, and allowed no time for the phase behavior to change. Sony camera with 14 M pixel was used for taking pictures of pipettes.

The tools consisting of:

- 10 ml measuring cylinders
- metal spoons
- glass rods
- glass cups
- Injections

3.5. Phase behavior Experimental Procedure

The concentrated stock solutions of surfactant, sodium carbonate and sodium chloride were prepared before mixing them together. All solutions were made by weight percentage. By mixing the stock solutions and DI water in different ratios, the solutions over a range of salinities were made. The solutions should be made in this order:

1. Sodium chloride and sodium carbonate stock
2. De-ionized water
3. Surfactant stock

The standard procedures for phase behavior study are:

1. Preparing surfactant solutions and alkaline solutions with different concentrations.
2. The surfactant solutions and crude oils are mixed at a specific Water Oil Ratio (WOR=1) into the pipettes.
3. After the mixing procedure, the tops of 10 ml glass pipettes are sealed by acetylene, so that water and volatiles in crude oil will stay in the samples.
4. Afterwards, the samples are shaken well by hand for 1 or 2 minutes and put on a rotating shaker for 24 hours to provide adequate mixing.
5. Then placing the mixture within the oven at reservoir temperature.
6. Finally, they are arranged on the racks to settle in an upright position.
7. Photos were taken to record the phase behaviors which would be used to calculate the solubilization ratios. The oil water interface changes with settling time. The equilibrium phase behavior is usually achieved after 7 days because no

further changes will be observed in the interface positions, i.e. phase volumes(Liu, 2008).

3.6. Correlation between Phase Behavior and IFT

The IFT measurement between micro-emulsion and water and/or crude oil is time consuming and more difficult than the phase behavior observations. Sometimes, it is almost impossible to measure the IFT between some crude oil and its lower phase micro-emulsion. By using phase behavior observation and measurements of the solubilization ratios, it is much simpler and faster to estimate the IFT of the oil/water/micro-emulsion system, especially for the surfactant screening.

IFT is related to the solubilization ratio that can be described by (Huh, 1979) equation as follows:

$$\sigma = \frac{C}{\left(\frac{Vi}{Vs}\right)^2} \qquad (3\text{-}1)$$

Where:

σ: Interfacial tension (IFT), dynes/cm.

Vi/Vs: Solubilization ratio

C: A constant with a typical value of 0.3 dynes/cm.

i : oil or water phase.

The solubilization ratio (Vo/Vs) is the ratio of solubilized oil volume to surfactant volume present (excluding soap) for the under-optimum samples. The volume of solubilized oil can be measured by the difference between the volume of the initial oil in the sample and that of the excess oil phase after equilibration. It represents a composite value for the combined lower or middle phase microemulsion and colloidal dispersion phase. For over-optimal samples, a similar calculation can be made to obtain the value (Vw/Vs).

In Huh's correlation, (Vo/Vs) is used for calculating the IFT between microemulsion and excess phase when the salinities are below the optimum condition and (Vw/Vs) is used as the solubilization ratio when the salinities are above the optimum condition, Vo/Vs increases with salinity, while Vw/Vs decreases with salinity. At optimum salinity, the amount of oil and brine solubilized in the surfactant phase are approximately equal. This is also another definition of optimum salinity. Also equal contact angles could be found at the optimum salinity(Reed.R.L. and Healy.R.N, 1984).

Chapter four

Results and Discussion

Chapter 4   Results and Discussion

4.1.   Selecting optimum Salinity (Salinity scan)

The previous prepared formulations of 3% surfactant, 2%Na_2CO_3 was used to carry out salinity scan using an oven at reservoir temperature (50° C) for equilibration time of one hour and two hours. The results of the experiments are shown in table (4-1) and table (4-2) with the solubilization ratio of both oil and water (v_o/v_s & v_w/v_s) are calculated. A camera was used to take snaps during the experiments as shown in figure (4-1) and figure (4-2).

Table 4-1: salinity scan with equilibration time of the first hour

$NaCl$ %				Solubilization ratio	
	Vo	Vw	Vem	Vo/Vs	Vw/Vs
0.5	0.2	1.1	1.3	1.33	7.33
1	0.2	0.9	1.1	1.33	6.00
1.5	0.3	0.8	1.1	2.00	5.33
2	0.6	0.5	1.1	4.00	3.33
2.5	1.3	0.4	1.7	8.67	2.67

Table 4-2: salinity scan with equilibration time of the second hour

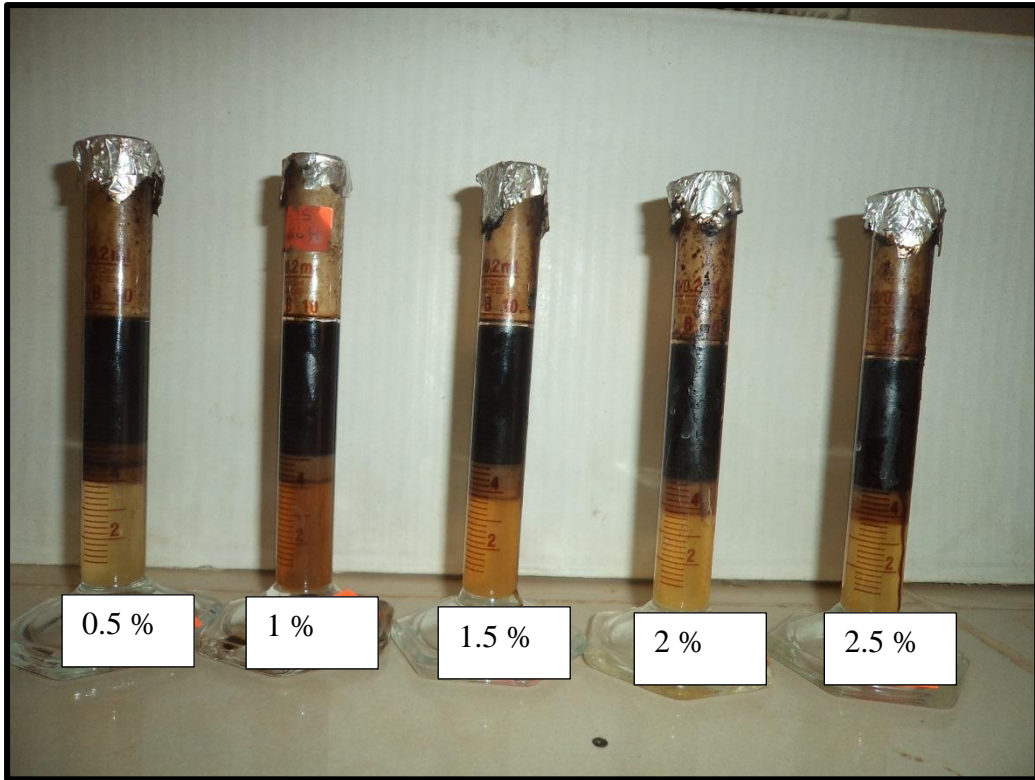| $NaCl$ %				Solubilization ratio	
	Vo	Vw	Vem	Vo/Vs	Vw/Vs
0.5	0.2	1.1	1.3	1.33	7.33
1	0.3	1.0	1.3	2.00	6.67
1.5	0.4	0.9	1.3	2.67	6.00
2	0.8	0.6	1.4	5.33	4.00
2.5	1.4	0.4	1.8	9.33	2.67

Figure 4-1: salinity scan with equilibration time of the first hour
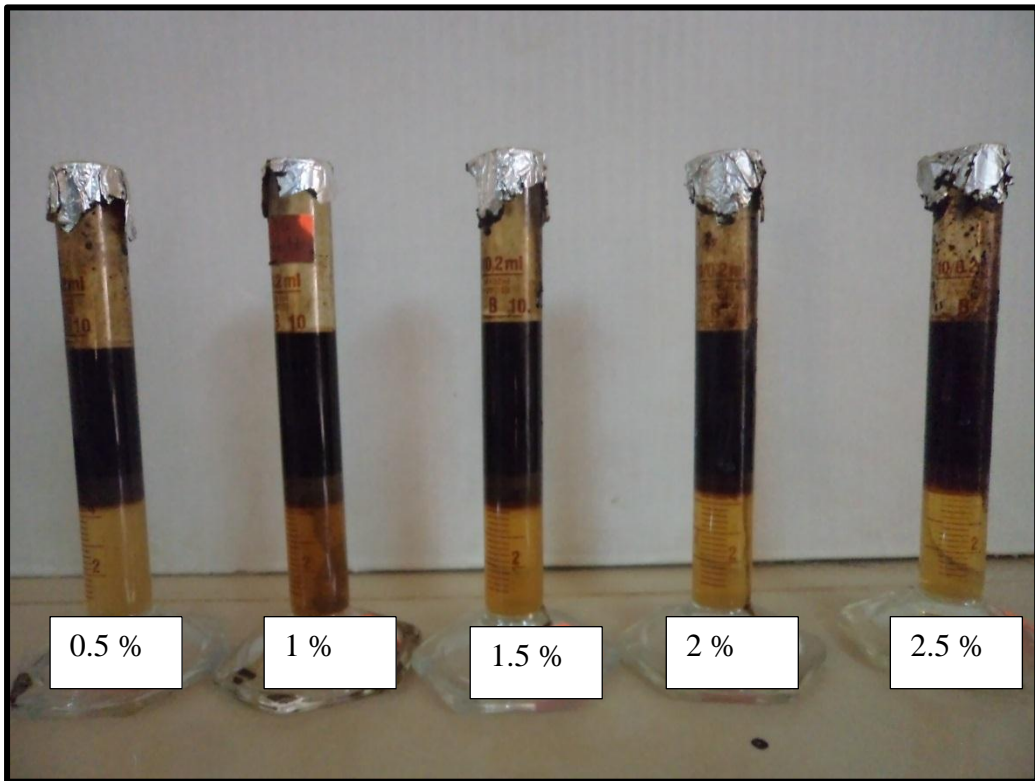

Figure 4-2: salinity scan with equilibration time of the second hour

Plotting the salinity vs. solubilization ratios of the set i.e., sodium chloride concentrations from 0.5% through 2.5%. Note that as the salinity increases the solubilization ratio Vo/Vs increases and Vw/Vs decreases this yields in an intersection of the two curves. The optimum salinity concentration is obtained from the intersection of the two curves during the first equilibration time and as shown in the figure (4-3) the value of the optimum salinity is 1.96%wt. Also the optimum salinity concentration is 1.9%wt from the second hour plot as shown in figure (4-4). It can be seen obviously from the two plots that the time has slightly effect on the optimum salinity concentration i.e., there is no large change in the optimum salinity concentration within equilibration period of two hours with respect to this set and that is due to the period of the experiment is relatively short.
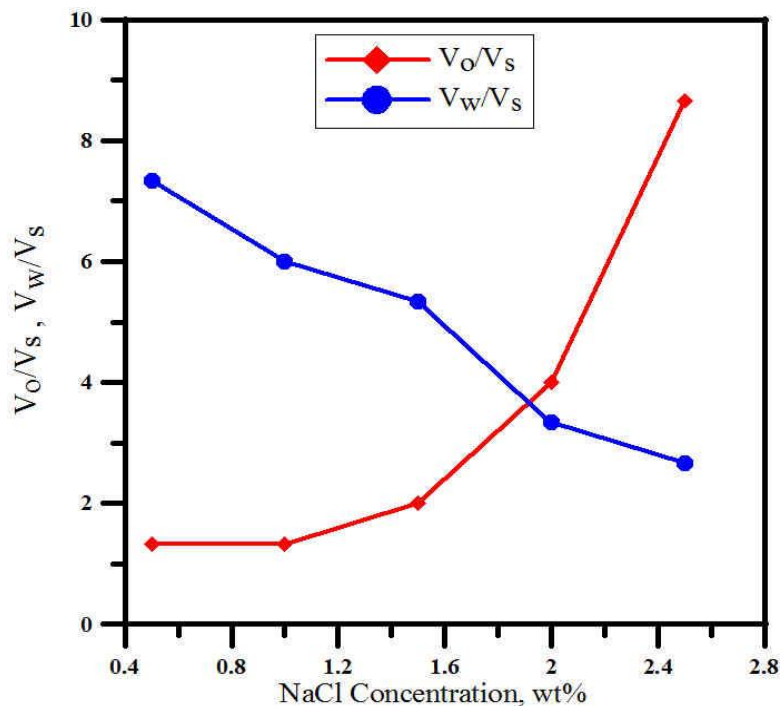

Figure 4-3: NaCl concentration wt% vs. solubilization ratio with 3%wt surfactant and 2%wt Na_2CO_3, at the first hour
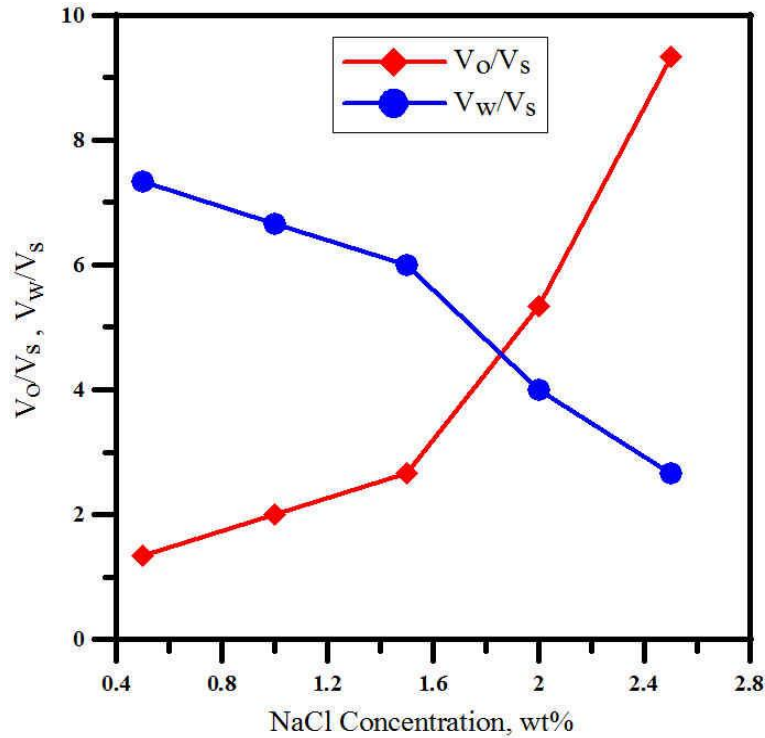
Figure 4-4: NaCl concentration $wt\%$ vs. solubilization ratio with 3%wt surfactant and 2%wt Na_2CO_3, at the second hour

4.2. Selecting optimum alkaline concentration

The optimum salinity concentration that is obtained from salinity scan is used to form a set of formulations with different sodium carbonate (Na_2Co_3) (alkaline) concentrations and the surfactant concentration is maintained constant at (3% wt.) in the hope of obtaining the best sodium carbonate concentration. The results of the experiment are obtained in the same manner to that of salinity scan and tabulated as shown in table (4-3) and table (4-4) below. In addition the snaps during the experiments are shown in figure (4-9) and figure (4-10).

Table 4-3: Na_2CO_3 concentration with solubilization ratio of the first hour

$Na_2CO_3\%$				solubilization ratio		Interfacial tension	
	Vo	Vw	Vem	Vo/Vs	Vw/Vs	$IFTom$	$IFTwm$
3	0.1	1.0	1.1	0.667	6.67	0.675	0.00675
4	0.3	0.8	1.1	2.00	5.33	0.07500	0.01055
5	0.5	0.7	1.2	3.33	4.67	0.02700	0.01378
6	0.7	0.5	1.2	4.67	3.33	0.01378	0.02700
7	0.8	0.3	1.1	5.33	2.00	0.01055	0.07500

Table 4-4: Na$_2$CO$_3$ concentration with solubilization ratio of the second hour

Na$_2$CO$_3$ %				solubilization ratio		Interfacial tension	
	Vo	*Vw*	*Vem*	*Vo/Vs*	*Vw/Vs*	*IFTom*	*IFTwm*
3	0.1	1.0	1.1	0.67	6.67	0.67500	0.00675
4	0.3	0.9	1.2	2.00	6.00	0.07500	0.00833
5	0.6	0.8	1.4	4.00000	5.33	0.01875	0.01055
6	0.8	0.7	1.5	5.33	4.67	0.01055	0.01378
7	0.9	0.4	1.3	6.00	2.67	0.00833	0.04219
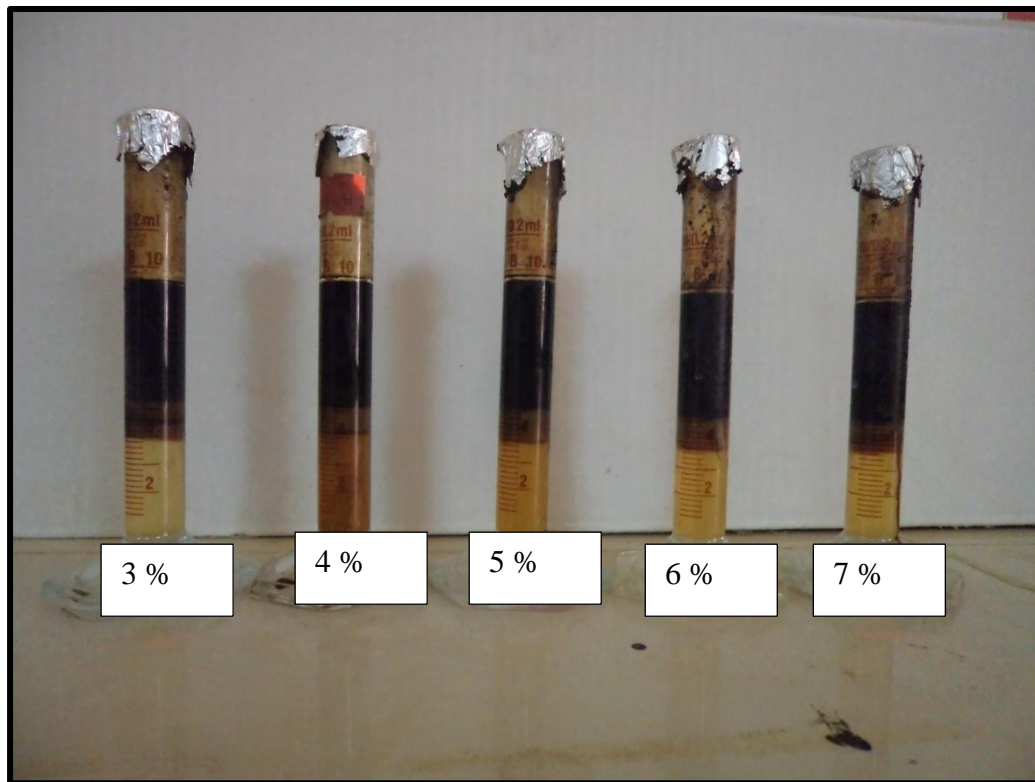
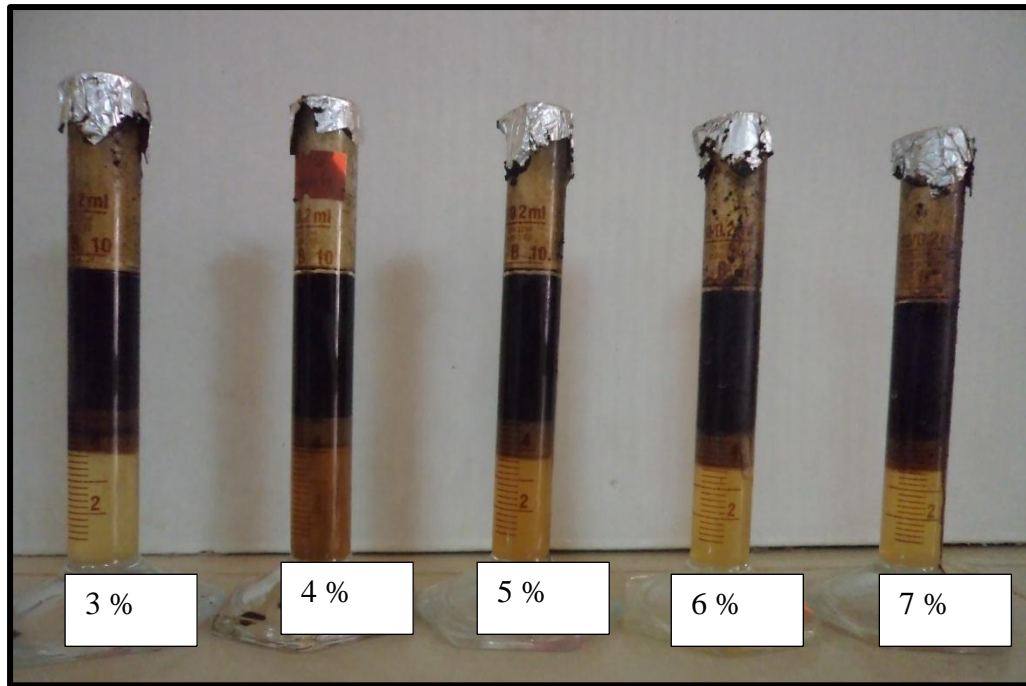**Figure 4-5**: different Na$_2$CO$_3$ concentration after the first hour

Figure 4-6: different Na_2CO_3 concentration after the second hour

Once again when plotting the sodium carbonate concentrations (Na_2Co_3 wt %) vs. the interfacial tension (IFT m-N/m) between oil and microemulsion, figure (4-7) and figure (4-8) are obtained.
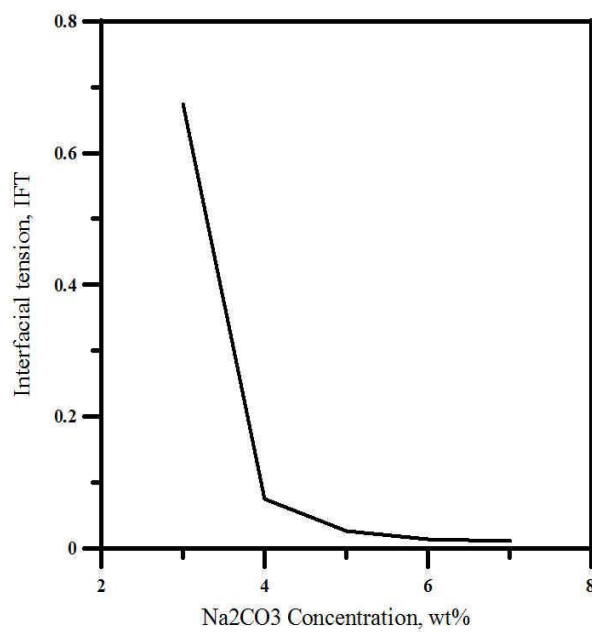

Figure 4-7: IFT as a function of Na_2CO_3 concentration with 2%wt NaCl and 3% *wt* surfactant, at the first hour
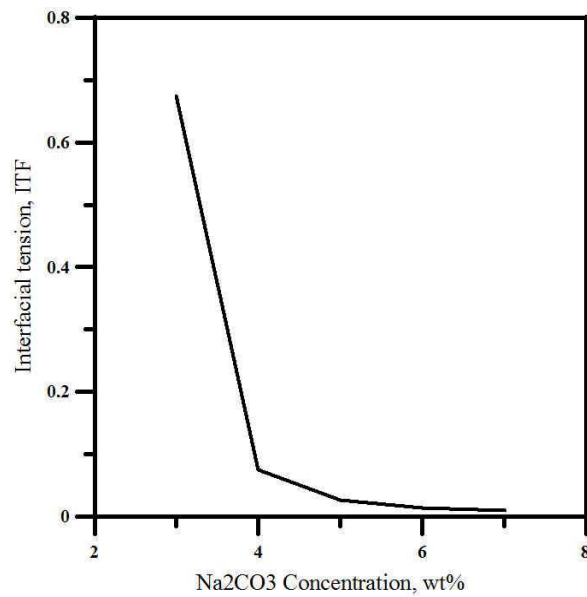
Figure 4-8: IFT as a function of Na_2CO_3 concentration with 2%wt NaCl and 3% *wt* surfactant, at the second hour

It's a clear cut evidence from the figures that as long as the sodium carbonate concentration increases the interfacial tension between oil and microemulsion decreases until a point where any addition in sodium carbonate concentration has no effect on the IFT, in other words the IFT stays constant and the concentration of the sodium carbonate at this point is the best practical concentration which has the value of 5%wt. As for the effect of time on the best concentration of sodium carbonate it shown in the figure (4-7) and figure (4-8) that the time has slight effect base on the two hours equilibrium time.

The other alkaline used i.e., sodium hydroxide ($NaOH$) was not effective, in other way around there wasn't any reaction with the crude oil and no emulsions were formed as shown in figure (4-9).
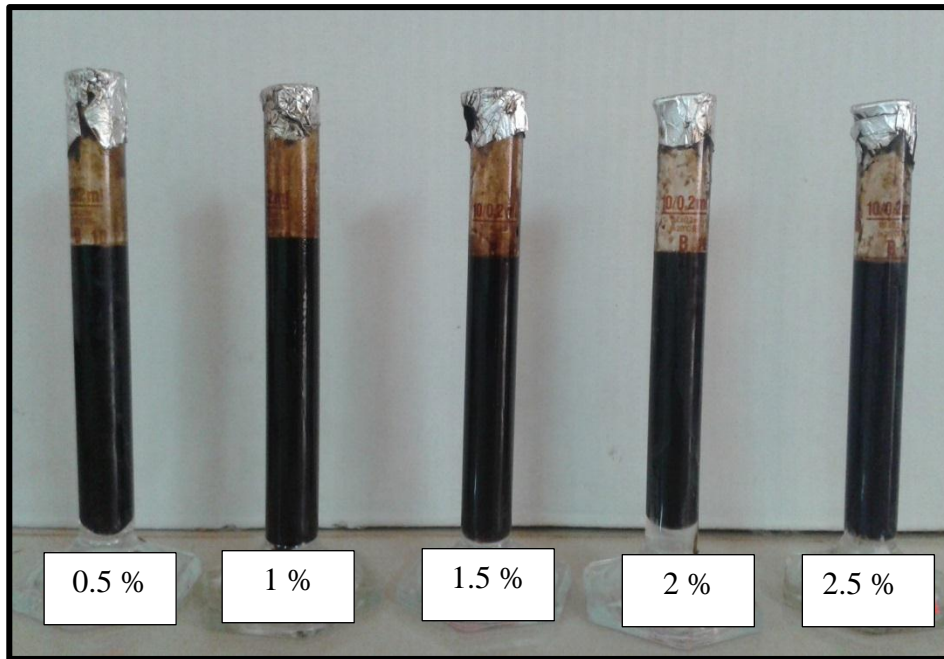
Figure 4-9: The result of NaOH

4.3. Selecting optimum Surfactant concentration

With regard to the last experiment that was conducted similarly to the previous experiments, the optimum salinity (2%wt) and sodium carbonate concentration (5%wt) obtained from the early experiments are used in new set of formulations that have different surfactant concentrations range from 3%wt to 7%wt these values of surfactant concentrations were selected based on preliminary experiments conducted at the early stage of the research which have shown that lower concentrations of surfactant exhibit low reactions. Figure (4-10) and figure (4-11) illustrate snaps taken during the experiment. And the results are tabulated in table (4-5) and table (4-6) below.

Table 4-5: IFT with surfactant concentration (equilibration time of the first hour)

Surfactant %wt	Vo	Vw	Vem	$IFTom$	$IFTwm$
3	0.1	5.0	5.1	0.67500	0.00027
4	0.4	1.8	2.2	0.07500	0.00370
5	0.8	1.4	2.2	0.02930	0.00957
6	0.9	1.2	2.1	0.03333	0.01875
7	1.1	0.9	2.0	0.03037	0.04537

Table 4-6: IFT with surfactant concentration (equilibration time of the second hour)

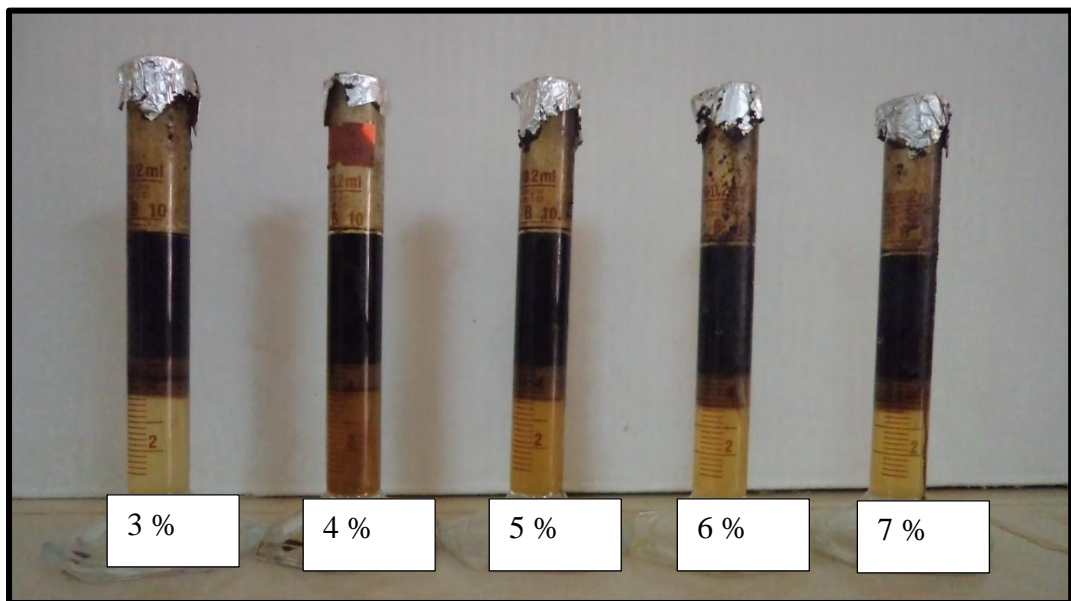| Surfactant %wt	Vo	Vw	Vem	$IFTom$	$IFTwm$
3	0.2	5.0	5.2	0.16875	0.00027
4	0.5	1.9	2.4	0.04800	0.00332
5	0.9	1.4	2.3	0.02315	0.00957
6	1.0	1.3	2.3	0.02700	0.01598
7	1.2	1.0	2.2	0.02552	0.03675

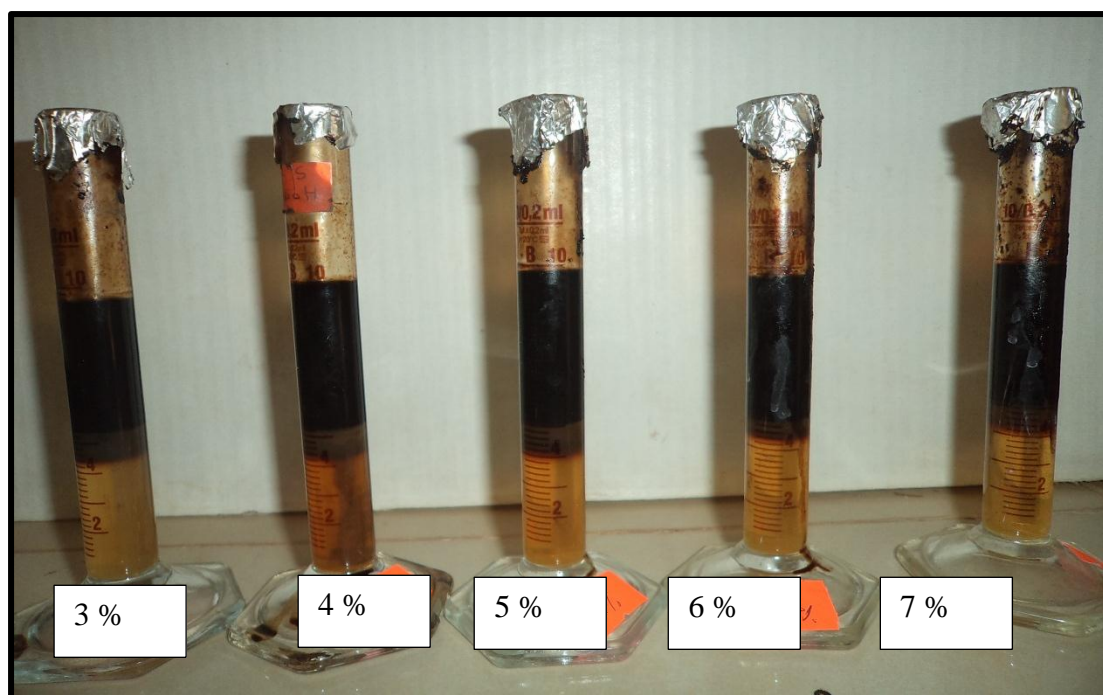**Figure 4-10**: result of different surfactant concentration after the first hour

Figure 4-11: result of different surfactant concentration after the second hour

The interfacial tension (IFT) is inversely proportional to the surfactant concentration i.e., as the surfactant concentration increases the IFT decreases until a point where any increase in surfactant concentration above this point relatively has no effect on the IFT, at this point the surfactant concentration is called Critical Micelles Concentration (CMC) as shown in figure (4-12) and figure (4-13) below.
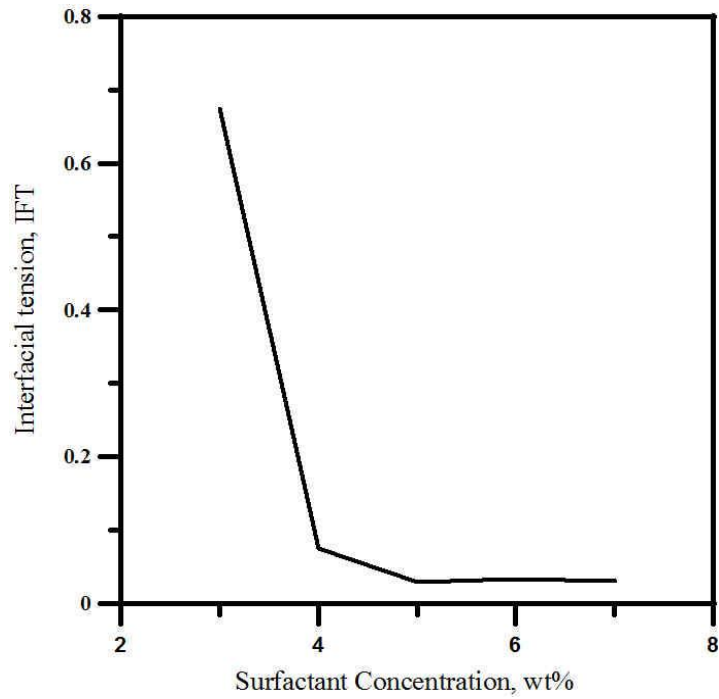
Figure 4-12: IFT as a function of surfactant concentration with 2% $wt\ NaCl$, 5%wtNa$_2$CO$_3$, at the first hour
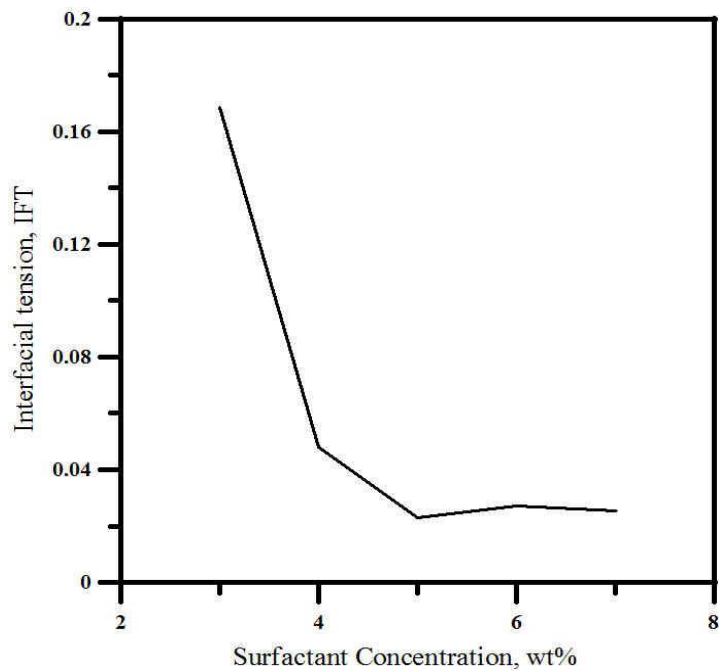

Figure 4-13: IFT as a function of surfactant concentration with 2%$wt\ NaCl$, 5%wt Na$_2$CO$_3$, at second hour

From both figure (4-12) and figure (4-13) the CMC is 5%wt which means the time has no effect on the value of CMC regarding to this equilibration period. The value of CMC can be considered as optimum surfactant concentration for ultra-low interfacial tension, beyond this value the IFT remains relatively constant. Note that from both figures the IFT exhibit slightly changes after the CMC, due to degree of the accuracy regarding to experiments procedures.

Chapter five

Conclusion &

Recommendations

Chapter 5   Conclusion & Recommendations

Conclusion

From the previous discussion:

1. The optimum salinity for crude oil of South Alnnajma 1 is $2\%wt$ with surfactant $3\%wt$ and $2\%wt$ Na_2CO_3.
2. Sodium carbonates are more effective with this crude than sodium hydroxide.
3. The optimum concentration of surfactant is $5\%wt$.
4. The optimum formulation of surfactant-alkaline is $5\%wt$ sodium carbonates and $5\%wt$ surfactant with $NaCl$ $2\%wt$.

Recommendations

1. Additional experiments should be conducted using several types of surface active agents; to investigate the best surfactant candidate.
2. Include more other types of alkali in the experiments; in order to achieve the ultra-low IFT.
3. The equilibration period should be longer enough to achieve a high degree of stability in the middle phase (micro-emulsion).
4. Rotating shaker should be used rather than manual shaking; to ensure a complete mixing of the system.

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