

MINISTRY OF HIGHER EDUCATION AND SCIENTIFIC RESEARCH



THESIS

**This Thesis is submitted as a Part of the Requirements
to Obtain Bachelor Degree From
Sebha University**

**Measure the Ability of Surfactant to Inject With Sea Water and form the
Emulsion**

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Sebha University

2018

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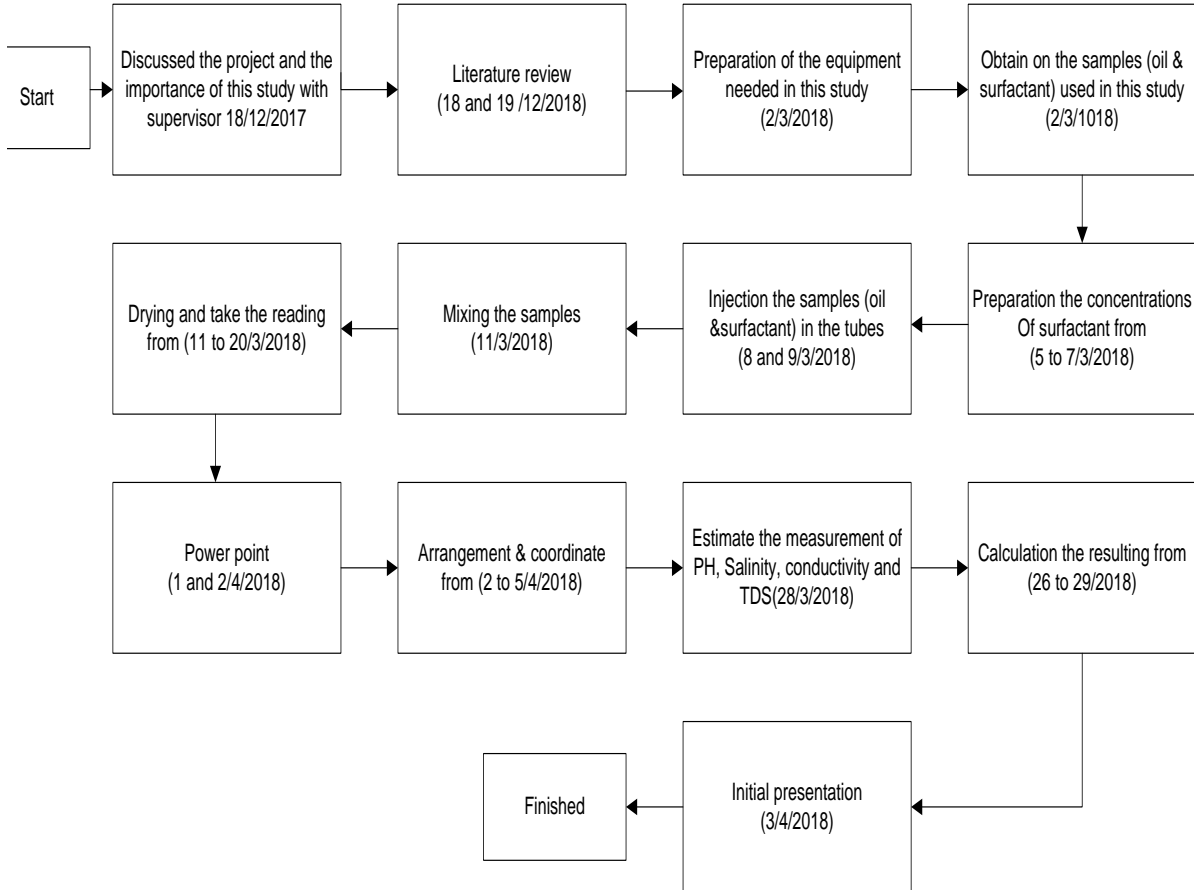
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Date :

RODING MAP



ABSTRACT

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There are many known EOR methods and every method has its criteria to use it. One of those methods is the chemical EOR. Chemical EOR has been widely used to global enhanced oil recovery. Chemical EOR can be classified into many main types such as surfactant, polymer and alkaline etc.

In this project Surfactant EOR (Cetyl Tri Methyl Ammonium Bromide soap) has been mixed with sea water and inject to crude oil that has been taken from Hamada field. Surfactant EOR was examine to test it is ability to form emulsion at different concentration and different temperature start from room temperature until 70 C⁰.

The results showed the ability of Surfactant EOR (Cetyl Tri Methyl Ammonium Bromide soap) to form emulsion. The screening criteria of surfactant concentration to form the emulsion was between the range 5% to 15 %. The best scenario has gave highest emulsion level was at 70 C⁰ and the surfactant concentration was at 7%.

Key words: EOR, Surfactant, Sea Water and PPT test.

DEDICATION

I would like to give my dedication to the people with their love and efforts who always support me and give me motivation :

To the spirit of my dear sister: Khlood.

To my beloved mother: Nagat Al-wrdany.

To my beloved father: Bashir Khir.

To my brothers and my sisters .

To my supervisor: Dr/ Mohammed samba.

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LIST OF NOTATION

Symbol	Mean	Unit
EOR	Enhanced Oil Recovery	//
PH	Power of Hydrogen	//
PPT	Part Per Thousand	//
TDS	Total Disolved Solids	Mg/l
CMC	Critical Micelle Concentration	//
MEOR	Microbail Enhanced Oil Recovery	//
GOR	Gas Oil Ratio	//
OOIP	Original Oil In Place	//

CHABTER I. INTRODUCTION

CHAPTER I INTRODUCTION

I. Literature Review

•**Enhanced Oil Recovery:** is a means of producing oil with the introduction of external fluids, substances and energy into the oil reservoir.^[1]

•**Objective of EOR:** to improve oil recovery by considering the economics .The most known EOR: Water flood (gives oil recovery as much as 15-40 % of initial reserve).^[1]

I.1 Sources of Reservoir Energy:

Oil production is separated into three phases: primary, secondary and tertiary, which is also known as Enhanced Oil Recovery (EOR). Primary oil recovery is limited to hydrocarbons that naturally rise to the surface, or those that use artificial lift devices, such as pump jacks.^[10]

I.1.1 Primary Recovery:

The first stage of oil and gas production, in which natural reservoir drives are used to recover hydrocarbons. Due to the difference in pressure within the reservoir and at the bottom of the well, hydrocarbons are driven towards the well and to the surface. During primary recovery, typically only 5-15% of initial hydrocarbons are produced for oil reservoirs. Also called primary production.

Primary recovery was the only method available during the early years of the oil industry and it is still the only method used in many oil fields such as in the Middle East. The natural energy or reservoir drive that is used during primary production can be visualized by considering that each unit volume of oil produced must be replaced by something in the reservoir since a vacuum cannot exist. The primary reservoir energy comes from five mechanisms. (a) Solution gas- drive reservoir (b) gas-cap drive reservoir (c) water drive reservoir (d) combination drive reservoir (e) Gravity

drainage reservoir. The most common methods of artificial lift methods are: Sucker-Rod Pumping, Gas Lift. ^[2,9]

I.1.1.1 Drive Mechanisms and Recovery:

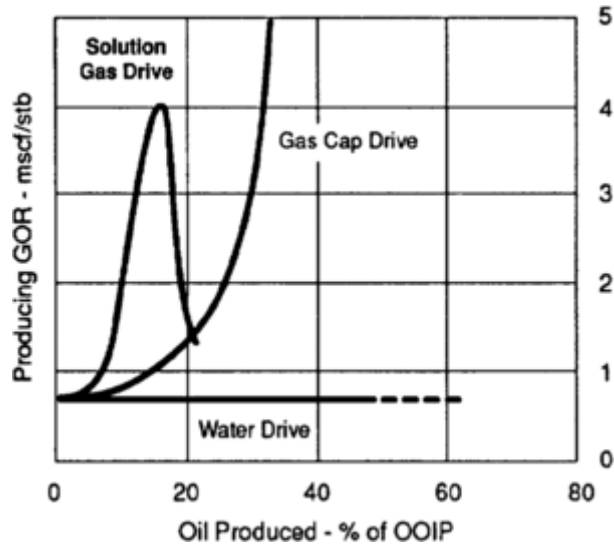


Figure 1.1. Producing Gas-Oil Ratio Trends by Drive Mechanism.

The natural energy of a reservoir can be used to move oil and gas toward the wellbore. Used in such a fashion, these sources of energy are called drive mechanisms. Early determination and characterization of the drive mechanism(s) present within a reservoir may allow a greater ultimate recovery of hydrocarbons. Drive mechanisms are determined by the analysis of historical production data, primarily reservoir pressure data and fluid production ratios.

The three primary oil reservoir drive mechanisms are solution gas drive, gas cap drive, and drives has mentioned.^[1] Reservoir pressure trends and producing gas-oil ratio trends of these three drive mechanisms are shown in Figure (1.1) .respectively. A combination or mixed drive occurs when two or more of the primary drive mechanisms are present in the same reservoir. A combination drive may also occur when one or more of the primary drive mechanisms are assisted by gravity drainage.^[2]

1. Solution Gas Drive:

In a solution (or dissolved) gas drive reservoir, the oil-bearing rock is completely surrounded by impermeable barriers. As the reservoir pressure drops during production, expansion of the oil and its dissolved gas provides most of the reservoir's drive energy (Figure1.2). Additional energy is obtained from the expansion of the rock and its associated water.

Depending on its discovery pressure, a solution gas drive reservoir can be initially either under saturated or saturated.^[2] In an under saturated reservoir, the reservoir pressure is greater than the bubble point of the oil. No free gas exists in the reservoir while the pressure remains above the bubble point. The reservoir drive energy is provided only by the limited expansion of the oil, rock, and water. In a saturated reservoir, the reservoir pressure is at the bubble point.^[2]

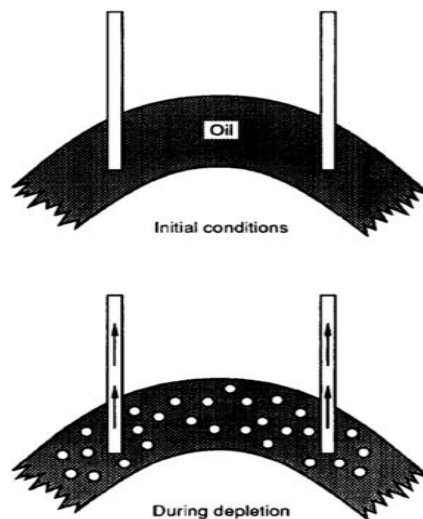


Figure1.2 Solution Gas Drive Reservoir.

Solution gas drive reservoirs show characteristic changes in reservoir pressure, producing gas-oil ratio, and oil and water production rates during the life of the reservoir. If the reservoir is initially undersaturated, the reservoir pressure falls quickly during oil production because of the small compressibility of oil, water, and rock. Pressure drops of several hundred pounds per square inch can easily occur over

a matter of months. Because the only gas produced is that which evolves from the produced oil in the wellbore, the gas-oil ratio (GOR) remains constant until the reservoir reaches the bubblepoint.

Once reservoir pressure reaches the bubblepoint pressure or if the reservoir was initially saturated, the reservoir pressure declines less quickly due to the large compressibility of the gas bubbles forming in the reservoir.

Oil production rates fall quickly once the producing GOR begins to rise. Wells must be placed on artificial lift early in their life.

Oil recovery from solution gas drive reservoirs is usually low, ranging from 5 to 30% of the original oil in place (OOIP). Typically less than 5% of the OOIP is recovered above the bubblepoint. In general, the better solution gas drive recoveries are obtained in reservoirs with relatively low oil viscosities and fairly homogeneous rock properties. Recovery can sometimes be improved with completion strategies that conserve reservoir energy by minimizing the producing GOR. ^[2]

2. Gas Cap Drive:

In a gas cap drive reservoir, the primary source of reservoir energy is an initial gas cap, which expands as the reservoir pressure drops (Figure 1.3). Additional energy is provided by the expansion of solution gas released from the oil. Less significant drive contributions are provided by the expansion of the rock and its associated water.

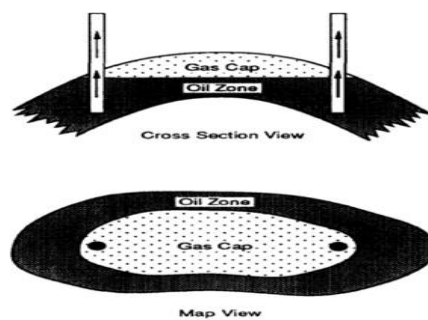


Figure 1.3. Gas Cap Drive Reservoir.

Gas cap expansion causes reservoir pressure to fall more slowly in a gas cap drive reservoir than in one producing in a solution gas drive. The rate of pressure decline is closely tied to the relative size of the gas cap, with larger gas caps resulting in a more gradual pressure decline as oil is produced.

Oil production rates fall less quickly than in a solution gas drive reservoir due to the slower decline in reservoir pressure. Artificial lift may not be required as early in the field's life since wells tend to have longer flowing lives.

Oil recovery from gas cap drive reservoirs typically ranges from 20 to 40% of the original oil in place. The actual recovery obtained depends on the size of the initial gas cap, the structural geometry of the reservoir, and the way the field is managed. ^[2]

3. Water Drive:

In a water drive reservoir, the oil zone is in communication with an aquifer that provides the bulk of the reservoir's drive energy. As oil is produced, the water in the aquifer expands and moves into the reservoir, displacing oil. Depending on the aquifer's strength, additional energy may be provided by solution gas expansion. Much less significant contributions are provided by the expansion of the reservoir rock and its associated water.

The geometry of the aquifer determines whether it is a *bottom water* or an *edge water* drive (Figure 1.4). In a bottom water drive, the aquifer is present below the entire reservoir and water influx moves vertically upward into the oil zone. In an edge water drive, the aquifer is located on the flanks of the reservoir and the water moves upward along the reservoir dip. Figure(1.4) Edge water versus bottom water drive reservoirs.

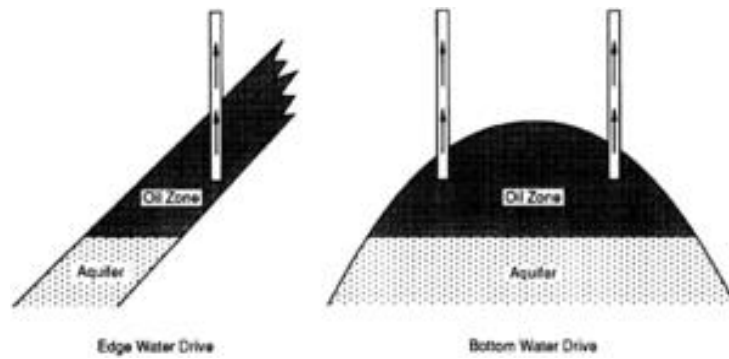


Figure 1.4. Edge Water Versus Bottom Water Drive Reservoirs.

In a water drive, the reservoir pressure response to production depends on the size and permeability of the aquifer and the rate at which the reservoir is produced.^[3] If the reservoir is produced at a low rate, the aquifer is able to replace the fluid volumes produced and reservoir pressure remains fairly constant. At high production rates, the aquifer is unable to keep up with withdrawals and reservoir pressure drops. If the rate is then reduced to a low level, reservoir pressure will rise. The magnitude of “high” and “low” production rates for a particular water drive reservoir are determined by the size and permeability of its associated aquifer.

Oil recovery from water drive reservoirs typically ranges from 35 to 75% of the original oil in place. The actual recovery obtained depends on the strength of the aquifer, the sweep efficiency of the encroaching water, and the way the field is managed.^[2]

4. Combination Drive:

Most oil reservoirs produce under the influence of two or more reservoir drive mechanisms, referred to collectively as a combination drive. A common example is an oil reservoir with an initial gas cap and an active water drive (Figure 1.5).

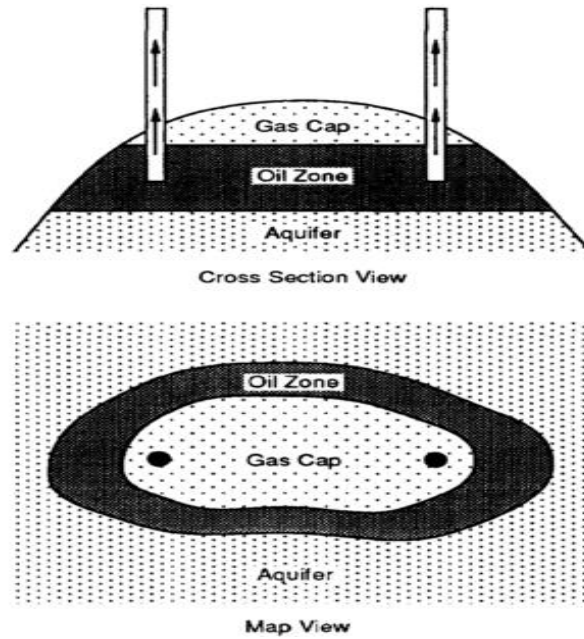


Figure 1.5. Combination Drive Reservoir.

The production trends of a combination drive reservoir reflect the characteristics of the dominant drive mechanism. A reservoir with a small initial gas cap and a weak water drive will behave in a way similar to a solution gas drive reservoir, with rapidly decreasing reservoir pressure and rising GORs. Likewise, a reservoir with a large gas cap and a strong water drive may show very little decline in reservoir pressure while exhibiting steadily increasing GORs and WORs. Evaluation of these production trends is the primary method a reservoir engineer has for determining the drive mechanisms active in a reservoir.

The ultimate recovery obtained from a combination drive reservoir is a function of the drive mechanisms active in the reservoir. The recovery may be high or low depending on whether displacement or depletion drive mechanisms dominate. Water drive and gas cap expansion are both displacement type drive mechanisms and have relatively high recoveries. Solution gas drive is a depletion type drive and is relatively inefficient.

Recovery from a combination drive reservoir can often be improved by minimizing the effect of depletion drive mechanisms by substituting or augmenting more efficient

ones through production rate management or fluid injection. To do this, the drive mechanisms active in a reservoir must be identified early in its life^[2]

5.Gravity Drainage:

Gravity drainage, or gravity segregation, is the tendency of oil, gas, and water to segregate in a reservoir during production due to their differing densities (Figure1. 6). As a secondary drive mechanism, gravity drainage occurs only in combination with one or more of the primary oil reservoir drive mechanisms.

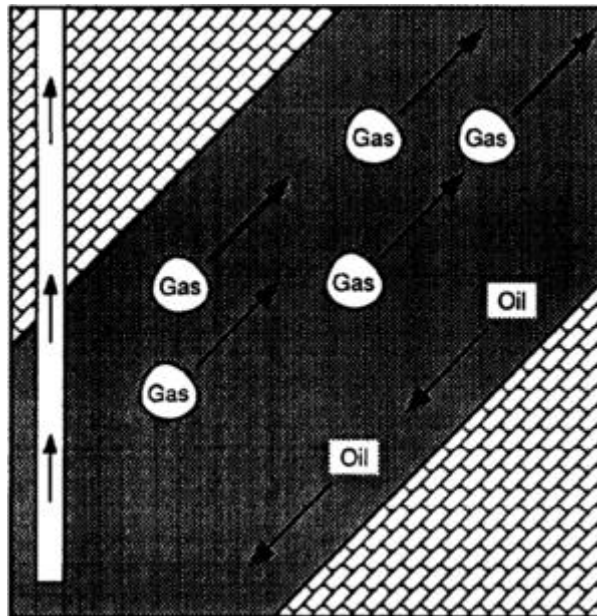


Figure1.6. Fluid Segregation by Gravity Drainage.

Conditions conducive to gravity drainage include thick reservoirs with high vertical permeabilities or thin reservoirs with steep dips. In a solution gas drive reservoir perforated down dip, gravity drainage can cause released solution gas to migrate upward and oil to flow downward, conserving reservoir energy and increasing recovery to near that of a water drive.

The rate of oil gravity drainage in the reservoir is usually low compared to field production rates. Over time, however, gravity drainage can be extremely efficient and recoveries higher than any of the primary drive mechanisms are possible.^[2]

***BREAKING DOWN 'Primary Recovery':**

Oil and gas companies will expend less money retrieving the resources from the ground during this initial phase. As production continues the reservoir pressure will decrease and hence the differential pressure decreases, which may necessitate the use of a pump to increase production. The limit for primary recovery is generally reached either when the reservoir pressure is too low, or the mix of gas or water in the output stream is too high. The next stage then involves the use of secondary recovery techniques such as gas injection or flooding.^[3]

I.1.2 Secondary Recovery:

The second stage of hydrocarbon production during which an external fluid such as water or gas is injected into the reservoir through injection wells located in rock that has fluid communication with production wells. The purpose of secondary recovery is to maintain reservoir pressure and to displace hydrocarbons toward the wellbore. The most common secondary recovery techniques are gas injection and water flooding. Normally, gas is injected into the gas cap and water is injected into the production zone to sweep oil from the reservoir. A pressure-maintenance program can begin during the primary recovery stage, but it is a form of enhanced recovery. The secondary recovery stage reaches its limit when the injected fluid (water or gas) is produced in considerable amounts from the production wells and the production is no longer economical. The successive use of primary recovery and secondary recovery in an oil reservoir produces about 15% to 40% of the original oil in place.^[4,9]

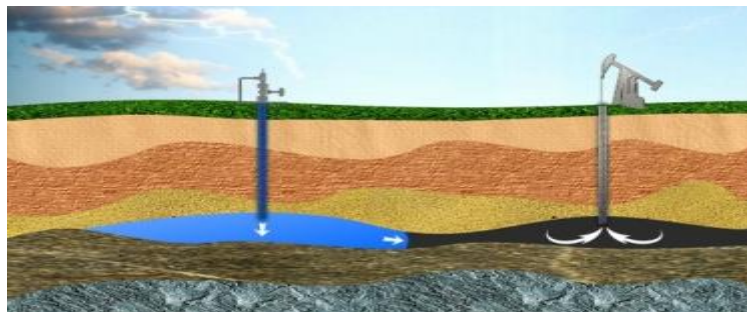


figure1.7. Secondary Recovery

1. Gas Injection:

Gas reinjection is the reinjection of natural gas into an underground reservoir, typically one already containing both natural gas and crude oil, in order to increase the pressure within the reservoir and thus induce the flow of crude oil or else sequester gas that cannot be exported. This is not to be confused with gas lift, where gas is injected into the annulus of the well rather than the reservoir. After the crude has been pumped out, the natural gas is once again recovered. Since many of the wells found around the world contain heavy crude, this process increases their production. The basic difference between light crude and heavy crude is its viscosity and pumpability - the lighter the crude the easier it is to pump. Recovery of hydrocarbons in a well is generally limited to 50% (heavy crudes) and 75-80% (light crudes). Recycling of natural gas or other inert gases causes the pressure to rise in the well, thus causing more gas molecules to dissolve in the oil lowering its viscosity and thereby increasing the well's output. Air is not suitable for repressuring wells because it tends to cause deterioration of the oil, thus carbon dioxide or natural gas is used to repressure the well. The term 'gas-reinjection' is also sometimes referred to as repressuring--the term being used only to imply that the pressure inside the well is being increased to aid recovery.

Injection or reinjection of carbon dioxide also takes place in order to reduce the emission of CO₂ into the atmosphere, a form of carbon sequestration. This has been proposed as a method to combat climate change, allowing mass storage of CO₂ over a geological timescale.^[4]

2. Water Flooding:

The principal reason for water flooding an oil reservoir is to increase the oil-production rate and, ultimately, the oil recovery. This is accomplished by "voidage replacement"—injection of water to increase the reservoir pressure to its initial level and maintain it near that pressure. The water displaces oil from the pore spaces, but the efficiency of such displacement depends on many factors (e.g., oil viscosity and rock characteristics). In oil fields such as Wilmington (California, US) and Ekofisk (North Sea), voidage replacement also has been used to mitigate additional surface subsidence. In these cases, the high porosity of the unconsolidated sandstones of the

Wilmington oil field's reservoirs and of the soft chalk reservoir rock in the Ekofisk oil field had compacted significantly when the reservoir pressure was drawn down during primary production.^[5]

I.1.3 Tertiary Recovery:

Tertiary process which is obtained after secondary recovery uses miscible gases, chemicals and/or thermal recovery to displace additional oil after the secondary recovery process become un economical. In classifying recovery processes care should be taken because many reservoir production operations are not conducted in the specified order above. A typical example is production operations of the heavy oils that occur throughout the world. If the crude oil is sufficiently viscous, it may not flow at economic rates under natural energy drives, so primary production would be neglected. Water flooding is also not useful thus; the use of thermal energy might be the only way to recover a significant amount of oil. In other words, a supposed tertiary process becomes the first stage. This can also apply in cases where the secondary process is skipped. Because of the situations described above, the term 'EOR' is used to replace 'tertiary recovery' in most cases. 'Improved Oil Recovery' is also another descriptive designation which not includes EOR but also encompasses a broader range of activities like reservoir characterization, improved reservoir management and infill drilling.^[10]

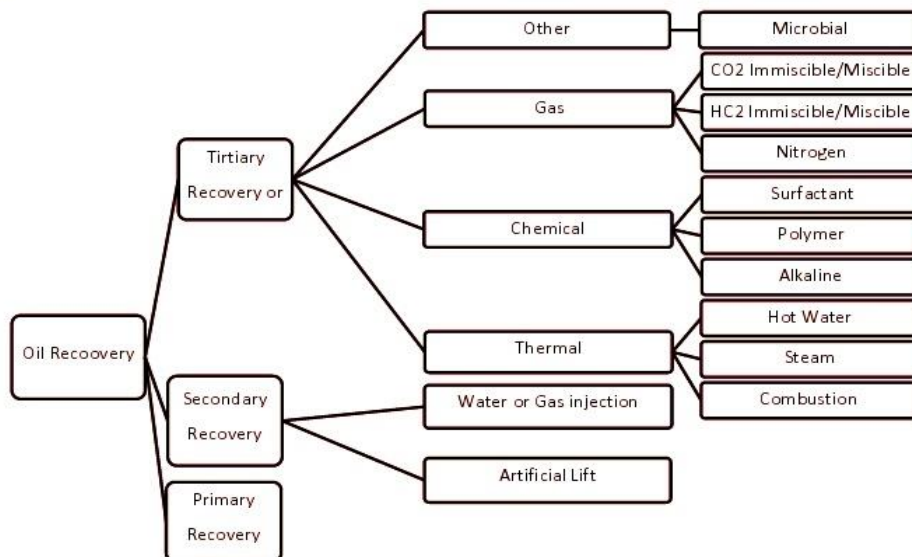


Figure 1.8. Shows a Classification of EOR Methods.

I.2 Factors Affecting EOR:

- »Wett ability.
- »Petro physical properties .
- »Rock type.
- »Oil type.
- »P & T of the reservoir.
- »Reservoir driving mechanism.
- »Formation water salinity.
- »Heterogeneity.
- »Present Oil Saturation.
- »Remaining Oil Reserves.
- »Reservoir Dip. ^[1]

I.3 Classification of EOR Processes:

There are five categories of enhanced oil recovery. These include chemical, gas, microbial EOR, and thermal processes. ^[5]

I.3.1 Chemical Processes:

Chemical processes target the reduction of IFT between the displacing liquid and oil. It comes from the injection of specific liquid chemicals which through their phase behavior leads to displacing of more oil. Surfactants and polymer have shown more potential for a higher EOR than any other method. In this process, a solution which contains surfactants is pumped in followed by polymer. The surfactant injection can only be justified when oil prices are relatively high and if the residual oil saturation after water-flooding process is high. This is because surfactants are expensive^[10]

I.3.2 Gas Processes:

The main objective in a gas process is to displace oil with a fluid that is miscible or immiscible with the oil in all proportions. This miscibility leads to a reduction in interfacial tension between oil and water thus leading to better oil sweep. Two major

variations are distinguished in this process. The first-contact-miscible (FCM) process where the injected fluid is directly miscible with the reservoir oil and the Multiple-Contact-Miscible process (MCM) where miscibility comes from modification of the composition of the injected fluid as it goes through the reservoir^[10]

I.3.3 Thermal Processes:

Thermal process involves the reduction of viscosity of oil so that it can flow towards producing wells. It may be sub-divided into steam flooding, hot-water floods and in-situ combustion. In the simplest form of steam flood, a single well is injected with steam for a certain period and then closed for a while to allow for the steam to act on the oil very well. The well is then opened for production which continues until the effect of the injected steam wears off and the process is continued again. ^[10]

I.3.4 Microbial Enhanced Oil Recovery (MEOR):

Microbes ferment hydrocarbons and produce by-products that are useful in the recovery of oil. MEOR uses the mechanism of channeling oil through preferred pathway in the reservoir by plugging off small channels so that oil is forced to migrate through larger pore spaces. Nutrients like sugar, phosphates or nitrates are injected to stimulate growth of microbes and aid their performance. The microbes generate surfactants and carbon dioxide that help to displace oil. ^[10]

I.4. Efficient Microscopic And Macroscopic Displacement:

The Overall Displacement Efficiency Of Any Oil Recovery Displacement Process Can Be Considered conveniently as the product of microscopic and macroscopic displacement efficiencies. In equation form,

$$E = E_D * E_V \dots\dots\dots(1.1)$$

Where

E = overall displacement efficiency(oil recovered by process/oil in place at start of process).

E_D =microscopic displacement efficiency expressed as a fraction.

E_V = macroscopic (volumetric) displacement efficiency expressed as a fraction.

Microscopic displacement relates to the displacement or mobilization of oil at the pore scale. That is, E_D is a measure of the effectiveness of the displacement fluid in moving (mobilizing) the oil at those places in the rock where the displacement fluid contacts the oil. E_D is reflected in the magnitude of the residual, S_{or} in the regions contacted by the displacing fluid.

Macroscopic displacement efficiency relates to the effectiveness of the displacing fluid(s) in the contacting the reservoir in a volumetric sense. Alternative terms conveying the same general concept are sweep efficiency and conformance factor.

E_V is a measure of how effectively the displacing fluid sweeps out the volume of a reservoir, both a really and vertically, as well as how effectively the displacing fluid moves the displaced oil toward production wells. Both areal and vertical sweeps must be considered, and it is often useful to further subdivide E_V in to the product of areal and vertical displacement efficiencies. E_V is reflected in the magnitude of average or overall residual oil saturation, S_{or} , because the average is based on residual oil in both swept and un swept parts of the reservoir. Consider the magnitude of these efficiencies in a typical water-flood. For an example in which initial oil saturation, S_{oi} , is 0.60 and S_{or} in the swept region is 0.30.

$$E_D = \frac{S_{oi} - S_{or}}{S_{oi}}$$

$$= \frac{0.60 - 0.30}{0.60} = 0.50 \dots \dots \dots (1.2)$$

A typical water flood sweep efficiency, E_V , At the economic limit is 0.7. There fore $E = E_D E_V = 0.50 * 0.70 = 0.35 \dots \dots \dots (1.3)$

Thus, for a typical water flood, the overall displacement efficiency is on the order of one - third, which also represents the oil recovery efficiency (neglecting volume changes associated with pressure changes).^[9]

CHABTER II. CHEMICAL EOR

CHAPTER II. CHEMICAL EOR

II.1 Chemical EOR:

II.1.1 Polymer:

- Improving water-oil mobility ratio (\downarrow).
- Increasing Sweep Efficiency (ES) – Macroscopic.
- Often used in combination with surfactant.
- Most widely used polymer in EOR.
- Poly acryl amide: artificial, flexible.
- Polysaccharide: fermentation, rigid, effective for reservoir with high viscosity oil .^[1]

II.1.2 Alkaline:

- Increase pH until 11 – 12
- Could reduce interfacial tension to 0.01 dyne/cm
- NaOH in water: 0.05 – 0.2% (500 – 2000 ppm).^[1]

II.1.3 Surfactant:

- mixture of polymer, alcohol, sulfonate
- reduce interfacial tension
- reduce capillary pressure
- increase microscopic displacement efficiency .^[1]

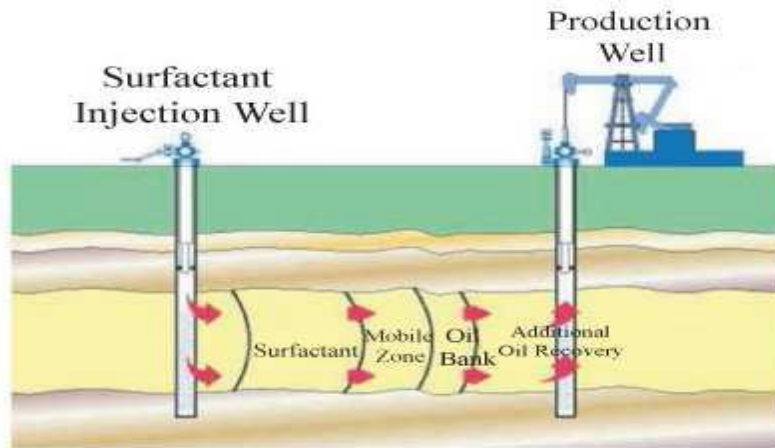


Figure 2.1. Surfactant Injection Well

Surfactant- active agents, or surfactants, are chemical substances that adsorb on or concentrate at a surface or fluid/ fluid interface when present at low concentrations in a system. They alter the interfacial properties significantly; in particular, they decrease the surface tension, or IFT. This section presents an introduction to surfactants and their effect on IFT. In their most common form, surfactants consist of a hydrocarbon portion (nonpolar) and a polar, or ionic, portion. Figure 2.2 a simplified sketch of the molecule. The hydrocarbon portion is often called the " tail " and the ionic portion the " head " of the molecule. The hydrocarbon portion can be either a straight chain or a branched chain. The non polar and polar portions are called lipophilic and hydrophilic moieties, respectively. (A moiety is simply a part or portion).^[9]

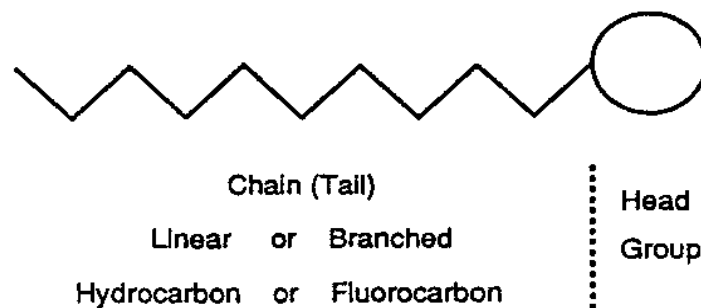


Figure 2.2. Schematic of Surface-Active Molecule

II.1.3.1 Classification and Structure of Surfactants:

Surfactants may be classified according to the ionic nature of the head group as anionic, cationic, nonionic, zwitterionic. This surfactant has two groups of opposite charge.

Anionics and nonionics have been used as surfactants in EOR processes. Anionic surfactants have been the most widely used because they have good surfactant properties, are relatively stable, exhibit relatively low adsorption on reservoir rock, and can be manufactured economically. Nonionics have been used primarily as cosurfactants to improve the behavior of surfactant systems. Nonionics are much more tolerant of high-salinity brine, but their surface-active properties (reduction of IFT) are not generally as good as anionics. Cationics are usually not used because they adsorb strongly on reservoir rocks.

The most common surfactants used in micellar/polymer flooding are sulfonated hydrocarbons. Figure 2.3 shows an example of a hydrocarbon sulfonate produced by sulfonating a relatively pure organic structure to form an organic acid followed by neutralization with sodium hydroxide.

The term "crude oil sulfonates" refers to the product when a crude oil is sulfonated after it has been topped.^[9]

Texas Number 1

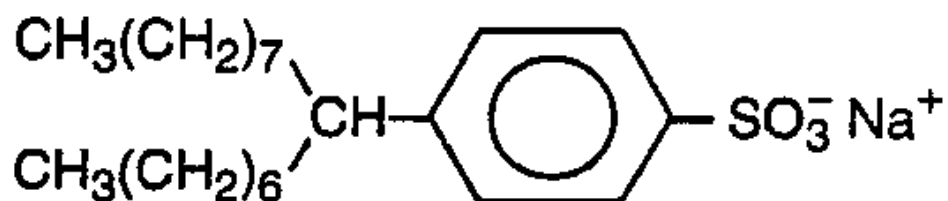


Figure 2.3. Example of a Hydrocarbon Sulfonate.

II.1.3.2 Type of Surfactant:

A. Anionic Surfactants : These have a negatively charged end of the molecule that gives it the hydrophilic part of the molecule. These negatively charged parts of the molecules are usually sulfonates, sulfates, or carboxylates that are usually neutralized by positively charged metal cations such as sodium or potassium. Examples include sodium alkyl benzene sulfonates, sodium stearate (a soap), and potassium alcohol sulfates. Anionic surfactants are ionic and are made up of two ions positively charged, usually metal, ion and a negatively charged organic ion.

B. Nonionic Surfactants: These are surfactants that have no ions. They derive their polarity from having an oxygen-rich portion of the molecule at one end and a large organic molecule at the other end. The oxygen component is usually derived from short polymers of ethylene oxide or propylene oxide. Just as in water chemistry, the oxygen is a dense electron-rich atom that gives the entire molecule a partial net-negative charge which makes the whole molecule polar and able to participate in hydrogen bonding with water (as discussed in the first chapter). Examples of nonionic surfactants are alcohol ethoxylates, nonylphenoxypolyethylenoxy alcohols, and ethylene oxide/propylene oxide block copolymers.

C. Cationic Surfactants: These are positively charged molecules usually derived from nitrogen compounds. They are not commonly used as cleaning agents in hard-surface cleaners because of the tendency of the cationic positively charged molecule to be attracted to hard surfaces (that usually have a net negative charge). Many cationic surfactants have bactericidal or other sanitizing properties that are useful in creating disinfectants that leave a cationic disinfectant film on the surface.

D. Cationic Surfactants- are usually incompatible with anionic surfactants, because they will react with the negatively charged anionic surfactant to form an insoluble or ineffective compound.

E. Amphoteric Surfactants: Those surfactants that change their charge with pH. They can be anionic, nonionic, or cationic depending on pH. Usually, any one amphoteric can be any two of the three charge states.^[6]

II.2 Interfacial Tensions:

Interfacial tensions the force per unit length required to create a new surface. Interfacial tension is commonly expressed in Newton's/meter or dynes/cm (Newton's /meter =1,000 dynes/cm).^[8]

II.2.1 Mechanism for IFT Reduction by Surfactants:

IFT is the force per unit length required to create new surface area at the interface between two immiscible fluids. IFT also is a condition of mechanical equilibrium at an interface. The description in this section was developed by Davis and shriven by analyzing stresses in the interfacial region between two fluids.

Consider the two-phase system separated by a planar interface shown in Figure2.4a. Phase1 is on the bottom because it has a higher density than phase2 . The interfacial zone has a thickness h_1 of 10 to several hundred angstroms. The system is at hydrostatic equilibrium.

The region shown in Figure2.4 a is assumed to be sufficiently thin that the bulk pressures in phases 1 and 2 are equal to p_b . This neglects any effect of fluid density on pressures above and below the interfacial zone.

The pressure distribution in the region shown in Figure(2.4 b) is affected by the process of the interface. The interfacial zone is considered to be inhomogeneous because the densities and composition of the fluids within the interfacial zone vary with position x . Because of this variation in fluid density, the stresses acting on molecules are not uniform within the interfacial zone and vary with both direction and position . These differences in stresses within the interfacial zone cause the pressure to vary with position and direction . For this geometry, the pressure has two components, a component P_N that is normal to the interface (x direction) and a second component, P_T that is transverse and lies in the plane of the interface. The magnitude of P_T depends on position in the interfacial zone, as depicted in Figure (2.6b).

At $x \gg h_1$, $P_T = P_B$.

The IFT properties of petroleum sulfonates, which are mixtures, generally are similar to those of single- component surfactant system. There is, however, a difference in that a sharp CMC is not usually observed. The IFT between an aqueous surfactant system and a hydrocarbon phase may decrease significantly at concentration well above the CMC, the point of onset of formation of micelles.^[9]

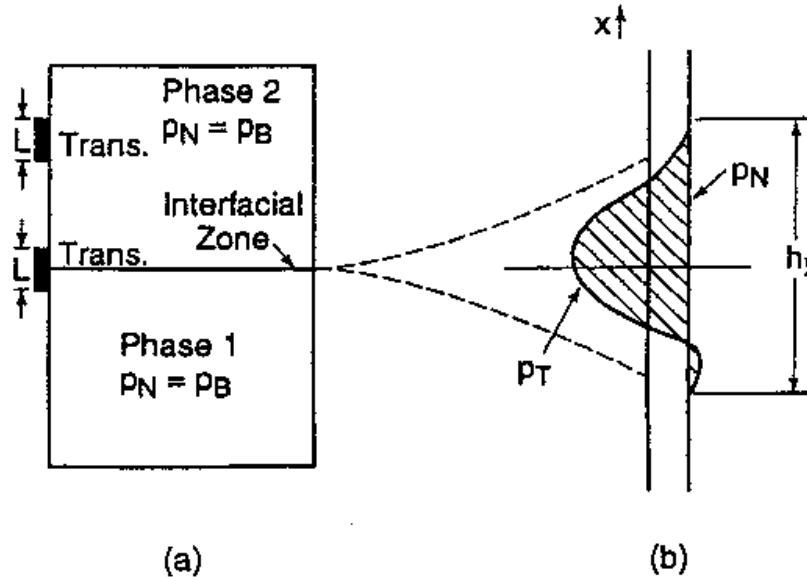


Figure 2.4.(a) Two Phase System Separated by a Planar Interfacial .

(b) Normal, P_N and Transverse, P_T , Pressure Profiles Across the Interfacial Zone.

II.2.2 Surfactants and IFT 's in EOR SYSTEM:

Surfactant systems that contain no alcohol or limited amounts of alcohol or co surfactant exhibit ultralow IFT 's. Puig et al . and Hall show that ultralow IFT 's observed under these conditions are caused by the presence of a finely dispersed phase at the interface between the oil and brine. This meso phase is liquid crystalline, surfactant- rich, and often exhibits birefringence under polarized light. Puig et al. found that ultralow tensions were observed only when the particles were large enough to cause turbidity in the solution. Davis et al. present an excellent report on the measurement of ultralow IFT. These systems have not been used successfully in field applications and are not considered further.

Micellar solutions, or micro emulsions, the type of solutions used in EOR processes, are complex. Characteristics of these solutions are discussed in the next section.^[9]

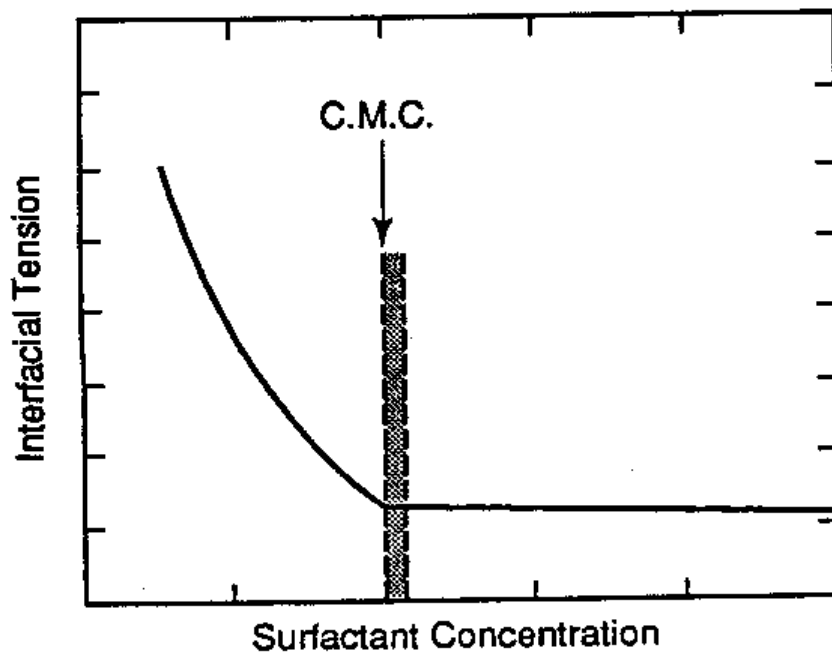


Figure 2.5. IFT as a Function of Concentration - Pure (Single-Component) Surfactant.

II.2.3 Capillary Pressure:

Capillary pressure defined capillary pressure as the difference in pressure across the interface between two phases. Similarly, it has been defined as the pressure differential between two immiscible fluid phases occupying the same pores caused by interfacial tension between the two phases that must be overcome to initiate flow. ^[8]

II.3 MicroEmulsion :

Definition of a micro emulsion is a stable, translucent micellar solution of oil, water that may contain electrolytes, and one or more amphiphilic compounds. ^[9]

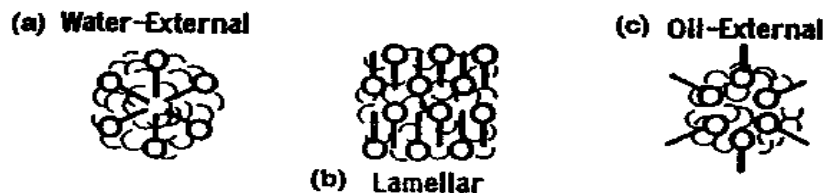


Figure 2.6. Definition and Structure of Micro Emulsion

II.3.1 Micelles and Micro Emulsions:

From the early days of the study of surface-active agents, it was recognized that their properties indicated that colloidal aggregates were in solution. Figure 2.7 depicts the formation of these aggregates, which are called micelles.

When a surfactant is added to a solvent at very low concentrations, the dissolved surfactant molecules are dispersed as monomers, as figure (2.7) shows. As the concentration of surfactant increases, the molecules tend to aggregate. Above a specific concentration, called the critical micelle concentration (CMC), further addition of surfactant results in the formation of micelles. The concentration of surfactant as monomers essentially remains constant above the CMC. That is, surfactant added at concentration above the CMC results in formation of additional micelles but relatively little change in monomer concentration.

If the solvent is water, the micelles form with the tail portion directed inward and the head (polar) portion outward. Water would be the continuous phase, as shown in the lower right side of Figure(2.7) .^[9]

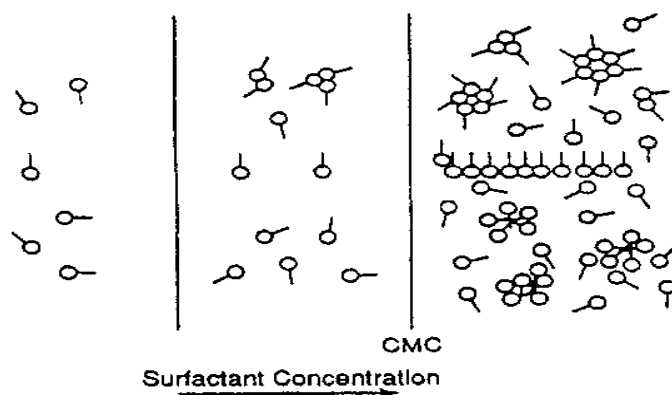


Figure 2.7. Formation of Micelles.

Chapter III. Experimental Materials and Equipments

Chapter III. Experimental Materials and Equipments

III.1 Experimental materials :

Materials that used in this experiment including :-

1. Sea Water:

Figure(3.1) shows the water used in this study, where taken from west Libya.



Figure 3.1 : Storage Sea Water Used in This Study.

2. Crude Oil:

Figure 3.2 shows the type of oil used in this study, were taken from Hamada field-V32. The analysis of composition of oil done at petroleum institute, as shown in the table(1)



Figure 3.2 :Crude Oil Used in This Study.

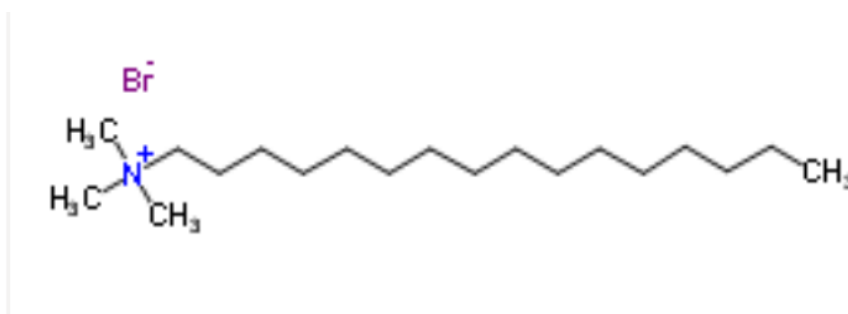
Table (3.1): Oil Composition Used in This Study

NO.	Component	Formula	Hamada field V32
			Flashed Liquid Mole%
1	Hexane	C_6H_{14}	3.24
2	Heptane	C_7H_{16}	6.94
3	Octane	C_8H_{18}	13.53
4	Nonane	C_9H_{20}	12.38
5	Decane	$C_{10}H_{22}$	11.05
6	n-Undecane	$C_{11}H_{24}$	8.78
7	n-Dodecanes	$C_{12}H_{26}$	6.83
8	n-Tridecanes	$C_{13}H_{28}$	6.87
9	n-Tetradecanes	$C_{14}H_{30}$	4.80
10	n-Pentadecanes	$C_{15}H_{32}$	4.17
11	n-Hexadecanes	$C_{16}H_{34}$	3.05
12	n-Heptadecanes	$C_{17}H_{36}$	3.04
13	n-Octadecanes	$C_{18}H_{38}$	2.76

14	n-Nonadecanes	C ₁₉ H ₄₀	2.48
15	n-Eicosane	C ₂₀ H ₄₂	1.59
16	n-Heneicosane	C ₂₁ H ₄₄	1.46
17	n-Docosane	C ₂₂ H ₄₆	1.32
18	n-Tricosane	C ₂₃ H ₄₈	0.99
19	n-Tetracosane	C ₂₄ H ₅₀	0.89
20	n-Pentacosane	C ₂₅ H ₅₂	0.74

3. Surfactant (Cetyl Tri Methyl Ammonium Bromide):

-Composition:



-Properties: Form is white crystalline solid, Purity is $\geq 98\%$, heavy metals is $\leq 0.001\%$ (as pb)

-Over view: cationic detergent suitable for the isolation of high molecular weight DNA in plants and other organisms . cetyl tri methyl ammonium bromide is action when dissolved in aqueous solutions and is an effective antiseptic against bacteria and fungi

- Applications: cetyl tri methyl ammonium bromide is partially soluble in water as well as in oil .This allows for the mixing of the two repelling phases which would not

be possible without the presence of the surfactant . This quality is utilized in the preparation of DNA.

Cetyl tri methyl ammonium bromide is used to form a buffer solution that is able to extract DNA. [7]



Figure 3.4. Soap Used in This Study.

4.Elastic Silicon: used for sealing joints between glass, aluminum and ceramics subjected to modest stresses. Temperature resistance: from -50°C to $+150^{\circ}\text{C}$, Application temperature: from $+5^{\circ}\text{C}$ to $+40^{\circ}\text{C}$



Figure 3.5. Silicon Used in This Study.

III.2 Experiment Equipments:

1. Capillary Tubes: are inserted into 1 ml and made of sterilin material and are used to inject the liquid into it.



Figure 3.6. Capillary Tubes Used in This Study.

2. Absorbent and Pipette Holder : are made of glass which is very thin and used for sucking liquid and used for sucking liquid and unloading in tube.

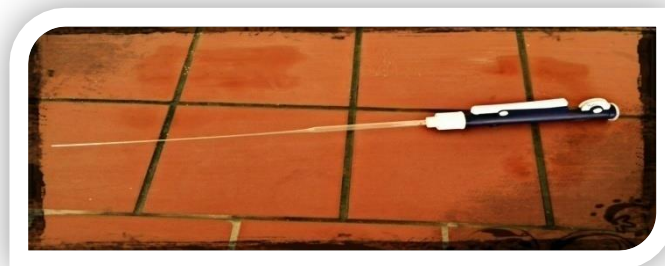


Figure 3.7. Absorbent and Pipette Holder Used in This Study.

3. Cups of Glass :used to prepare solutions



Figure 3.8. Cups of Glass Used in This Study.

4. Nylon Laboratory : to close cups evaporate them to the outside.



Figure 3.9. Nylon Laboratory Used in This Study.

5. Base of Cork : used to fix pipes on them.



Figure 3.10 : Base of Cork.

6. Spoons : to carry chemical materials.



Figure 3.11. Spoons Used in This Study.

7. Nomination Paper : it is very light used in the study to put on the balance and neglect the weight and place the surfactant over it.



Figure 3.12. Nomination Paper Used in This Study

8. Glass Stick : to stir solution and mix well inside the cup.

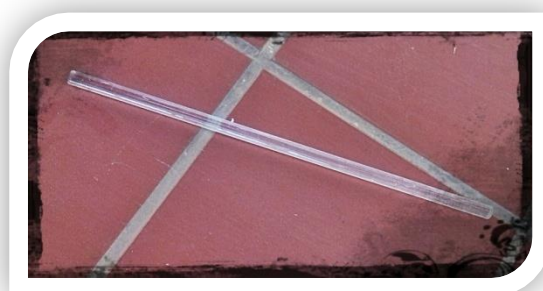


Figure 3.13 : Glass Stick Used In This Study.

III.3. Experimental Devises:

1. Electronic Balance : Accurate balance where the device can be zeroed when you need to neglect a certain weight, weighs from 0 to 200 grams .



Figure 3.14: Electronic Balance Used in This Study.

2. Aquarium Water : heats and mixes and contains moles to things inside him, the mixing index from 0 to 300.



Figure 3.15 : Aquarium Water Used in This Study.

3. Electric Oven: Heats up to 200°C and is supplied with a timer for two hours, (120 min)



Figure 3.16. Electric Oven Used in This Study.

4. Ion Meter 3025 JENWAY : to estimate PH.



Figure 3.17. Ion Meter 3025 JENWAY.

5. Thermo Scientific Orion 4-Star:To estimate conductivity, salinity and T.D.S .

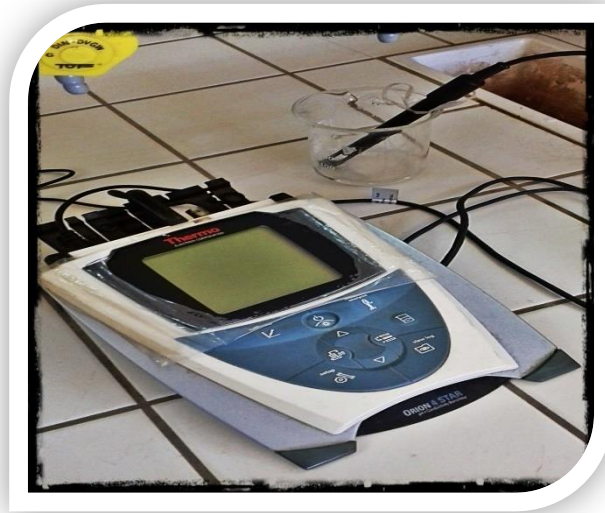
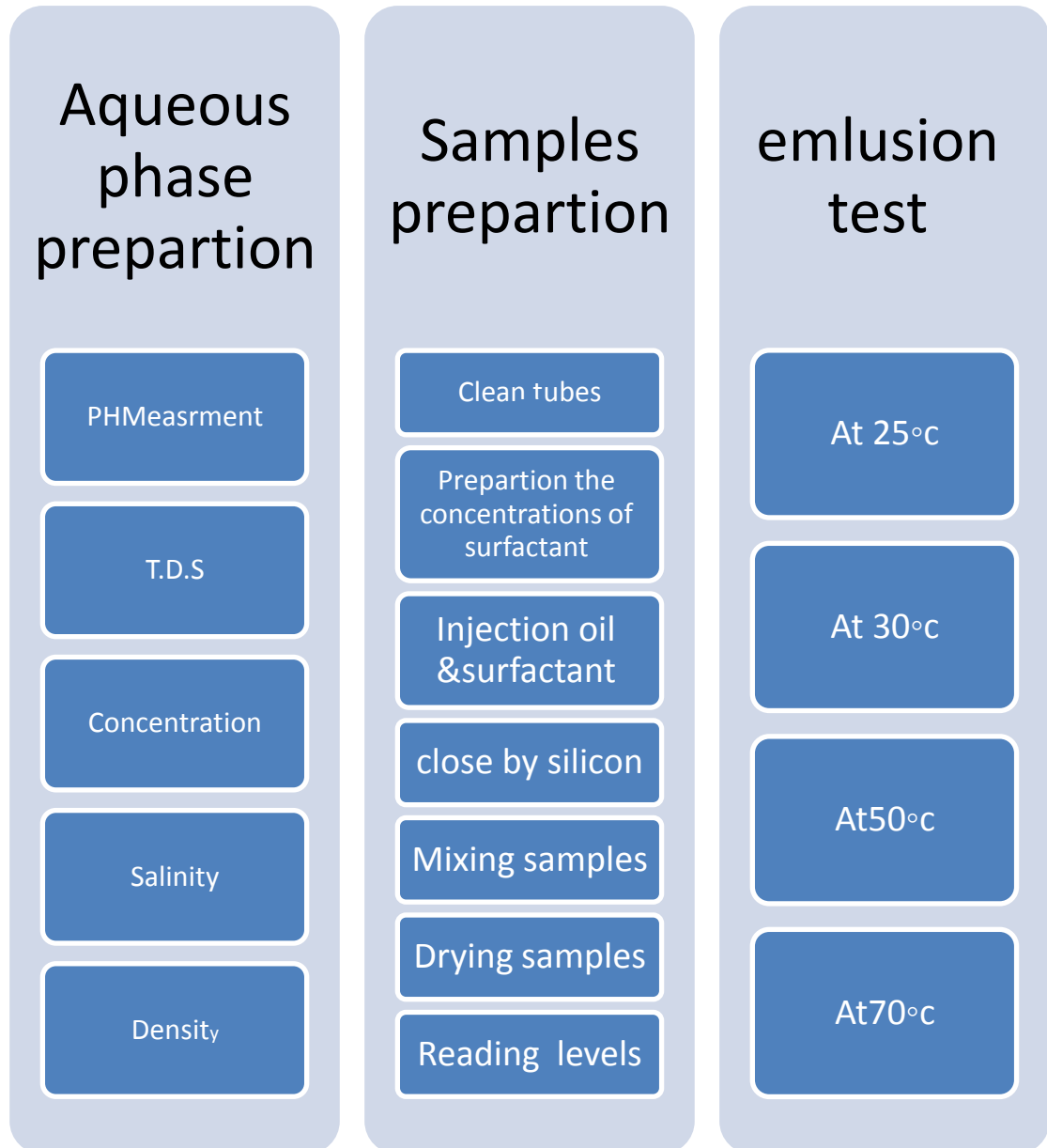


Figure 3.18. Thermo Scientific Orion 4-star

CHABTER IV. Methodology and procedures

CHAPTER IV

Methodology and Procedures



IV.1 Procedures of Estimate PH, Salinity, Conductivity and T.D.S:

This Experiment done by using(Ion Meter 3025 JENWAY) for estimate PH and(Thermo Scientific Orion 4-star), for estimate conductivity, salinity and T.D.S.

The procedures of this experiment as follow:

- A. Clean electrode that use of measurement using distilled water as shown in the figure 4.1.
- B. There are two types of electrodes, the first one use for measure PH ,the other use for conductivity, salinity and T.D.S.
- C. Put sample in small baker 40ml as shown in the figure 4.2.
- D. Put the electrode in the baker that contains the sample (sea water or surfactant), Figure (4.3 a: shown the estimates of PH) , (4.3 B: Shown the estimate of salinity, T.D.S, conductivity) .
- E. Press on measure bottom.
- F. Read the measurements.



Figure 4.1: Clean the Electrode.



Figure 4.2. Put Small Sample in Baker 40ml.



Figure 4.3a. Shows Estimate of PH.



Figure(4.3 b), Shown Estimate of Salinity, T.D.S, Conductivity.

IV.2 Procedures to Measure Density:

Measure the density of sea water and surfactant . Figure 4.4 shows baker 50ml used to measure density. The procedures of this experiment as follows:

A. 50 ml baker has been used to measure the density.



Figure 4.4.Baker 50ml.

- B. Measure the weight of the baker without sea water as shown in the figure 4.5.
- C. Fill the baker with sea water known volume 10ml.
- D. Measure the weight of the baker with sea water as shown in the figure 4.6.
- E. By using this equation $\text{density} = [\text{weight of the baker with sea water} - \text{weight of the baker without(dry) sea water}] / \text{volume of sea water (10ml)}$.
- F. Repeat the last steps for measure density of the surfactant for each concentration.



Figure 4.5. Weight of Baker Dry



Figure 4.6.Weight of Baker Filled 10ml

IV.3 Procedures the Surfactant with Different Concentration :

1. Put 25ml of sea water in a glass cup.
2. Weight amount of soap(acetyl tri methyl ammonium bromide)by0.05% (0.0125gr)as shown in figure 4.7.
3. Grind the soap for small particles to facilitate melting in to the solution. as shown in figure 4.8.
4. Add the soap after grinding it in a glass of sea water as shown in Figure 4.9.
5. Mix soap with sea water with continuous stirring by glass stick . as shown in figure 4.10.
6. Repeat previous steps for other concentrations (1%, 2%, 4%, 5%, 7%, 10%, 15%, 20%).Figure4.11. shown all the concentration prepared in solution.

7. calculations of concentrations equations:

$$\text{Amount of (acetyl tri methyl ammonium bromide)} = \frac{(\text{wt}\%) * (\text{salt water with ml})}{(100\% - \text{wt}\%)}$$

a) concentration (0.05%) = $\frac{0.05\% * 25\text{ml}}{100\% - 0.05\%} = 0.0125$ gram

b) concentration (1%) = $\frac{1\% * 25\text{ml}}{100\% - 1\%} = 0.252$ gram

c) concentration (2%) = $\frac{2\% * 25\text{ml}}{100\% - 2\%} = 0.510$ gram

d) concentration (4%) = $\frac{4\% * 25\text{ml}}{100\% - 4\%} = 1.041$ gram

e) concentration (5%) = $\frac{5\% * 25\text{ml}}{100\% - 5\%} = 1.315$ gram

f) concentration (7%) = $\frac{7\% * 25\text{ml}}{100\% - 7\%} = 1.881$ gram

g) concentration (10%) = $\frac{10\% * 25\text{ml}}{100\% - 10\%} = 2.77$ gram

h) concentration (15%) = $\frac{15\% * 25\text{ml}}{100\% - 15\%} = 2.9$ gram

i) concentration (20%) = $\frac{20\% * 25\text{ml}}{100\% - 20\%} = 6.25$ gram



Figure 4.7. Weight of Concentration the Surfactant.



Figure 4.8. Grinding of the Surfactant.



Figure 4.9. Add the Soap on Sea Water.



Figure 4.10. Mixing Soap with Sea Water.



Figure 4.11. All Concentration of the Surfactant.

IV.4 Procedures Injection the Surfactant and Oil inside the Capillary Tubes.

1. Clean the capillary tube with distilled water to remove any impurities inside the tube.
2. Close the tubes from the bottom by silicon until does staging mark is 0.1ml to ensure that the fluid does not leak as shown in figure 4.12.
3. Enter the solution of the surfactant first from the top of the tube by pipette as shown in the figure 4.13.
4. Enter the oil in the tube and size is equal to the size of the surfactant as shown in figure 4.13.
5. Close the tubes from the top with silicon matter until the mark is shown to ensure tight sealing as shown in figure 4.14.
6. Install the tubing on the cork vertically as shown in the figure 4.15.
7. Let the tubing until the silicon dries well.



Figure 4.12. Close the Tubes with Silicon of Bottom.



Figure 4.13. Injection the Surfactant and Oil.

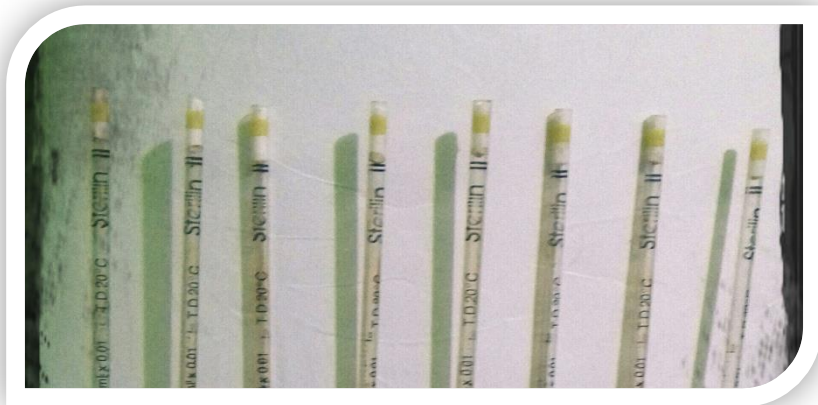


Figure 4.14. Close the Tubes with Silicon of Top.

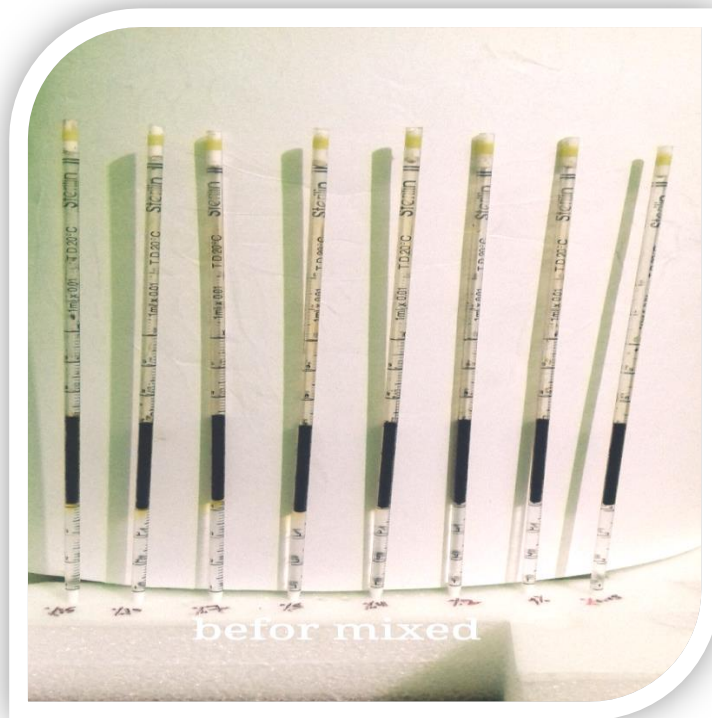


Figure 4.15. Install the Tubing on the Cork Vetically.

IV.5 Procedures for mix up and heating of tubes:

1. Put the tubes inside the aquarium water
2. Install all the tubes by moles founded in the a aquarium water as shown in the figure 4.16.
3. Operation of the water basin on temperature 40°C as shown in the figure 4.17.
4. Turn the (mix bottom) and place it on 250 as shown in the figure 4.17.
5. Let the tubes in (mix) for 4hr continuously.
6. Take the read of the tubes after passing 48hr at room temperature (25°C) as shown in the figure 4.19.
7. Put the tubes inside the oven at 30°C.
8. Take the read after passing 48hr as shown in the figure 4.20.
9. Put the tubes again inside the oven at 50°C, then take theread after passing 48hras shown in the figure 4.21.
10. Put the tubes inside the oven at 70°C, then take the read after passing 48hras shown in the figure4.22.



Figure 4.16. Install The Tubes Inside Basin Water.



Figure 4.17. Turn Temperature and Mixing Button.

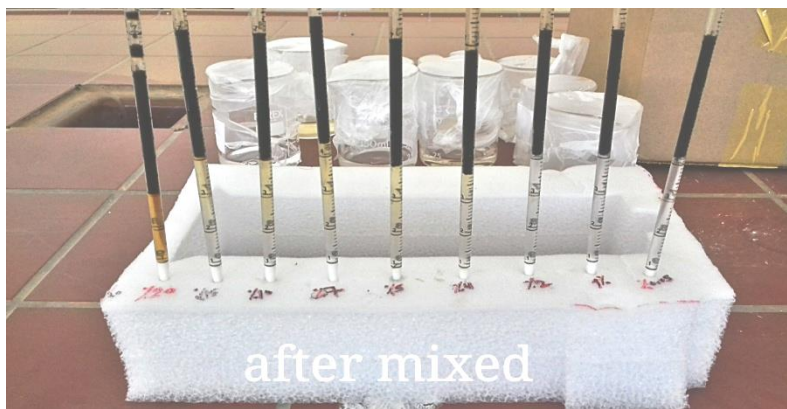


Figure 4.18. Samples after the Mixing.

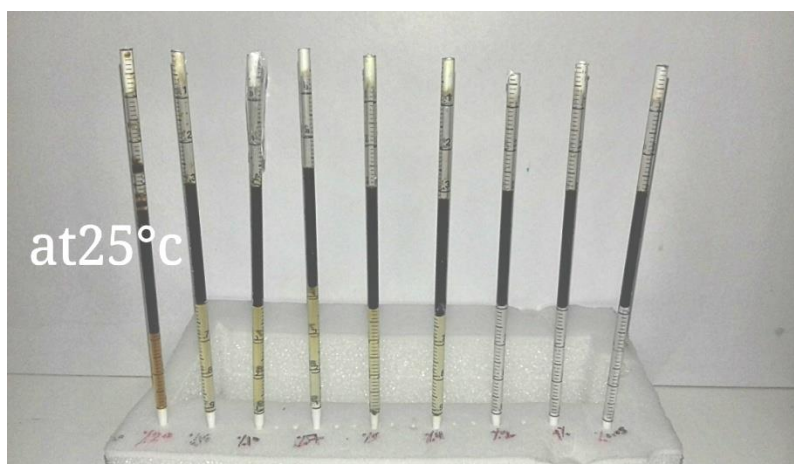
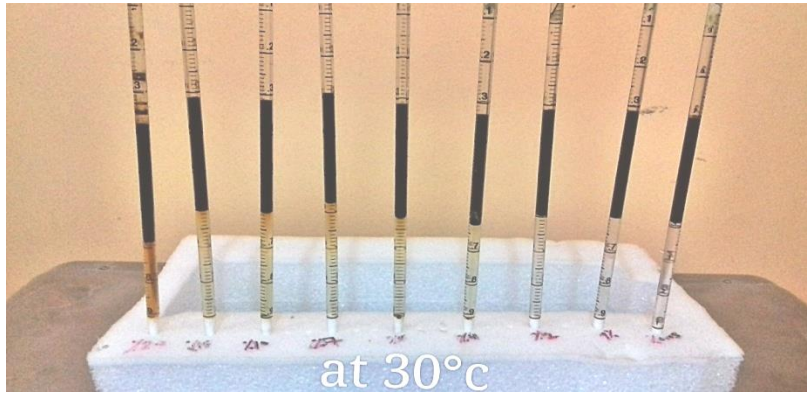


Figure 4.19. Samples after 48hr at 25°C



Figure(4.20): Samples after 48hr at 30°C

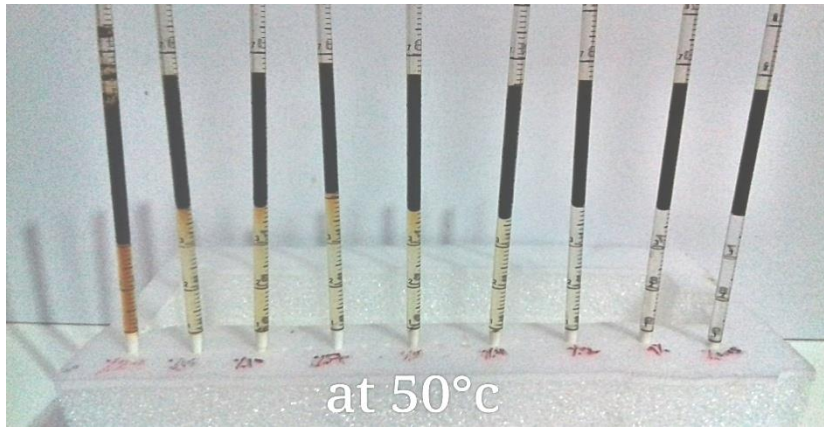


Figure 4.21. Samples after 48hr at 50°C

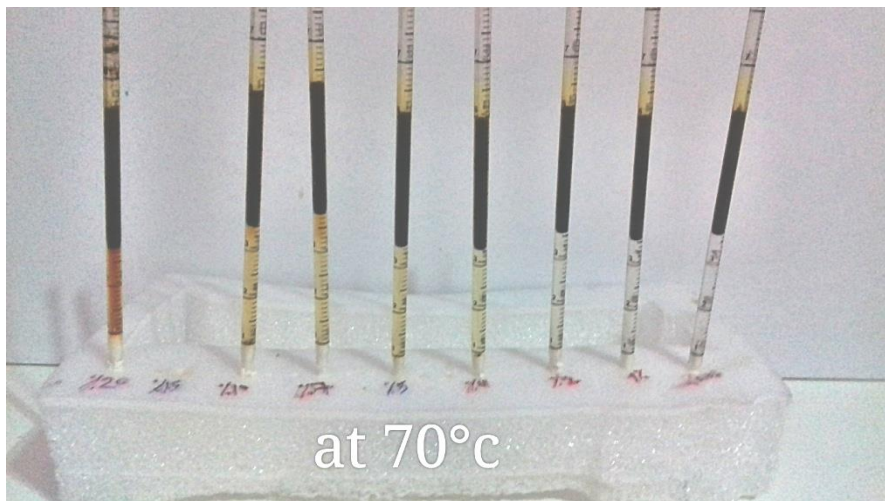


Figure 4.22. Samples after 48hr at 70°C

CHAPTER V RESULTS AND DISCUSSIONS

CHAPTER V RESULTS AND DISCUSSIONS

V.1 Results:

V.1.1 Results of PH:

Table (5.1) shows the results of PH experiment.

Table (5.1) : PH Results.

Sample	PH
Storage sea water	5.9
surfactant 0.05%	6.29
surfactant 1%	5.81
surfactant 2%	5.42
surfactant 4%	4.59
surfactant 5%	5.52
surfactant 7%	5.16
surfactant 10%	5.24
surfactant 15%	5.62
surfactant 20%	5.3

V.1.2 Results of Conductivity:

Table (4.2) shows the results of conductivity experiment. The conductivity is direct proportional with the surfactant concentration. If the soap concentration increase, the conductivity will increase.

Table (5.2) : Conductivity Results.

Sample	Conductivity(ms/cm)
Sea water	442.65
surfactant 0.05%	764
surfactant 1%	956
surfactant 2%	1351
surfactant 4%	1630
surfactant 5%	1734
surfactant 7%	2752
surfactant 10%	2873
surfactant 15%	2083
surfactant 20%	3337

V.1.3 Results of Salinity:

Table (5.3) shown the results of salinity experiment. The salinity is direct proportional with the surfactant concentration. If the soap concentration increase, the salinity will increase.

Table (5.3) : Salinity Results

Sample	salinity,(ppt)
sea water	247
surfactant 0.05%	410
surfactant 1%	500
surfactant 2%	830
surfactant 4%	1000
surfactant 5%	1170
surfactant 7%	1690
surfactant 10%	1810
surfactant 15%	1820
surfactant 20%	2060

V.1.4 Result of T.D.S (Total dissolved salt):

Table (5.4) shown the results of total dissolve salt experiment.

Table (5.4) : Total Dissolved Salts (T.D.S).

Sample	T.D.S (mg/l)
sea water	4
surfactant0.05%	33
surfactant 1%	155
surfactant 2%	170
surfactant 4%	144
surfactant 5%	501
surfactant 7%	194
surfactant 10%	264
surfactant 15%	215
surfactant 20%	487

V.1.5 Result of Density:

Table (5.6) shows the results of density experiment. Since the density = $\frac{mass}{volume}$ in this case we take the weight of bottle dry - weight of bottle filled with salt water or surfactant or oil , by divided on volume of bottle which 10 ml.

Table (5.6) : Storage sea water , Oil and Surfactant Density

Sample	W dry (g)	W filled(g)	w water(g)	V water(ml)	Density
sea water	31.739	40.647	8.728	10	0.8728
Oil	31.739	36.192	4.453	10	0.4453
surfactant0.05%	31.739	39.119	7.38	10	0.738
surfactant 1%	31.739	38.467	6.728	10	0.6728
surfactant 2%	31.739	37.91	6.171	10	0.6171
surfactant 4%	31.739	38.632	6.893	10	0.6893
surfactant 5%	31.739	39.41	7.671	10	0.7671
surfactant 7%	31.739	39.355	7.616	10	0.7616
surfactant 10%	31.739	39.644	7.905	10	0.7905
surfactant 15%	31.739	39.168	7.429	10	0.7429
surfactant 20%	31.739	40.116	8.377	10	0.8377

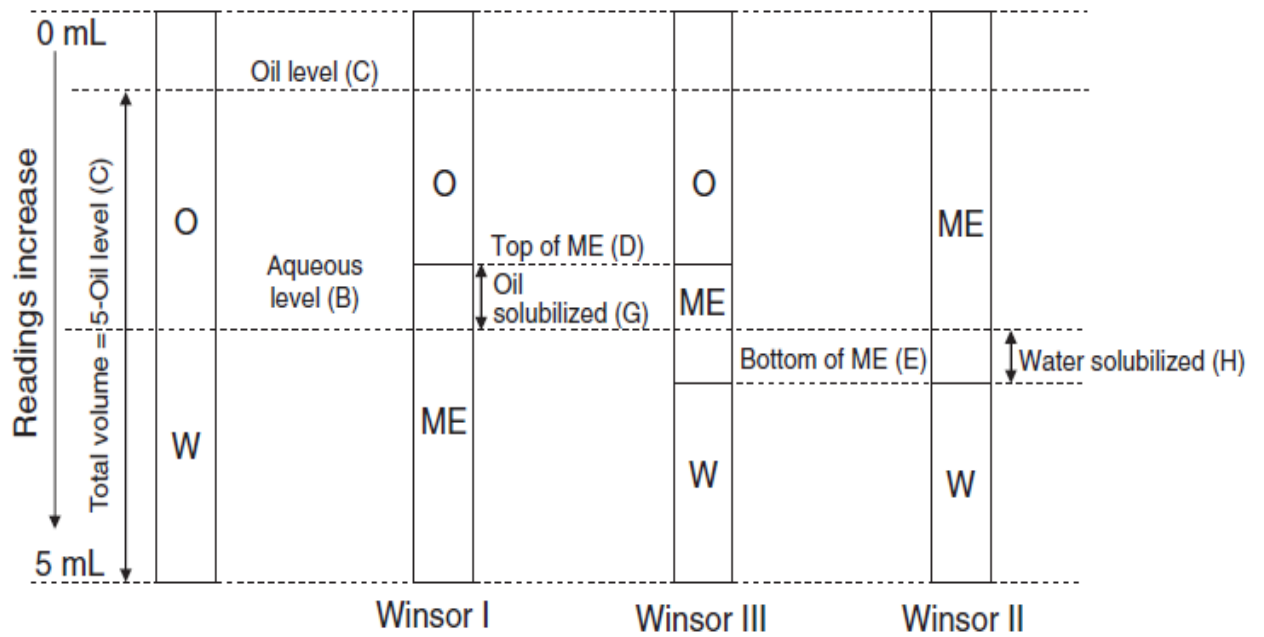


Figure (5.1): Schematic to show how salinity scan test data are measured and calculate

Table(5.7).Samples at Room Temperature before Mixed

	B	C	D	E	R	emulsion volume
concentration	aqueous level	oil level	top level	top of ME	bottom of ME	Emulsion volume
0.05	0.32	0.29	0.61	0	0	0
1	0.32	0.29	0.61	0	0	0
2	0.32	0.28	0.6	0	0	0
4	0.31	0.31	0.62	0	0	0
5	0.3	0.31	0.61	0	0	0
7	0.34	0.3	0.64	0	0	0
10	0.3	0.31	0.61	0	0	0
15	0.32	0.3	0.62	0	0	0
20	0.23	0.33	0.56	0	0	0

Table(5.8). Samples at Room Temperature after Mixed

	B	C	D	E	R		
Concentration	aceques level	oil level	top level	top of ME	bottom of ME	emulsion volume	Type
0.05	0.32	0.29	0.61	0.32	0.32	0	I
1	0.31	0.3	0.61	0.31	0.31	0	I
2	0.31	0.29	0.6	0.31	0.31	0	I
4	0.28	0.3	0.58	0.28	0.28	0	I
5	0.29	0.31	0.6	0.29	0.29	0	I
7	0.33	0.3	0.63	0.23	0.33	0	I
10	0.3	0.3	0.6	0.3	0.3	0	I
15	0.3	0.3	0.6	0.3	0.3	0	I
20	0.22	0.33	0.55	0.22	0.22	0	I

Table(5.9). Samples at 30c° .

	B	C	D	E	R		
concentration	aceques level	oil level	top level	top of ME	bottom of ME	Emulsion volume	Type
0.05	0.31	0.28	0.59	0.31	0.31	0	I
1	0.3	0.28	0.58	0.3	0.3	0	I
2	0.3	0.28	0.58	0.3	0.3	0	I
4	0.28	0.29	0.57	0.28	0.28	0	I
5	0.27	0.29	0.58	0.29	0.27	0.02	III
7	0.195	0.28	0.515	0.235	0.195	0.04	III
10	0.265	0.285	0.58	0.295	0.265	0.03	III
15	0.275	0.285	0.58	0.295	0.275	0.02	III
20	0.21	0.31	0.52	0.21	0.21	0	I

Table(5.10). Samples at 50 c° .

	B	C	D	E	R		
concentration	Aceques level	oil level	top level	top of ME	bottom of ME	Emulsion volume	Type
0.05	0.3	0.27	0.57	0.3	0.3	0	I
1	0.29	0.27	0.56	0.29	0.29	0	I
2	0.29	0.27	0.56	0.29	0.29	0	I
4	0.265	0.28	0.545	0.265	0.265	0	I
5	0.25	0.28	0.56	0.28	0.25	0.03	III
7	0.27	0.27	0.58	0.31	0.27	0.04	III
10	0.255	0.275	0.56	0.285	0.255	0.03	III
15	0.25	0.27	0.55	0.28	0.25	0.03	III
20	0.2	0.295	0.495	0.2	0.2	0	I

Table(5.11). Samples at 70 c° .

	B	C	D	E	R		
concentration	aceques level	oil level	top level	top of ME	bottom of ME	Emulsion volume	Type
0.05	0.275	0.235	0.51	0.275	0.275	0	I
1	0.25	0.255	0.505	0.25	0.25	0	I
2	0.26	0.25	0.51	0.26	0.26	0	I
4	0.245	0.25	0.495	0.245	0.245	0	I
5	0.245	0.265	0.51	0.245	0.245	0	I
7	0.23	0.245	0.525	0.28	0.23	0.05	III
10	0.23	0.26	0.51	0.25	0.23	0.02	III
15	failed	Failed	Failed	failed	failed	Failed	Failed
20	0.18	0.265	0.445	0.18	0.18	0	I

CHABTER VI

Conclusion and Recommendation

CHABTER VI. Conclusion and Recommendation

VI.1 Conclusion:

From this study we noted the following :

1. The conductivity is direct proportional with the surfactant concentration. If the soap concentration increase, the conductivity will increase.
2. The salinity is direct proportional with the surfactant concentration. If the soap concentration increase, the salinity will increase.
3. The oil is dissolved in surfactant after mixing and passing 48 hour at 25°C and is considered the type I.
4. The emulsion has been formed at 30°C and 50°C after passing 48 hr in the concentrations from 5% to 15% and is considered the type III, while the other concentrations between 0.05% to 4% and at 20% are considered the type I.
5. nonionic surfactant are much more tolerant of high- salinity brine
6. The best composition of the emulsion was recorded at a concentration 7% at 70°C , as shown in figure(6.1).

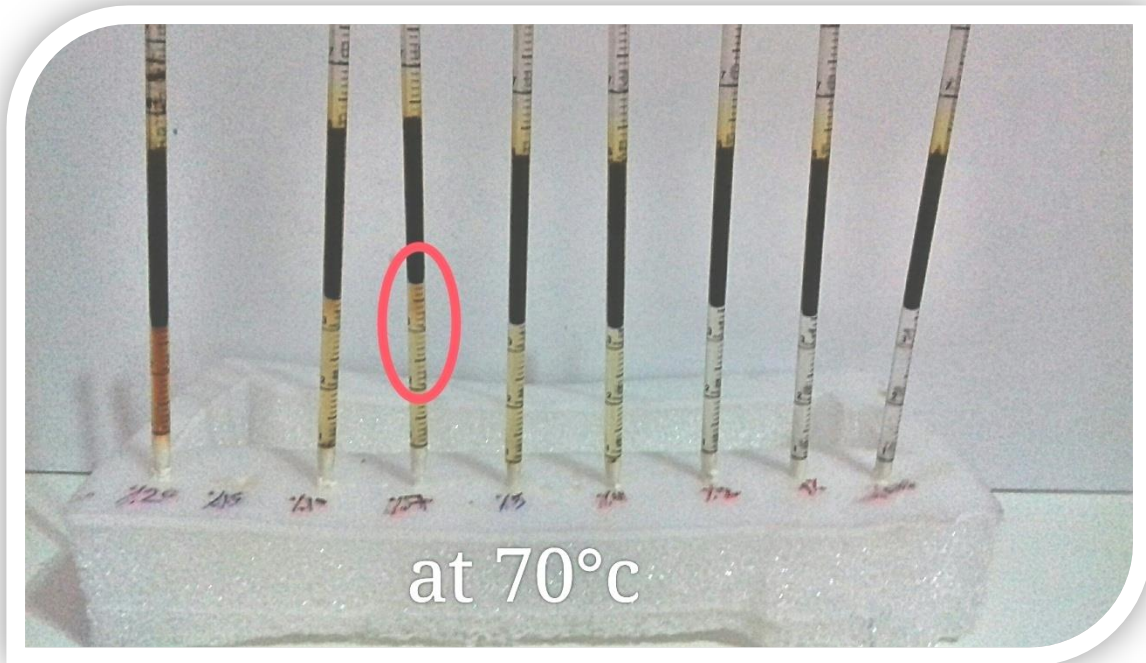


Figure (6.1).Shown Best Consist Of Emulsion.

VI.2 Recommendation:

For this who will serve the same research it is recommended to :

1. compare the results with fresh water results.
2. Use a wooden rack for pipe taps especially for the upper temperature of 50°C.
3. When the pipes are sealed with silicon it is a advisable to leave them a full day to ensure their drying.

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