Experimental Assessment of Heavy Crude Oil Production using Emulsion Flooding

MSc(50/50) RESEARCH THESIS

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Submitted to

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ABSTRACT

In many crude oil exploitation oil cannot be produced using its own natural drive after many years due to pressure depletion. In order to maintain the reservoir pressure and optimize the oil production, secondary oil recovery methods are usually used i.e. water injection, gas lift and reinjection of natural gas. Although, secondary oil recovery methods increase hydrocarbon production by about 35 - 45 %, they do not provide a definitive solution due to continuous pressure decrease and the excessive amount of water required. An alternative recovery technique known as tertiary recovery or enhanced oil recovery is usually used at this stage and focuses on increasing the mobility of the oil. Chemicals such as surfactants, polymers and nanoparticles are injected to improve recovery. These chemicals help improve properties of the injected fluid and its interactions with the rocks. Surfactants are well known for reducing interfacial tension formed between oil and water and polymers for improving sweep efficiency. Moreover, addition of nanoparticle is said to further reduce interfacial tension between water and oil and help reduce the capillary pressure.

This study looked at emulsion stability of crude oil with cationic surfactants and non-ionic surfactants. The objective was to analyse how stable the solution with surfactants only is and also how the stability is affected by temperatures, nanoparticles and stirring mechanism. It further investigates which surfactant type is best suitable to stabilise emulsions and whether or not the combination of surfactant and nanoparticle can provide a more stable emulsion than surfactants only

In the study, experiments were conducted to test emulsion stability based on temperature variation, water to oil ratios differences and droplet size formation. Cationic dodecyl trimethyl ammonium bromide (DTAB) and non-ionic Triton®X-100 surfactants were used; nanoparticle zinc oxide (ZnO) was later added into the two types of surfactants aqueous solutions and emulsion stability tests conducted. Temperature was raised from 250C to 60C to look at the effect this will have on emulsion stability. Water/ Oil ratios were analyse the effect/impact the different ratios had on emulsion stability. Droplet size distribution was analysed using a microscope to see how tight the emulsions are.

The experimental results suggest that cationic DTAB is not a good candidate for emulsion stability especially at 60^0C. The potential application of non-ionic surfactant Triton®X-100 alone gave better stability. Addition of nanoparticle ZnO to DTAB did not help stability and when ZnO is added to non-ionic surfactant Triton®X-100 the stability was good at all temperatures but did not last for a longer periods vs having non-ionic surfactant Triton®X-100 only , suggesting that Triton®X-100 is best suitable to keep emulsions formed stable and further microscopic work supported this finding.

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1. INTRODUCTION

When an oil field is discovered, a thorough study of the profitability is normally carried out to justify its exploitation. Initially the drilling of the sedimentary layers and the cover rock may give a direct access to the reservoir and the natural pressure within the reservoir allows then the flow of oil in the production well. This phase of production is called primary recovery. The secondary recovery of oil happens when the pressure of the reservoir is no longer sufficient to drive the hydrocarbons in the well. Water or gas is injected in the reservoir to increase the pressure and allow oil extraction. Lastly, tertiary recovery or enhanced oil recovery (EOR), is used to allow an even thorough oil extraction via mainly chemical or thermal methods. However; during tertiary recovery various problems can disturb, even temporarily stop the oil production and lead to a significant loss of earnings namely the formation of solid deposits and the formation of stable emulsions. A first potential problem of solid deposits is due to the formation of gas hydrates. Gas hydrates are crystalline compounds, formed of gas molecules (methane, ethane, propane...) imprisoned in " cages " made up of water molecules, and whose fields of stability correspond to the conditions of pressure and temperature typically found in marine resources. The formation and the accumulation of hydrates in the oil transport pipelines can lead to the blockage of pipelines and eventually stop the production. The available preventive (treatment) methods are both expensive, time consuming and difficult to implement. In the case of installations where the risk of formation of hydrates is proven, preventive methods generally based on the injection of chemicals (thermodynamically and/or kinetically inhibiting) are used to avoid or delay the formation of the hydrates. The second problem is that water co-produced with oil can lead to the formation of emulsions, generally water-in-oil (W/O), which, in certain cases, can be extremely stable. The presence of emulsions causes several problem, the first being a loss of productivity. Indeed, if the separation between the aqueous and oil phases is not complete, produced oil can contain a considerable quantity of water (dispersed in the shape of fine droplets) and not adhere to the necessary specifications of maximum water content in crude oil (in general less than 2% in mass) to be able to be sold to refineries. Additionally, time consuming and expensive treatments may be further required. The second problem due to the presence of emulsions concerns environmental preoccupations. The water separated from oil maybe re-injected (when that possible) in the well, and used for the secondary phase of recovery. It is very important to break the emulsion into two continuous phases to be able to re-use water without further losing oil. The demulsification can often be very difficult particularly in presence of additives used in EOR methods. In the worst case, the recovered water must be rejected into nature, and for that it must still adhere to strict environmental specifications. Often the required treatments consist in eliminating the remaining hydrocarbons as well as other polluting elements (i.e. metals). In this case, the presence in the water of stable oil droplets can complicate the treatment operations. To limit the presence of emulsions, additional separation units are required upstream the production chain and at the wells exit.

A further major problem is the formation of stable emulsions in the desalting unit which is intended to wash the entering crude in order to eliminate salts which may in the long term induce the corrosion of equipment and the poisoning of catalysts used downstream. When a stable emulsion appears in the desalting unit, the principal associated problems are:

i. The rejected water contains oil
ii. The maximum water content specification of the crude is not respected any more
iii. Oil can contain solids (silica, sand, asphaltenes precipitated) which can, in the long term, accumulate in the pipelines
iv. Desalting is no longer effective and hydrolysis of residual salts can occur during distillation.
v. The quality of the desalting water worsens and water cannot be recycled any more.

It is therefore imperative to limit the formation of stable emulsions in the desalting unit or at least to ensure a fast and effective breaking of the formed emulsion. The formation of emulsions (stable or unstable) is a major preoccupation for oil production and refining and this the motivation behind this work: to assess stabilization of surfactant and nanoparticle based emulsions using real crude oils systems in order to find out which mixture of surfactant with crude oil would give more stable emulsion over time and then which one could be separated easily by using various temperatures but also to find out if the addition of nanoparticles to aqueous surfactant solution would give more stable emulsion compared to the use of surfactants alone.

1.1. Crude Oil

Crude oil is characterised by an API value, this is the American Petroleum Institute (API) gravity commonly used to specify crude oil products (Silset, 2008).

$$\text{API} = (141.6/\text{SG}) - 131.5$$

On the basis of API (see figure 1), crude oil is graded as light (API >31^0), medium (API 22.3^0-31.1^0), heavy (API<22.3^0) and extra heavy/bitumen (API<10^0). The higher the API value the higher the commercial value for that crude oil, crude oil with API values <10^0 sinks in water whereas those with values >10^0 floats in water and therefore easily accessible/extracted (Speight, 2007).

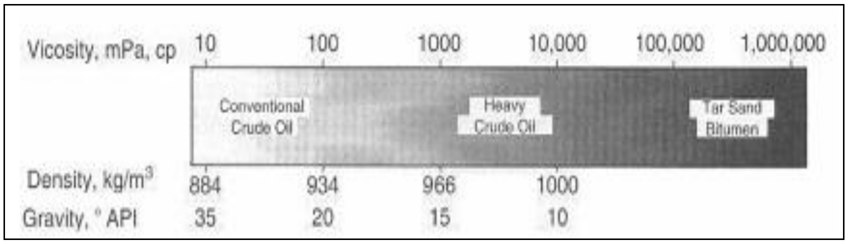

Figure 1. Properties of Crude Oil (Speight, 2007)

Low API crude oil has large amounts of impurities and low distillates yields; light crude oil has a better quality (Ancheyta, 2011), this makes processing of heavy crude oil different from light conversional crude oil. New reservoir wells that are now being explored and drilled have heavy crude oils and this require different extraction methods and different refinery processing.

In a life cycle of a reservoir/well, the crude oil that flows to the surface is naturally recovered by using either a pump or artificial lift system. Overtime the well naturally depletes and alternative recovery methods are required. A well undergoes three phases/ stages of oil recovery during its life span: primary, secondary and tertiary.

- *Primary recovery* involves pumps and artificial lift systems; this is where “easy oil” is produced with recovery of the original oil in place (OOIP) ranging between 10-30%.

- *Secondary recovery* introduces fluids to the system; this is when the easy oil can no longer be produced by natural pressure underground, the most common method is waterflooding where water is injected via an injection well to enhance flow by sweeping and maintaining bottom hole pressure. This recovers 30-50% of original oil in place (OOIP) (Green and Willhite 1998)
- *Tertiary recovery* methods on the other hand are applied when secondary methods start to be exhausted or recover less original OOIP. Tertiary methods are also referred to as Enhanced Oil Recovery (EOR) method; this method aims at reducing viscosity of the oil to recover what is left behind after primary and secondary recovery methods are no longer economical by recovering 50-80% of OOIP (Silset ,2008).

1.2. Objective of research

The application of enhanced-oil recovery (EOR) methods during oil production lead to the formation of water-in-crude oil emulsions. The pros and cons of emulsion formation have motivated significant research in the oil industry in the last few decades. Therefore, the objective of this study is to contribute to the understanding of water-in-crude oil emulsions stabilizing mechanisms. In this regards, several parameters affecting the stability of water-in-oil emulsions were examined including oil-to-water ratio, surfactant type (Cationic dodecyl trimethyl ammonium bromide (DTAB) and non-ionic Triton®X-100 surfactants were used), aqueous phase composition and temperature.

On the other hand, it has been suggested that solid content is a good predictor of emulsion stability in oil operations. Generally, the most stable emulsions are found when interfaces are stabilized by the smallest particles. Therefore, stabilization mechanisms for water-in-crude oil emulsions were also investigated in the presence of zinc oxide (ZnO) nanoparticles.

LITERATURE REVIEW

2.1. Overview of Enhanced Oil Recovery (EOR) Methods

EOR methods are tertiary recovery methods that involve injection of fluids of some type such as chemicals, gas (CO_2) or heat into the reservoir (figure 2.1). This injected fluid/gas act as a supplement to the natural energy present in the reservoir to displace oil to a producing well, they interact with the reservoir rock/oil system to create conditions favourable for oil recovery. The interaction will lower the interfacial tension, reduce viscosity and modify wettability (Green and Willhite, 1998).

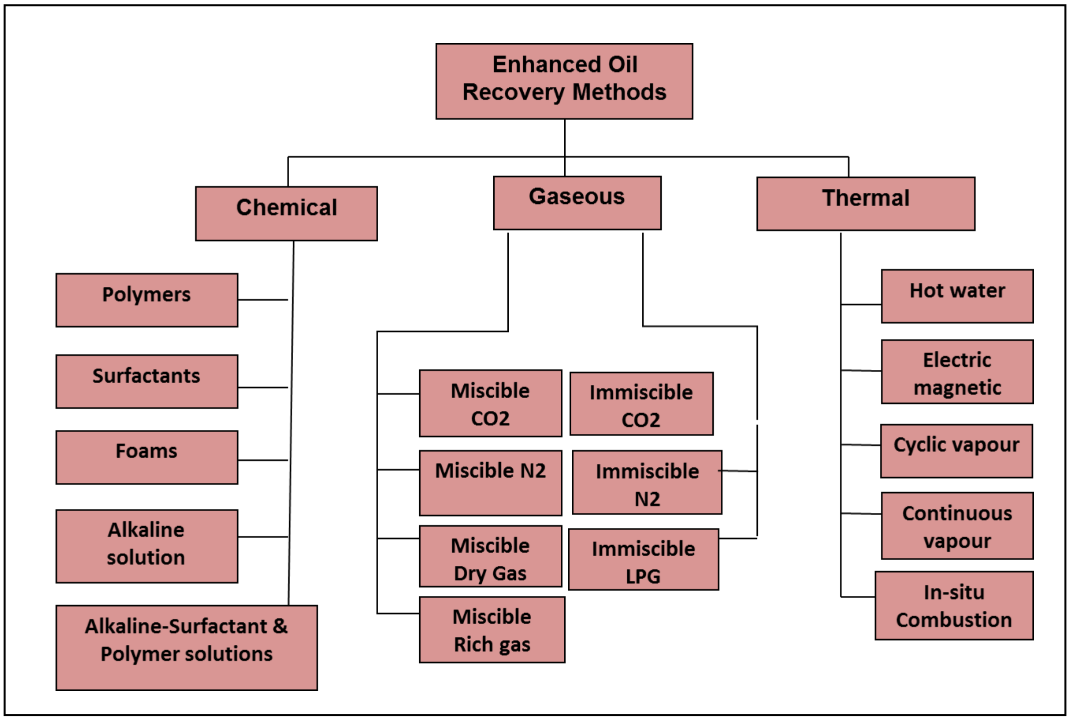

Figure 2.1 Enhanced Oil Recovery Methods (EOR)

Thermal Injection: Reservoir temperature is increased by injecting steam; as the steam comes in contact with the cold environment it condenses and a hot water bank is formed. This hot water bank acts as a water flood and pushes additional oil to the producing wells. There are three stages involved in this EOR method: 1) steam injection, 2) soaking and 3) production. Steam is injected and let to soak for 3-6 days upon that production can take place. The steam heats up the crude oil thus lowering the viscosity, crude oil is hot and produced with water. The schematic diagram (figure 2.2) shows the three different stages of thermal injection. This method is the most commonly used method for viscous crude oil. It is important to calculate the heat injection and heat loss to ensure consistent heat throughout the production.

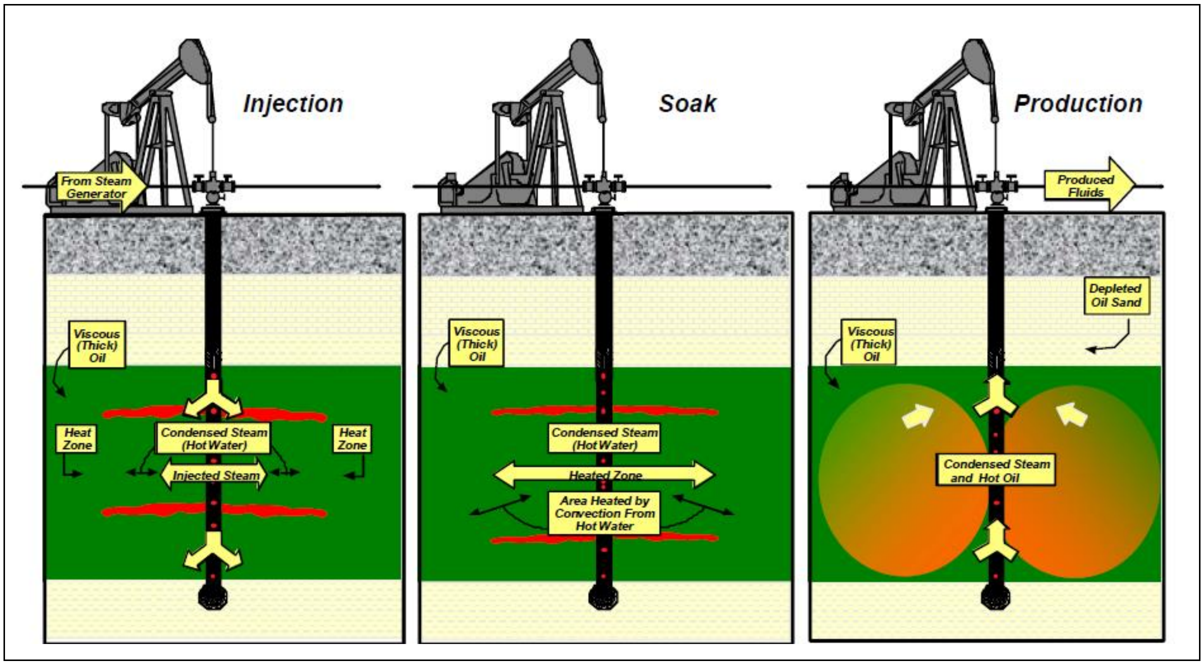

Figure 2.2 Cyclic Steam Injection (Berry Petroleum ,2012)

Gaseous Injection: When looking at the CO_2 gas injection in the reservoir (figure 2.3), the CO_2 dissolves in the oil, swells and viscosity of any hydrocarbon will be reduced and hence it will be easier to sweep to the production well**.**

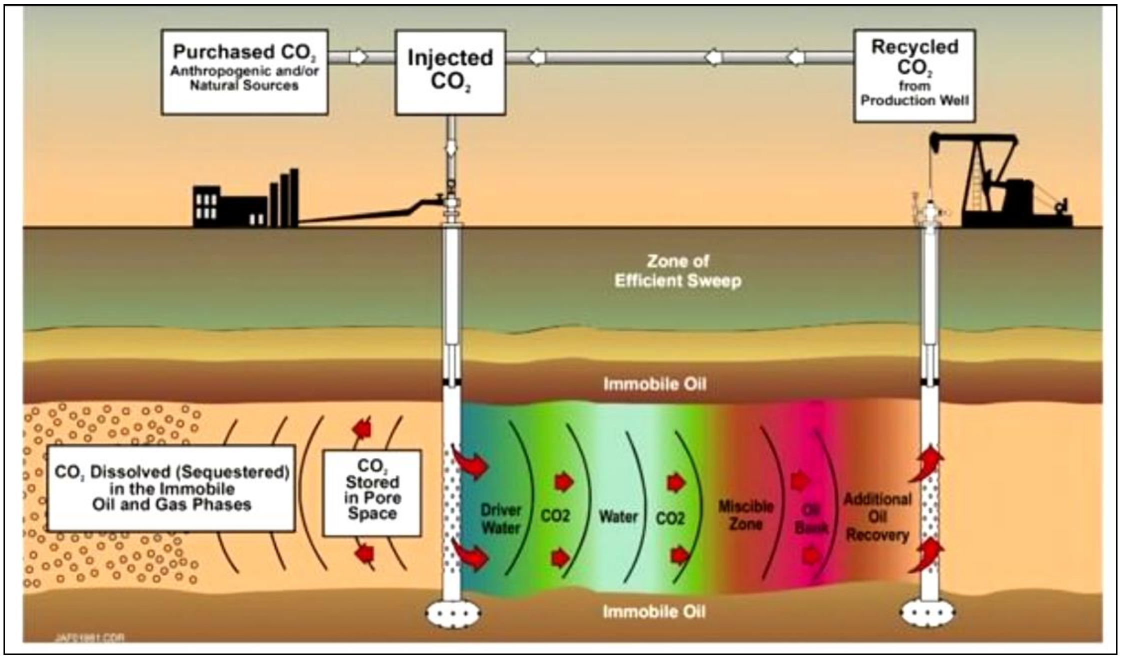

Figure 2.3 CO_2 gas Injection EOR method (Godec, 2011)

Chemical Injection: This involves an injection of various chemicals, usually dilute solutions to aid mobility and the reduction in surface tension. This is looked at in more detail in the section 2.2 below.

2.2. Overview of Chemical injection for EOR

Different chemicals are injected to the reservoir that aid in the recovery of original oil in place (OOIP) namely: polymers, surfactants, alkalis and nanoparticles. These chemicals can be injected separately or together depending on the type of system and the type of hydrocarbon to be recovered. When these chemicals are injected the process is normally referred to as flooding.

a) Polymer flooding

Polymers that are injected into the water phase of the reservoir trap (figure 2.4) are chemicals characterize by large molecules which when injected into water they add to the bulk of the water (they increase the viscosity of the water). The water is thickened and becomes heavier than the hydrocarbon (Wilson, 1977) and is able to sweep or wash the hydrocarbons from the pores within the reservoir. The polymer helps reduce water fingering into the hydrocarbon and therefore reduces water production with the crude oil.

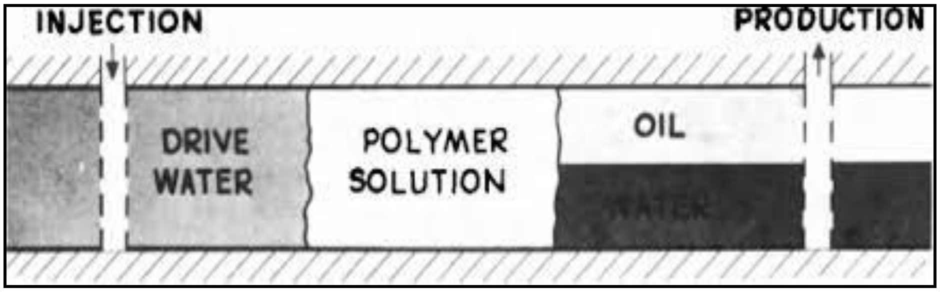

Figure 2.4. Polymer flooding (Wilson,1977)

b) Alkali Flooding

With an Alkali flooding process (figure 2.5), a slug of water that contain caustic is injected into the reservoir and followed by brine or water; this slug may contain up to 5% NaOH and approximately 15% of the pore volume (Wilson,1977). The caustic effects will increase the recovery of OOIP by one or more of the following mechanism: (a) improved sweep, (b) a favourable change in the wettability of the rock and (3) a low tension displacement.

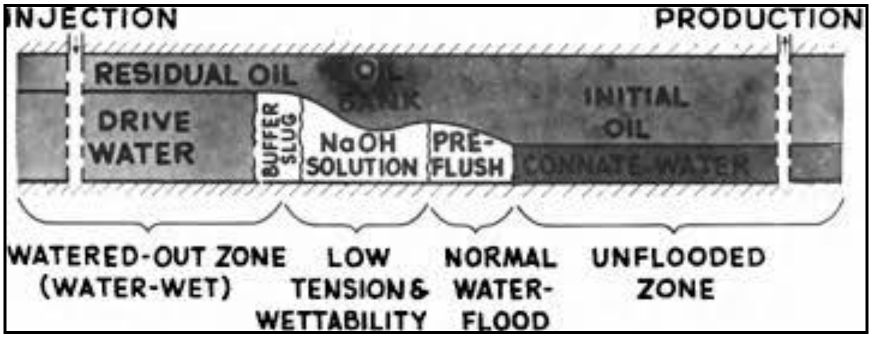

Figure 2.5. Alkali (NaOH) waterflooding (Wilson, 1977)

c) Surfactant Flooding

Surfactants play a key role in the formation of nano-emulsions. They are used (following polymer flooding) to mobilize the residual oil that can be displaced and produced (figure 2.6); it reduces adhesive forces of the water molecule to solid substances. Detergents are used as surfactant and are sometimes injected to produce what is known as surfactant flooding or emulsion flooding (Wilson, 1977). Sometimes these detergents are injected in combination with polymers to recover residual oil and this is commonly known as Surfactant Polymer (SP) Flooding. The surfactant causes the oil to flush more easily through the porous materials to enable the carbon that were adhering to rock grains to be released. This is then displaced by brine or water.

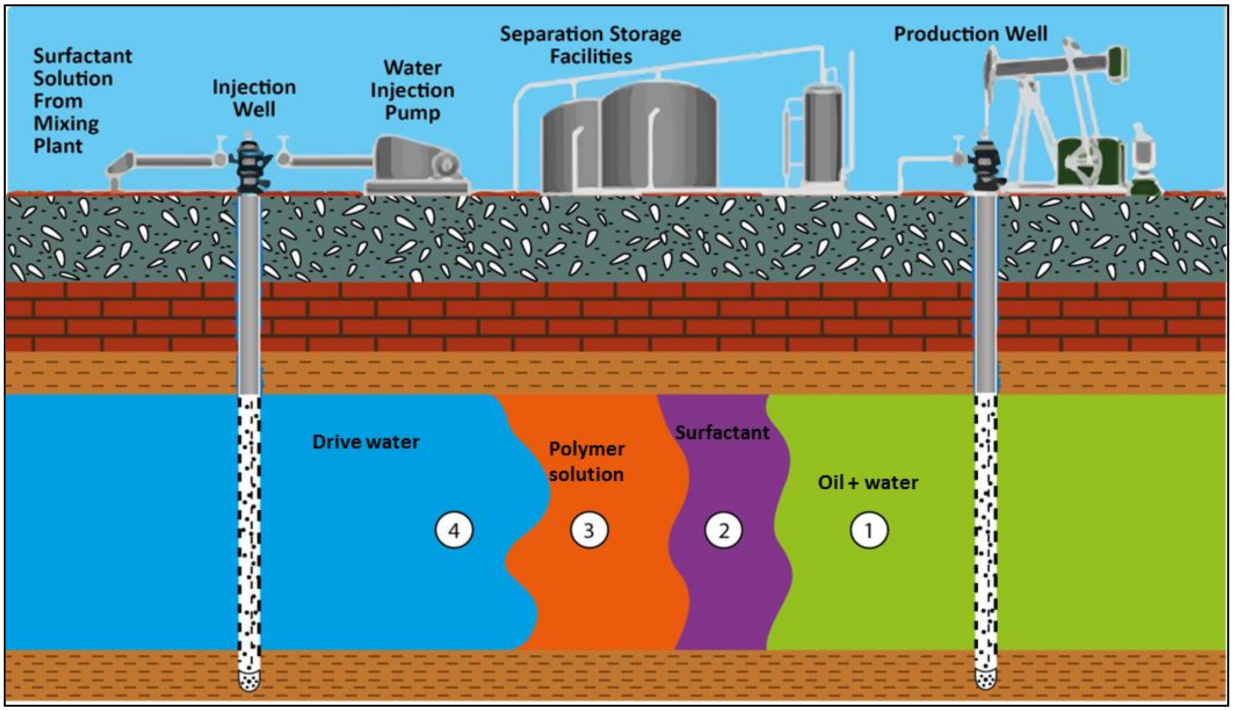

Figure 2.6. Polymer-Surfactant flooding (Farhadi, 2016)

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2.3. Emulsion Flooding for Crude Oil Recovery

An emulsion is a thermodynamically unstable system consisting of at least two immiscible liquid phases one of which is dispersed as globules in the other liquid phase stabilizes by a third substance called emulsifying agent. The droplets phase is called the dispersed phase / internal phase and the liquid in which droplets are dispersed is called the external (continuous) phase.

Crude oil emulsions form the moment when crude oil gets in contact with brine/water. Emulsions can be classified as either water in oil (w/o) or oil-in-water (o/w). W/O emulsion is when water forms the dispersed phase and oil acts as a dispersion medium. O/W emulsion is when oil is present as the dispersed phase and water as the dispersing medium i.e. continuous phase (Abdel-Raouf, 2012). Most crude oils produced in the world are commonly w/o and a few are o/w emulsions (macroemulsions). Figure 2.7 show a schematic representation of emulsion structures, encircled is an enlarged view of a surfactant monolayer siting at the oil-water interface.

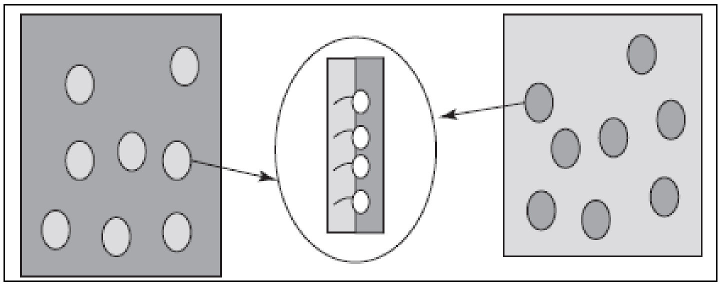


Figure 2.7. Representation of emulsion structures O/W emulsion (left) and W/O emulsion (right). Adapted from Langevin et al., 2004

In order for crude oil emulsion to form, certain criterion needs to be met:

- **a)** There must be two immiscible liquids (oil and water -brine) that interact with each other,
- **b)** There must be sufficient mixing or agitation effects to disperse one liquid into another as droplets and
- **c)** A mixing agent or an emulsifier must be present

The amount of mixing and the presence of emulsifier are critical for the formation of emulsion (Abdel-Raouf et al., 2011). Some of the factors that affect emulsion stability are temperatures, droplet size and droplet-size distribution and brine (pH and composition). Emulsions are generally unstable and the heavier liquid will settle to the bottom over time, a stabilizing agent is required to keep this emulsion from separating.

Oilfield emulsions are categorised based on their degree of kinetic stability:

- Tight emulsions, separation occurs after several hours or days
- Medium emulsions, separation occurs within minutes
- Loose emulsions, separation occurs after a few minutes. The separation is free of water.

One needs to note that w/o or o/w crude oil emulsions are self-emulsification processes and a spontaneous formation process, this is different from *chemical flooding* process where the emulsion is via chemical injection and the objective is to keep the emulsion stable during production. Additives that can be used to stabilize an emulsion are referred to as emulsifiers or emulsifying agents.

Emulsion consists of three phases: the internal or discontinuous phase of finely divided droplets. The external or continuous phase is the medium that keeps droplets in suspension. The interphase consists of an emulsifier that keeps the emulsion stable, binding the internal and external phase together and preventing droplets from approaching each other and coalescing (Udonne, 2012).

While emulsification process is of interest to EOR, demulsification processes shouldn’t be overlooked. This process breaks up crude oil emulsion into oil and water phases. There are several factors such as temperature; emulsifying agents’ concentration and solids removal that enhances emulsion break up. The mechanisms that are involved in this process have been categorised into three processes as follows:

a) Sedimentation and creaming, these are processes produced by external forces such as centrifugal and gravitation. When such forces exceed the thermal motion of droplets, a concentration gradient tends to build up where there are larger droplets moving faster to the top or bottom (depending on the density of the medium)

b) Flocculation, this is when droplets get too close to each other (cluster together) to a point of almost touching due to differences in oil and water densities, temperature, water cut and oil viscosity (Kokal , 2002)

c) Coalescence, this occurs when droplets fuse together forming a large drop. This leads to complete demulsification due to a decrease in the number of water droplets

2.4. Emulsifying agents: Surfactants

Surface active agents (surfactants) are compounds that are partially soluble in both water and oil; they have a *hydrophilic* part that attracts water and a long chain *hydrophobic* end that attracts oil. This allows the surfactant to be concentrated at the o/w interface where they form interfacial films lowering interfacial tension promoting dispersion and emulsification of droplets (Kokal, 2005). This means that the surfactant must create a very low IFT (figure 2.8) to mobilize residual oil creating an oil bank of both water and oil that flows as a continuous phase (Bourrel and Schechter, 1998). The hydrophilic part of the structure is sometimes represented by non-ionic polar groups or ionic groups whereas the hydrophobic par usually consists of hydrocarbons.

There are many possibilities to be examined when it comes to surfactants due to the capability of the molecules to absorb onto surfaces and modify their properties i.e. self-assemble in solution (Gugel et al, 2008) and their ability to interact with polymers and other chemicals.

When surfactants are dissolved they reach a certain value of concentration and the molecules begin to associate and organise themselves into complex units called "*micelles*". The point where the association process takes place is referred to as the *critical micelle concentration,* abbreviated CMC. The CMC is discussed in detail below (Section 2.6).

Surfactant (as mentioned above) can be classified into four types according to the ionic structure of the head group, namely *Anionic*(carrying negative charge with low absorption on sandstone rock),*Cationic* (carrying positive charge that strongly absorb on rocks such as sand stones) ,*Non-ionic*(doesn't carry any ionic charge) and *Zwitterionic* also known as Amphoteric (carrying both negative and positive charges.

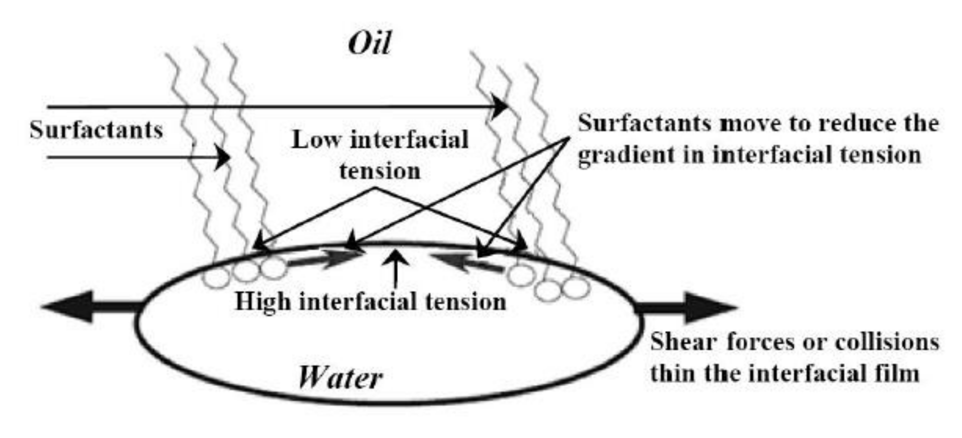


Figure 2.8. Gibbs-Marangoni effect at o/w interface (Aske, 2002)

Polymers can also be used as emulsifying agents, they are chemicals characterised by large molecules which, when injected into water, add bulk to the water. The water is thickened and is able to sweep or wash the hydrocarbons from the pores within the reservoir. Polymers add to sweep efficiency by improving the mobility ratio and recovery efficiency. Commercially available polymers include (1) Polyacrylamide (PAM) (2) partially hydrolysed polyacrymides (HPAM) a water soluble polyelectrolyte with a negative charge on the polymer chains; (3) Xanthan gums are excellent viscosifying agents and have high tolerance to temperature and salinity.

There are some crude oils that contain enough naphenic acid fractions to generate natural surfactants upon addition of alkaline components to serve as stabilizing agent (Kokal, 2005). Asphaltenes, resins and bases are also some of the naturally occurring emulsifiers in crude oil. The ability of surfactant molecules to interact with polymers and other chemical species, to absorb onto surfaces and modify their properties (Gugel et al., 2008) gives a compelling reason why surfactants remain the most widely used chemical for the EOR method.

Other emulsifying agents are fine solids, these are mechanical stabilizers that are smaller than emulsion droplets; they collect at the o/w interface and are wetted by both oil and water. These fine solid particles are clay particles, asphaltenes, waxes, corrosion products, drilling muds and sand (Kokal, 2005). A phenomenon used to explain these emulsifiers is called Pickering emulsion (figure 2.9), this consist of solid particles-nanoparticles (sub-micron, 100nm) that are used in the place of surfactant.

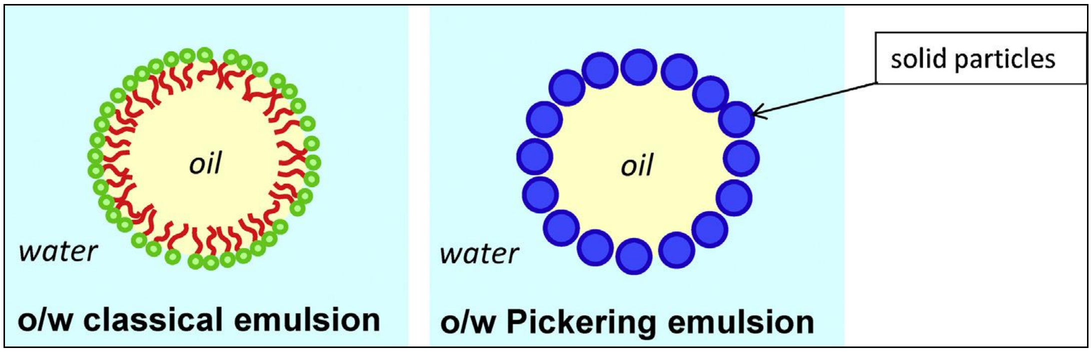


Figure 2.9. Pickering emulsion with solid particles absorbed at the oil-water interface stabilizing the droplets in place of the surfactant molecules. Chevalier and Bolzinger (2013)

The development of EOR methods was for the purpose of destroying the capillary forces that are responsible for the retention of a high amount of residual oil in the reservoirs (Nazar et al. 2011). Stable emulsion can significantly improve oil recovery.

Work done by Usman and Jimme (2016) has showed that emulsion flooding remains the best method for tertiary recovery. Challenges found by previous researchers was to obtain the o/w emulsion stability but Usman and Jimme conduced experiment to investigate the level or concentration of salinity that influences viscosity and stability of oil-in-water emulsions and found that the low salinity (low concentration of polymers) reduces the viscosity of heavy crude oil and thus achieving o/w emulsion stability. This research proposal aims to look at achieving similar results for crude oil stability imported

2.5. Commonly used Surfactant for EOR

This section looks at the different types of surfactants used in the oil and gas industry for EOR and why the surfactants used in this research were chosen.

A surfactant molecule is made up of two functional groups (hydrophobic and hydrophilic) and classified under four different groups (cationic, anionic non-ionic and *Zwitterionic),* see figure

2.10. This research paper will focus only the cationic, anionic and non-ionic surfactant groups as these were available surfactant groups to conduct the experimental work.

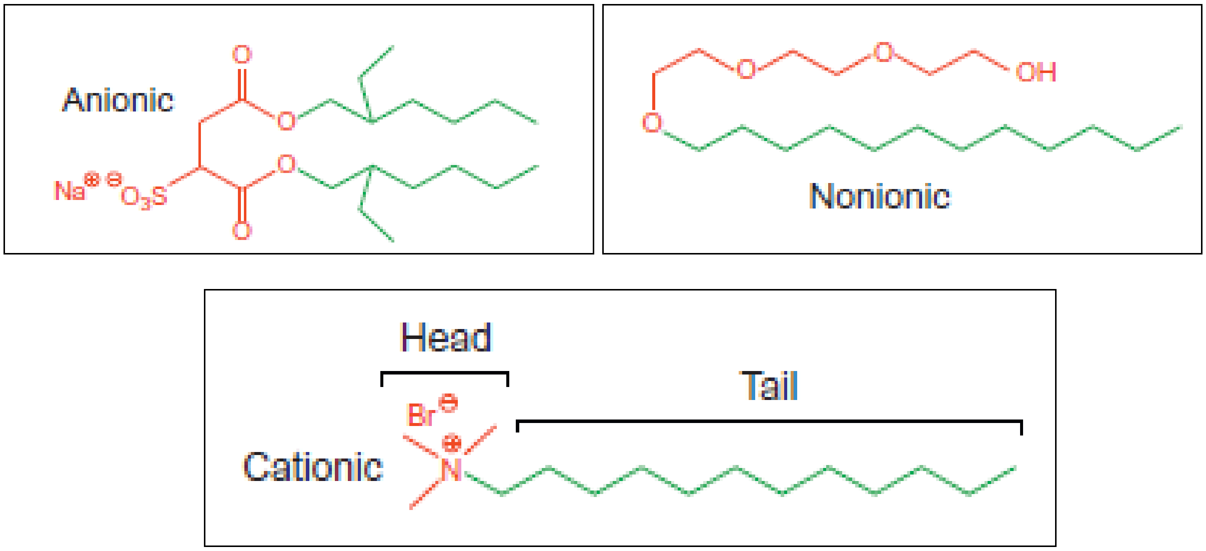


Figure 2.10. Examples of surfactant chemical structures (Eastoe and Tabor, 2014)

Cationic Surfactant

These are positively charged surfactants that dissociate into an amphiphilic anion and cation, a very large portion of this class corresponds to quaternary ammoniums and nitrogen compounds with one or several long chain of the alkyl type coming from nitrogen compound (Salager, 2002). They are generally expensive and are usually only used in applications that require a positive charge and cannot be substituted by other surfactants. Alkyltrimethyl ammonium chloride or bromide (figure 2.11) is used as sterilizing, antiseptic and disinfectants agents and can act as corrosion inhibitors when incorporated as additives in non-ionic detergents.

Further studies conducted by Sharma and Mohanty (2013) supported other researchers like Langevin et al,(2004), that cationic surfactant such as Dodecyl Trimethyl Ammonium Bromide (DTAB) is able to alter the wettability from oil-wet to intermediate water-wet in carbonate rocks. In dilute concentrations with non-ionic surfactant it can recover up to 80% of the original oil in place (OOIP).

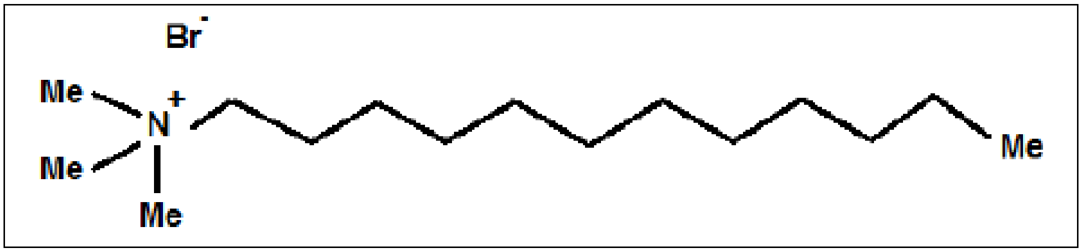


Figure 2.11. Molecular Structure of DTAB (ChemNet)

Anionic Surfactant

These surfactants are dissociated in water in an amphiphilic anion and a cation which is generally an alkaline metal (Na^+, K^+) or quaternary ammonium.

One of the most commonly used anionic surfactant is Sodium Dodecyl Sulfate (SDS), this surfactant belong to the alkyl sulfate group. Research done by Esmaeilzadeh et al., (2014), show that SDS is a good partner for nanoparticles when injected as part of EOR process.

Liu et al.,(2006) tested several anionic surfactants (alkyl sulfates, linear alkylbenzene sulfonate, alpha olefin sulfonates, alkyl ether sulfates and alkylbenzene sulfonate), upon his screening tests it was evident that alkyl ether sulfates provided the best performance in emulsifying the heavy oil in brine. Liu et al., (2007) conducted more experiments adding surfactant to enhance alkali flooding of heavy oil recovery in Canada, his experimental work showed that alkyl ether sulfate was necessary to initiate emulsification. When sandpack flooding tests were conducted, this surfactant reduced the IFT and allowed the oil to easily disperse into formation brine showing (again) that the anionic surfactant is necessary to obtain high tertiary recovery.

It is important to note that when dealing with carbonate reservoirs, anionic surfactants are not good candidates for EOR; when combined with cationic surfactants they tend to reduce production. However, when dealing with sandstone reservoirs then anionic surfactants are most effective candidates (on their own or in a mixture with other anionic surfactants)

Non-ionic surfactant.

These surfactants are effective for surfactant flooding in formations that contain high salinity water and reservoirs that contain carbonate rocks. Non-ionic surfactants don’t have any charges and therefore do not ionize in aqueous solution because of their hydrophilic group made up of alcohol, ether, ester or amide. They are made hydrophilic by the presence of a polythoxylated glycol chain. A well-known non-ionic surfactant used is the Triton® X-100 synonymously known as Octylphenol ethylene oxide condensate. This group is hydrophilic as it forms hydrogen bonds with water; however, these bonds can break with increasing temperature (Kokal, 2002)

There are several research papers highlighting the uses and benefits of surfactants in EOR, with cationic surfactant being the most common. Work by Standnes and Austad (2000) have compared the uses of cationic, anionic and non-ionic surfactants and they’ve showed that the most efficient surfactants are cationic.

2.6. Critical Micellar Concentration (CMC)

The critical micellar concentration (CMC) is defined as the concentration of surfactant solution at which molecules self-aggregate above which spherically shaped micelles form (Domoniquez et al., 1997).

At low surfactant concentration the surfactant molecule assemble on the surface; when more surfactant is added then the surface tension of the solution starts to rapidly decrease because more and more surfactant molecules will be on the surface. When the surface becomes saturated, the addition of the surfactant molecules will lead to formation of micelles (creating a concentration point called CMC), see figure 2.12.

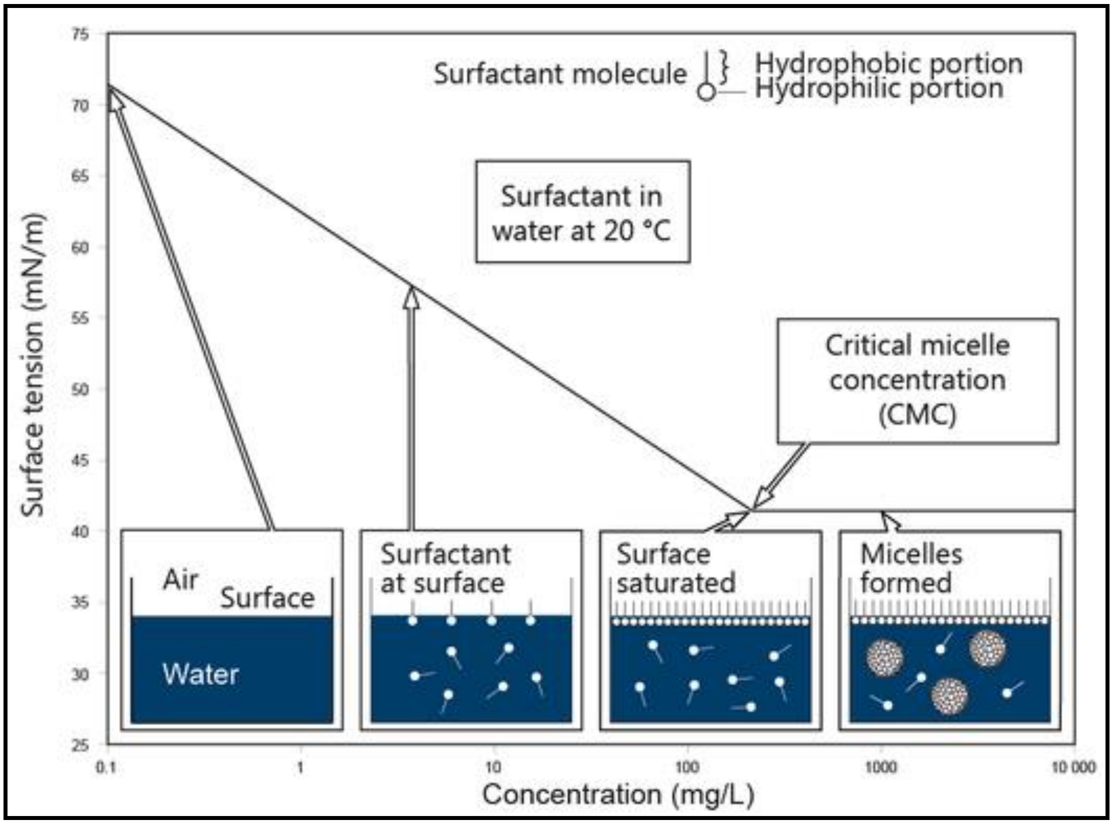


Figure 2.12. Formation of Critical micelles Concentration (CMC) (Krűss company, 2017)

Surfactants having higher concentrations than their CMC are known to achieve ultra-low IFT, these are however expensive. Researchers have all come to conclude that the concentration of surfactant in a chemical slug needs to be greater than the CMC so that the micellization can be initiated.

The CMC for a given alkyl chain increases in the order non-ionic < Zwetterionic < ionic (anionic or cationic) (Winterbom, 1972)

2.7. Interfacial Tension (IFT)

Interfacial tension (IFT) is defined by Udeagbara (2010) as the force that exists between the molecules of the interface between two fluids.(IFT holds these molecules together).This phase can be that of two immiscible liquids such as oil and water. This force can be reduced by surfactants by getting absorbed at the interface between two liquids. When the IFT force is lowered enough it can increase OOIP significantly because the IFT gives rise to capillary forces in the porous (Troy et al., 2006). The IFT is normally measured in dynes/cm, the surface tension between a gas and crude oil ranges from near zero to approximately 34dynes/cm. To measure o/w IFT, a drop spin tensiometer is used.

2.8. Overview of Nanotechnology used for EOR

Nanotechnology has gained vast interest in the petroleum industry through the use of nanoparticles particularly in the drilling, completion and production operations, this has enhanced the rheological properties of fluids at favourable and elevated temperatures (Cheraghian and Hendraningrat, 2016). Nanotechnology deals with the application, design, characterization and production of materials and devices based on nanometre scale. Nanoparticles have distinctive properties due to their small sizes and greater surface area per unit volume; they have dimensions in the order of 1-100nm (Singh and Ahmed, 2010). For EOR, nanotechnology has become the cutting-edge technology, adding nanoparticles to fluids can benefit EOR significantly and improve well drilling by changing fluid properties, wettability alteration of rocks, interfacial tension reduction, mobility increase of capillary-trapped oil and drag reduction. According to Zhang et al, (2010) nanoparticles are used to stabilize emulsion droplets which are small enough to pass typical pores, flow through the reservoir rock without much retention and also remain stable under hard conditions in the reservoir due to irreversible adsorption of the nanoparticles on their droplet surface. Nanoparticles that are less than 30nm in diameter can be either hydrophilic or hydrophobic.

2.8.1. Commonly used Nanoparticles for EOR

In previous work done by Cheraghiam and Hendraningrat (2016), Negin et al.,(2016) were applications of nanotechnology for EOR was investigated, commonly used nanoparticles were found to be from the metal oxide group: Silicon dioxide (SiO_2), Aluminium oxide (Al_2O_3) , Nickel Oxide (Ni_2O_3) and Iron Oxides (Fe_2O_3). The metal oxides are popular and considered as polar molecules or hydrophilic. They are known to significantly reduce the viscosity of the crude oil when dispersed in brine solution. Research by Negin et al.,(2016) summarises the application of nanotechnology and classifies the most commonly used nanoparticles for EOR. In listing the dominant mechanism of surfactants which leads to EOR, nanoparticles CuO, Al_2O_3, Ni_2O_3 and Fe_2O_3 are best for viscosity reduction. When needing to effectively reduce the IFT, then SiO_2 and Polymer coated nanoparticles are best. SiO_2 has another advantage/dominant mechanism to alter wettability of the formation rock.

Zinc Oxide (ZnO) is other nanoparticles known in the industry but not much work is done on them. This nanoparticle can have a polar and non-polar structure therefore can be hydrophilic or hydrophobic. Studies done by Ogolo et al., (2012) looked at ZnO as EOR agent in sandstones, they found that when injected it negatively affected the permeability of samples used. Furthermore, their study saw a additional decrease in permeability when brine was used. Ogolo et al., (2012) argued that the injection of ZnO could lower the overall oil recovery factor.
Negin et al., (2016) made a recommendation for further investigation into ZnO nanoparticles. For this reason, this research paper focuses on the application of ZnO nanoparticle with surfactant to stabilise crude oil emulsion.

A review by Cheraghian and Hendraningrat, (2016) gave evidence that nanoparticles enhances the function the stimulation fluids due to easy access of the nanoparticles into the o/w interface to reduce the IFT (Amulla and Al-Tahini, 2009) between the oil and water and enhance the oil production.

Further experimental studies by Le et al.,(2011) using different types of surfactants with nanoparticle SiO_2 showed great potential for EOR application on rock surfaces as this displayed a resistance to adsorption. Some researchers took surfactant solutions and investigated the effects of adding nanoparticles on IFT; they've found that the presence of nanoparticles changed the rheological properties (Al-Raoush and Wilson, 2005).

2.8.2. Effects of nanoparticles on Interfacial tension (IFT) reduction

Typical nanoparticles used in the petroleum industry are SiO_2, CO_2, Al_2O_3, MgO and Fe_2O_3. Silica nanoparticles are widely used in EOR methods. At the interface between the injected fluid and oil, surfactants form a mixed layer with nanoparticles; this result in increasing the interface and thus contribute to further reducing the IFT (Cheraghian and Hendraningrat, 2016). Studies done by Suleimaniv et al., show that surfactant contribute to the stability of nanoparticles and emulsions to decrease IFT, these two emulsifiers complement each other.

2.9. Oil Droplet Measurement

Droplet Size distribution (DSD) in an emulsion depends on several factors such as IFT, emulsifying agents, bulk properties of oil and water, presence of solids and shear. DSD of an emulsion should be taken into consideration as it determines the stability of the emulsion Emulsions generally look dark and less bright when they have large diameter droplets (low total interfacial surface area) (Kokal, 2005). As a rule of thumb, the smaller the average size of the dispersed water droplets, the tighter the emulsion. Emulsions that have smaller size droplets (≤10 micron) will generally be more stable, see figure 2.13 below. The droplet size distribution affects emulsion viscosity because it is higher when droplets are smaller. Mixing using Ultrasonic stirrer also affects the droplet sizes formed.

There are different methods used to determine DSD for oilfield emulsions and they are:

- Physical separation
- Scattering techniques such as X-ray and light scattering, these technique measures droplet sized 0.4nm to > 100µm
- Microscopy and image analysis.

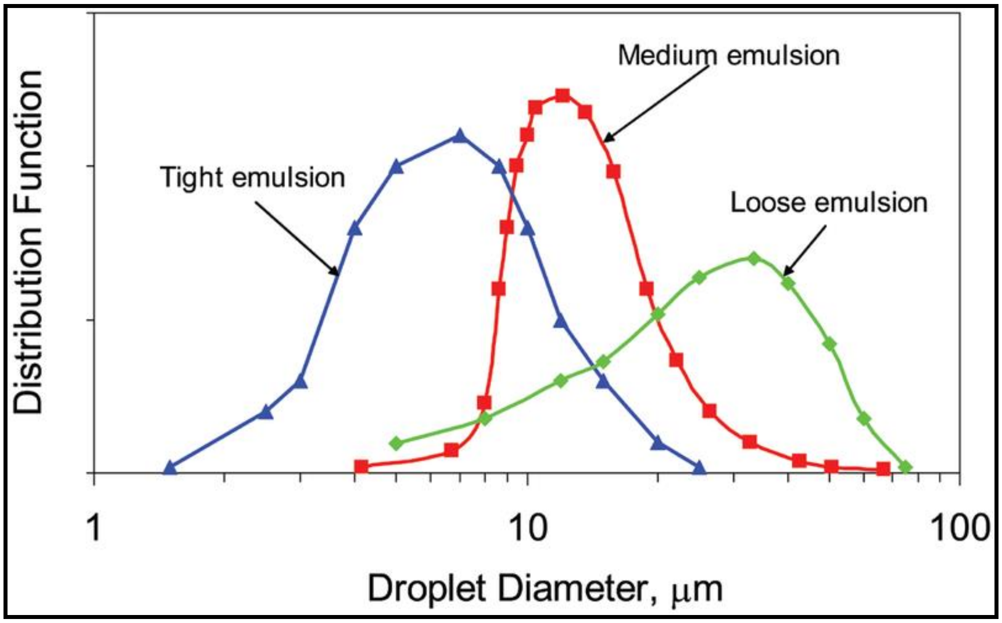


Figure 2.13. Droplet-size distribution of petroleum emulsions (Kokal, 2007)

2.10. Problems associated with Heavy Crude Oil production

Although polymers and surfactants play a large role in heavy oil production, these emulsifiers do not provide long term stability of emulsion. Commonly used polymers such as HPAM and PAM have poor shear resistance and therefore don't have high tolerance to temperatures, salinity and don't possess tremendous viscosifying ability (Cheraghiam and Hendraningrat, 2016). During production the polymer molecular chains tends to be cut off when polymer solution passes through the porous medium, perforations, pipeline and the pump at high speed. This leads to the reduction in viscosity of polymer solution. Crude oil is not produced alone, it is comingled with water, and the water creates (and) usually increases the unit cost of oil production. The produced water must be separated from the oil, treated and dispose-off properly. Heavy oil production can cause problems in both upstream and downstream. For upstream operations, figure 2.14, issues such as wax precipitation, viscous emulsion, corrosion, hydrate formation, asphaltene precipitation and emulsion breaking can occur in pipelines and production tubes disturbing flow (Ancheyta, 2011). In downstream operations the process of upgrading heavy oil or residual can be expensive especially when looking at processes such as hydrogen addition or carbon injection.

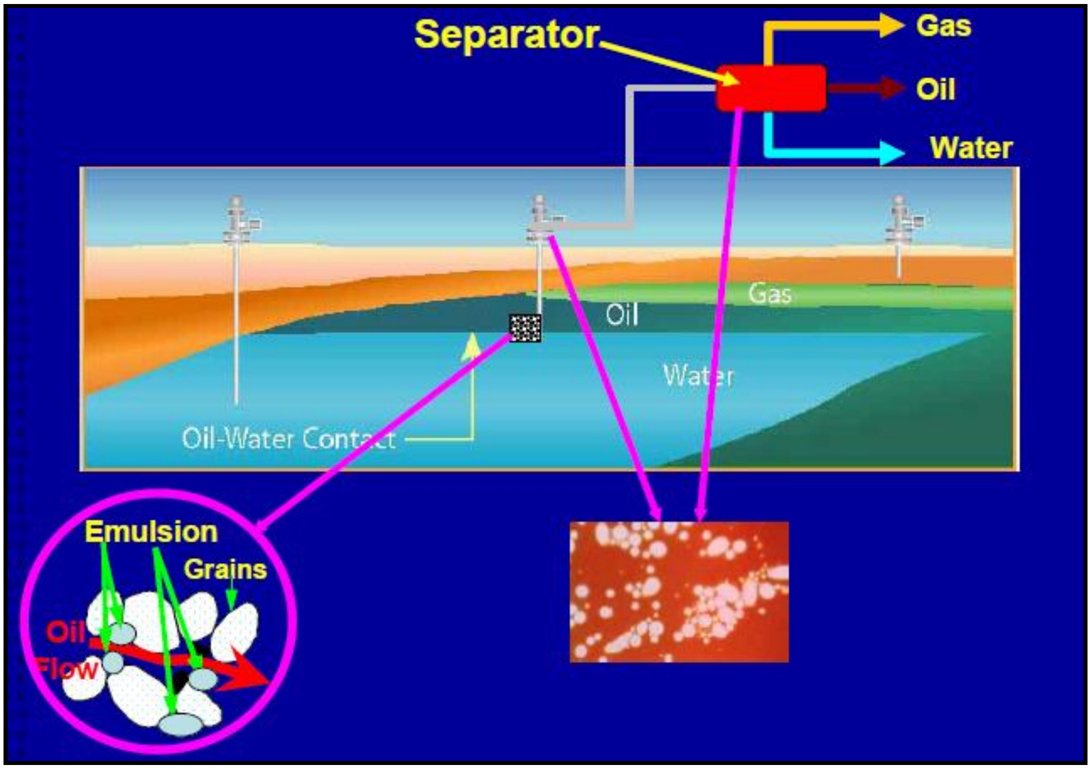


Figure 2.14. Occurrence of emulsions during production in the reservoir and separator (Kokal , 2005)

2.11. Origin of Crude oil Sample

The crude oil sample used in this research was obtained from NATREF (refinery tank F29107) and it is a blend of different crude oils from Nigeria, Angola and Saudi Arabia (table 1). These crude oils have different properties due to the different origins and consequently their formation brines differ as well. Table 2.1 lists the crude oil blend properties including and their gravity API values.

Nigeria Crude Oil

Nigeria produces high value low sulfur content and light crude oils and they include the 1)Brass River Blend,(2)Bonny Light, (3) Escravos, (4)Forcados, (5)Qua Iboe and (6) Erha crude oil., these crude oil have different API^0 gravity specifications ranging from30-36. (Eastern Union energy). Out of the crude oil blend received from NATREF, 60.79% of the crude is of Nigerian origin, with average API gravity of 35.

Table 2.1 Crude oil Sample : Crude oil Blend from NATREF (refinery Tank F29107)

Crude feed	Country of origin	Mass	Mol wt%	API ^{0}
BONNY LIGHT (BLT)	Nigeria	32.37	5.15	34.6
ESCRAVOS (EST)	Nigeria	240.04	38.10	33.7
FORCADOS (FBT)	Nigeria	1	0.11	30
QUA IBOE (QIT)	Nigeria	1	0.15	36
ERHA (ERT)	Nigeria	12	1.94	
BRASS RIVER (BRT)	Nigeria	97	15.34	38
NEMBA (NET)	Angola	7	1.09	38.6
ARAB EXTRA LIGHT (AET)	PG-Saud Arabia	15.67	2.49	30
ARAB LIGHT (ALT)	PG-Saud Arabia	88.36	14.03	39
ARAB MEDIUM (AMT)	PG-Saud Arabia	70.84	11.24	20
ARAB HEAVY (AHT)	PG-Saud Arabia	65	10.37	10
Total Feed		**630.00**	**100**	

60.79%

38.13%

Angola Crude Oil

Angola has different types of crude oil from heavy to light crudes. Heavy crude is known as Kuito (very viscous crude with medium sulphur content with API values of 19^0 and 0.66^0 respectively). The Nemba crude oil is a light crude oil with API gravity of 38^0 and makes up only 1% of the crude oil blend provided for this research (Sunga Energy). Due to the existence at this low percentage, the crude oil will not be discussed further as it has very insignificant effects to the blend.

Saudi Arabia Crude Oil

The Saudi Arabian crude oil is very diverse, from the Saudi oilfields there are five types of crude oil produced; namely Arabian (1)Heavy, (2)Medium, (3) light, (4)extra light and (5) super light crude oil. Arabian heavy and medium crude oil are produced offshore and have API gravity that range from 6^0 -10^0 for heavy crude and 10^0 -21^0 for medium crude oil. The light, extra light and super light crude oil are produced onshore from different field; their API gravity range from 21-30, 30-39 and 39-50 respectively.

Saudi Arabia crude oil makes up 38.13% of the crude blend provided for this research, this in essence makes the blend light with an average API gravity of approximately 35.

3. EXPERIMENTAL WORK

3.1. MATERIALS

Surfactants: Two surfactants were used in this research: cationic Dodecyl Trimethyl Ammonium Bromide (DTAB) and non-ionic Triton® X-100.

The DTAB with the formula of $C_{12}N(CH_3)_3Br$ 0.22 has a molecular weight 308.34g/mol at 25^0C.

Triton® X-100 with the formula $C_{14}H_{22}O(C_2H_4O)_n(n=9\text{-}10)$ and average molecular weight of 625g/mol. The viscosity is 240cps at 25^oC with pH 6-8 (5% aqueous solution). The HLB of the surfactant is 13.5, so this can help generate oil in water emulsions. Properties for all surfactants are shown in Table 3.1.

Nanoparticles**:** ZnO nanoparticles were selected, supplied by Sigma Aldridge. This was in a white powder form with formula weight of 81.39g/mol and particle size <10nm. Properties are summarised in Table 3.2.

Brine**:** 1 wt% of NaCl and $CaCl_2$ were mixed together with distilled water to prepare the brine solution. Surfactant and nanoparticle aqueous solutions were prepared using brine solution.

Test bottles**:** 20 poly vial test bottles were used to mix the crude oil and aqueous solutions..

Crude Oil sample**:** The crude oil sample used was collected from NATREF (refinery tank F29107), crude oil properties are summarised in Table 2.1 (in Chapter 2)its properties.

A water bath: A hot water bath (figure 3.1) was used to maintain the system at a fixed (room) temperature. The temperature was increased to 40^0C measure the stability of emulsion under higher temperatures. A cold ice bath (-10^0C) was also used to measure the stability of the emulsion under cold environments.

Figure 3.1. Water bath with thermometer and Controller

Instruments: A hielscher UP200S Ultrasonic Processor (200 watts, 24kHz) was used to mix the aqueous solutions and the crude oil. An Ohaus Explorer EP413 milligram balance was used to weigh the chemicals in preparation of the aqueous solutions. Olympus BX 63 OFM microscope was used to analyse the samples with the most stable emulsions formed to determine the tightness of the emulsion by looking at the droplet size distribution of emulsions formed.

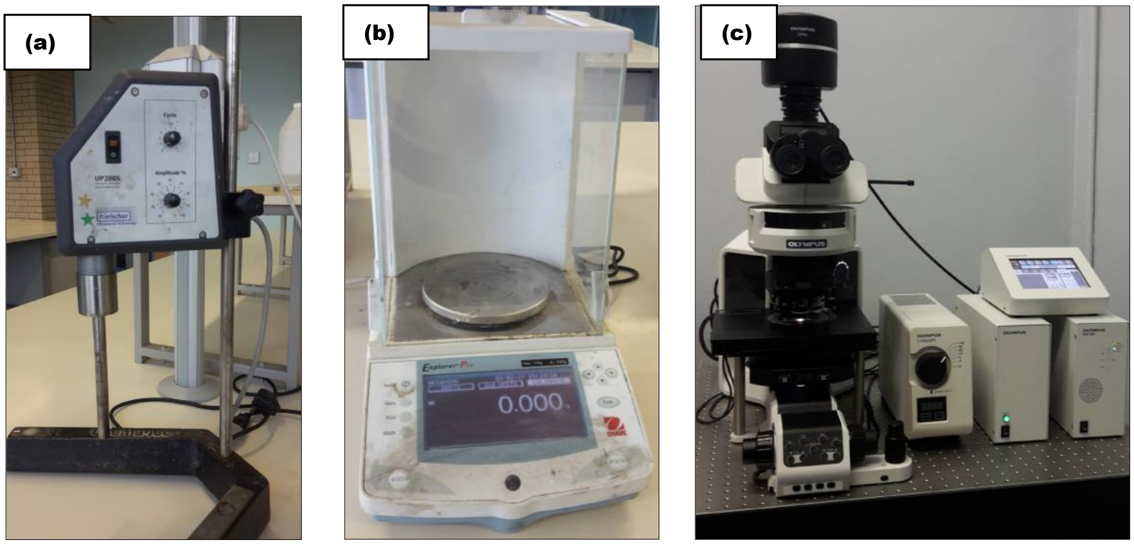


Figure 3.2. (a) Hielscher UP200S Ultrasonic Process (b) Ohaus Explorer EP413 balance (c) Olympus BX 63 OFM

Table 3.1 Properties of Surfactant

Name of Surfactant	Type of surfactant	Description	Supplier
Dodecyl Trimethyl Ammonium Bromide (DTAB) [CH3(CH2)11N(CH3)3Br]	Cationic	White Powder	Sigma Aldridge
Triton® X-100	Non-ionic	Liquid/Colourless	Sigma Aldridge

Table 3.2: Properties of Nanoparticles

Type of nanoparticle	Particle size (nm)	Description	Supplier
Zinc Oxide (ZnO)	<10nm	White powder	Sigma Aldridge

3.2. Experimental Procedure

Two types of surfactants were used, non-ionic Triton® X-100 and cationic DTAB to conduct the first part of the experiment. Tables 3.1 show properties of surfactants used. Samples were weighed to 1wt% using the weight balance shown in figure 3.2. Four aqueous solutions were prepared as follows:

Mixture 1

100g Distilled water + 1wt% NaCl + 1wt% $CaCl_2$ + 1 Wt% DTAB

Mixture 2

100g Distilled water + 1wt% NaCl + 1wt% $CaCl_2$ + 1 Wt% Triton® X-100

The second part of the experiment made use of surfactant with nanoparticle ZnO;

Mixture 3

100g Distilled water + 1wt% NaCl + 1wt% $CaCl_2$ + 1 wt% DTAB + 1wt% ZnO

Mixture 4

100g Distilled water + 1wt% NaCl + 1wt% $CaCl_2$ + 1 wt% Triton® X-100+ 1wt% ZnO

3.2.1. Preparing the aqueous solution mixtures with crude oil

Emulsification tests were conducted using poly vial bottles. In each set of tests, a group of bottles was used to contain different aqueous phases with the different chemicals and concentrations. In preparation of an emulsification bottle test, different ratios of aqueous phase were added to a test bottle first; see Table 3.3 for ratios used. Then different ratios of crude oil were carefully added to the top of the aqueous phase with a syringe so that minimal mechanical disturbance occurs. An ultrasonic stirrer was then used to mix the crude oil and aqueous solutions.

Table 3.3: Water to Oil (W:O) ratios of samples prepared

	Aqueous solution (DTAB)	Oil		Aqueous solution (Triton® X-100)	Oil
1	9	1	**6**	9	1
2	7.5	2.5	**7**	7.5	2.5
3	5	5	**8**	5	5
4	2.5	7.5	**9**	2.5	7.5
5	1	9	**10**	1	9

3.2.2. Preparing the aqueous solution mixtures and Zinc Oxide with crude oil

Another 10 samples containing different ratios of aqueous solution (brine, Triton® X-100,DTAB and ZnO) were prepared with crude oil, Table 3.2 shows properties of the ZnO used. The aqueous solutions including ZnO were mixed using the ultrasonic stirrer (figure 3.2.a.) and immediately transferred using a syringe into the test bottles containing different ratios of crude oil. This was to avail the settling of ZnO nanoparticle in the aqueous solution since it is not soluble in water. These solutions (containing crude oil) were then further mixed with an ultrasonic stirrer for 2-3minutes each and results of emulsion stability were then observed at 25^0C over 24hour period. If separation occurred then temperatures where increased, this was the case for all samples at 25^0C. Re-emulsification was conducted and samples placed in a hot bath for analysis under higher temperatures of 45^0C and 60^0C to observe any differences in emulsion stability at difference temperature conditions.

3.3.Microscopic Observations

The droplet size distribution for oilfield emulsions is determined by several techniques, for this research microscopy and image analysis technique was used. The microscope used for this was the Olympus BX 63 OFM , figure 3.2. Thin section slides were prepared for samples with W:O ratios of 9:1,5:5, 2.5:7.5 for all four solution mixtures containing DTAB with brine and crude oil, Triton® X-100 with brine and crude oil, dodecyl trimethyl ammonium bromide + brine + Zinc Oxide + crude oil and Triton X-100 + brine + Zinc Oxide + crude oil.

Preparing microscopy slides for the aqueous solution mixtures with crude oil

A pipette was used to collect aqueous solutions from test bottles. The thin section slides were used to place the solution drops of the emulsion formed (continuous phase) with a microscope slip placed on top of it to seal the aqueous solution in place. Different oil droplet sizes of samples were measured to obtain an average droplet size distribution (DSD), this was then used to graph a distribution curve to determine the degree of kinetic stability (tight medium or loose emulsions formation).

4. RESULTS AND DISCUSSION

Emulsions are generally unstable and the heavier liquid will settle to the bottom over time, the surfactant will act as stabilizing agents to keep the emulsion from separating. Bancroft proposed that when surfactant is mixed with crude oil and water then the continuous phase of the emulsion that forms is the phase where the surfactant is more soluble.

Non-ionic surfactants are made hydrophilic by the presence of a polythoxylated glycol chain which is hydrophilic and will create more surface contact with aqueous phase. Triton® X-100 is soluble in all proportions at 25^0C in water and gives a clear to slightly hazy solution. It is more viscous than water so should mix well with crude oil and form a more stable emulsion for hours. At higher temperatures, the bond that forms (hydrogen and water) is expected to break. Based on literature study cationic surfactants have been chosen over non-ionic due to their success in EOR therefore it is expected that the cationic Dodecyl trimethyl ammonium Bromide to stabilise the emulsion better than non-ionic Triton® X-100. Nanoparticle added to the surfactant aqueous solution is expected to increase the emulsion stability due to their hydrophilic characteristics.

4.1. Emulsion stability of surfactants only with crude oil

Visual observations were done to compare the effect of temperature on emulsion stability and it was found that a water phase forms and the emulsion does not stay stable. Mixture 1 (dodecyl trimethyl ammonium bromide) and mixture 2 (Triton® X-100) were placed in poly vial bottles with crude oil with water-to-oil ratios of 9:1, 7.5:2.5, 5:5, 2.5:7.5 and 1:9. When the aqeous solution was mixed with crude oil, a homogeneuous solution formed within 2 minutes of stirring. The bottles were then placed in a water bath at various temperatures (25^0C, 45^0C and 60^0C respectively). This was to test if emulsion stability increases at higher temperatures or decreases. Some percentage (~10%) of the solution was lost during re-emusification process and was accounted for. Samples with water-to-oil ratio 1:9 and 2.5:7.5 displayed an oil continous phase and those with 9:1 and 7.5:2.5 displayed a water continuous phase.

In order to obtain the graphs' effect of temperature on emulsion stability, the following equation was used:

Equation 1:

$$\boxed{Emulsion\ Stability\ (\%) = (Height_{max} - Height_{brine}) \div Height_{max}}$$

4.1.1 <u>The effects of temperature</u> on emuslion stability of DTAB

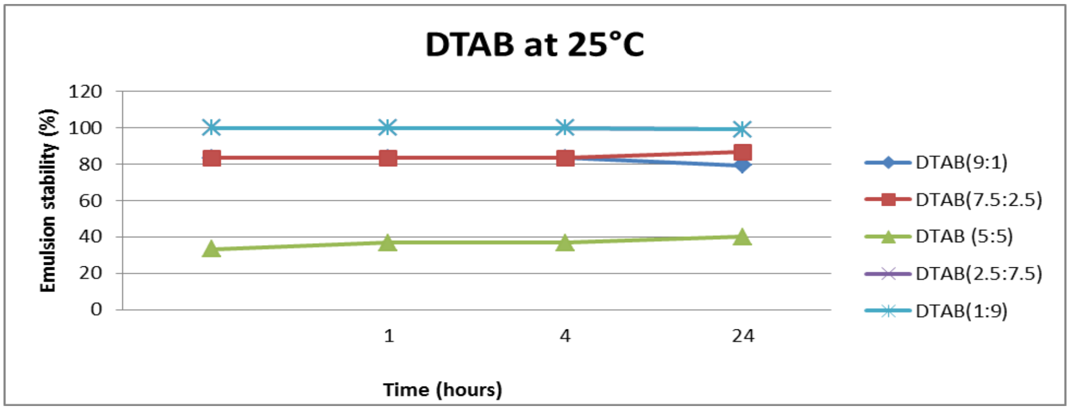


Figure 4.1. Stability of DTAB at 25^{0}C over 24hours

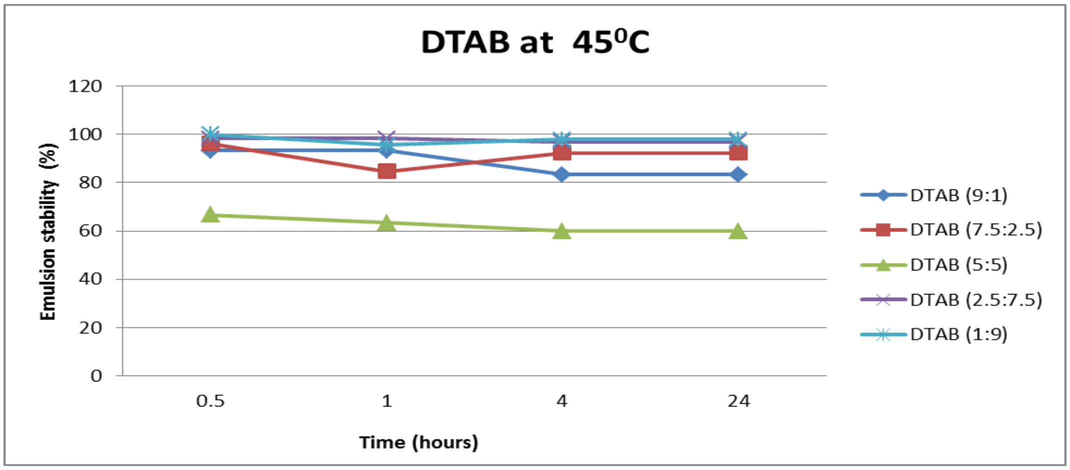


Figure 4.2. Stability of DTAB at 45^{0}C observed over 24hours

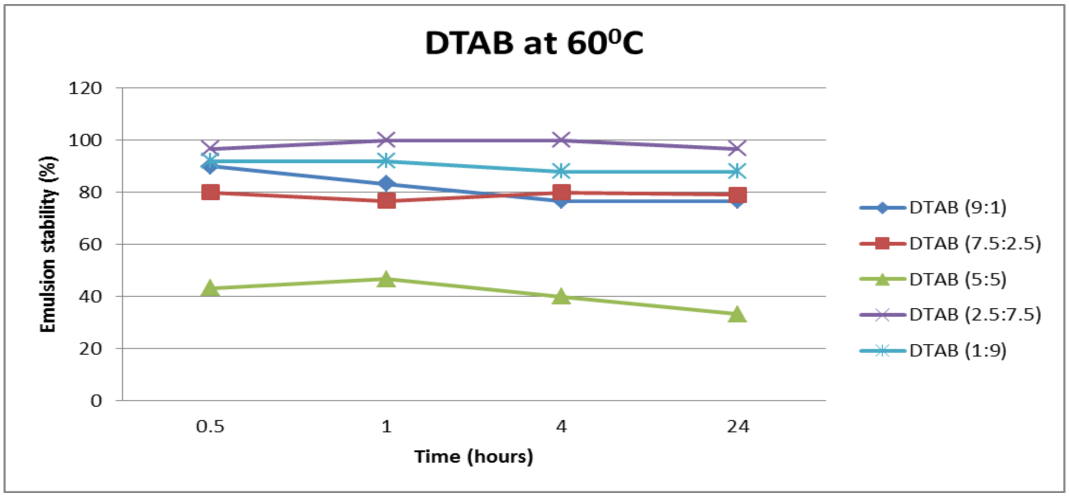


Figure 4.3. Stability of DTAB at 60^{0}C observed over 24hours

Sample with water-to-oil ratio of 5:5 had emuslion stabilty of 33% under 25^0C (figure 4.1) , this slightly increased to 40% and remained constant over 24 hours. At 45^0C, figure 4.2, emulsion stability was much higher reaching 66% to remain constant at 60% for 24 hours. When temperatures were increased to 60^0C (figure 4.3) the stability decreased to 33%.

Sample with water-to-oil ratio 9:1 exhibited 83% emulsion stability under 25^0C for 4 hours and remained constant at 80% for 20 hours (a similar trend was seen for 7.5:2.5). However, under a much higher temperature of 45^0C the samples' emulsion stability was 93% in the first 4 hours and dropped to 83% to remain constant over 20 hours. Under 60^0C the emulsion formed wasn't as stable (77%) and remained constant over 24hours.

The sample with 7.5:2.5 showed emulsion stability of 83% under 25^0C and increased to 93% under 45^0C**.** The sample however did not perform well under 60^0C as only 80% of the emuslion was stable over 24hours. For 1:9 and 2.5:7.5 , emuslion stability was stable at 100% over 24hours, on the graph the two overlap under 25^0C, a similar trend is seen under 45^0C.

The greater the continuous phase the stable the emuslion. Sample 7.5:2.5 is water(aqeuous) continuous with a thin oil rim at surface. This is expected since the concentration of crude oil is far less than the aqeuous.

Once the samples became accustomed to the new temperature, the emulsion stabilty becomes stable and constant. A much more stable emulsion is seen with samples that have oil as the continuous phase compared to aquoues solution as the continuous phase. This is due to the viscosity of the crude oil itself. Samples 9:1, 7.5:2.5 and 5:5 formed unstable emulsions as phase separation occurred. The temperature had no effect.

4.1.2. The effects of temperature on emulsion stability of Triton® X-100

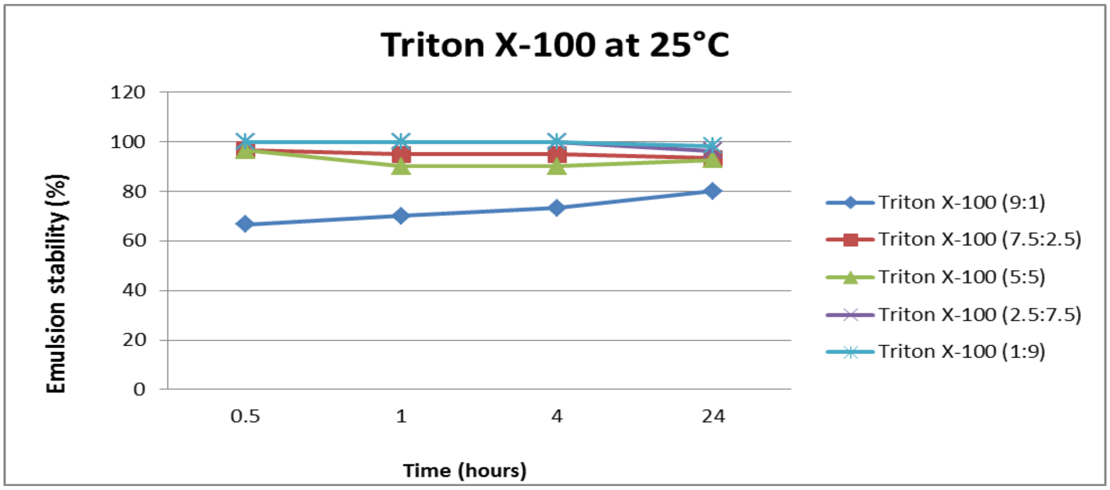


Figure 4.4. Stability of Triton® X-100 at 25^{0}C over 24hours

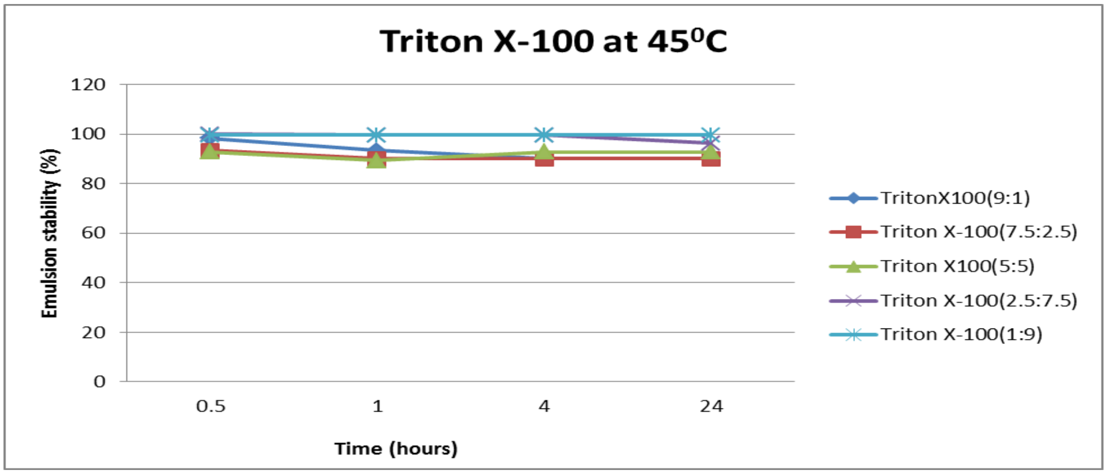


Figure 4.5. Stability of Triton® X-100 at 45^{0}C over 24hours

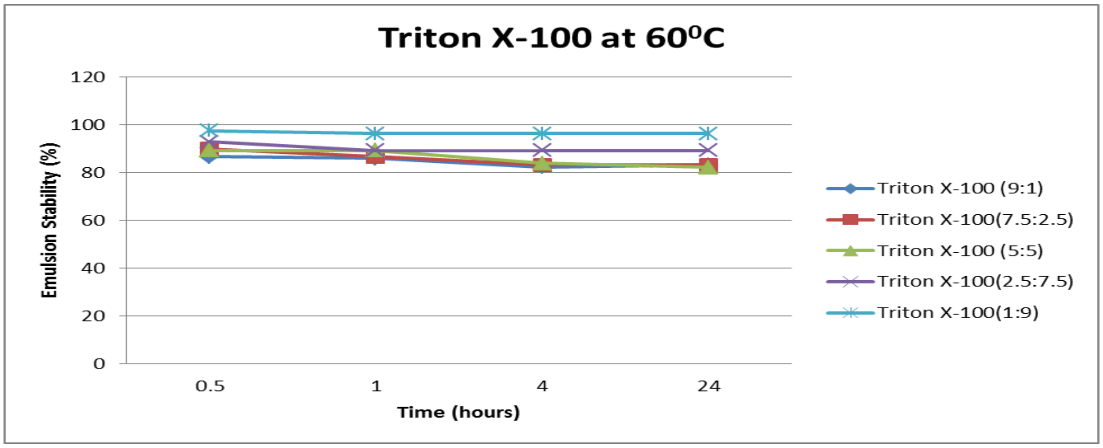


Figure 4.6. Stability of Triton® X-100 at 60^{0}C over 24hours

At 25^0C (figure 4.4 above) , sample with water-to-oil ratio 5:5 is more stable with emulsion stability of 93% over 24hours. The same trend is seen again under 45^0C (see figure 4.5 above) where emulsion stability remainied constant at 93% over 24hours. However, this was changed under 60^0C where the emulsion stability dropped to 89% and remained constant after 4 hours reaching 83% emulsion stability (see figure 4.5 below).

For 1:9 and 2.5:7.5 emuslion is stable and no clear phase separation is seen with the naked eye. Ony at 60^0C the emuslions become unstable reaching only 96% and 89% stability over 24 hours respectively. A different stability is seen in sample with ratio 9:1 where stability of emuslion increases with time then decreasing. This could be due to coalescence. There was no significant change in emulsion stability when comparing solutions at 60^0C and when they were first mixed at room temperatures.

As seen from the graphs above (figure 4.1-4.6) , temperature has a great impact on emulsion stability; according to Kokal (2002) temperature affects the rate of build-up of interfacial films by varying the absorption rate and characteristics of the interface. Also, it influences the film compressibility by changing the solubility of the crude oil surfactants in the continuous phase. Application of heat can promote demulsification because heat increases droplet collisions and favours coalescence and settling of water droplets. Table 4.1 gives a summary of these emulsion stability results of surfactants only under these various temperatures.

4.2. Emulsion stability of <u>nanoparticle ZnO and surfactant</u> with crude oil

ZnO is not soluble in water; it is expected for the nanoparticle powder to not reach full homogeneity with samples having a higher volume of the aqueous phase and to settle at bottom. Since the nanoparticle is less than 30nm in diameter, it can either be hydrophilic or hydrophobic; in this case it is showing characteristics of being hydrophobic

Addition of ZnO gave a more stable emulsion for the first hour under 25^0C and thereafter the stability decreased, although at a lower rate and percentage than when the mixture had surfactant only. This rapid decrease is attributed to the insolubility of ZnO. The nanoparticle did not mix well with the aqueous solution as expected and thus some of it had settled at the bottom. This had a major influence on the emulsion stability formed as seen in figure 4.7-4.12.

4.2.1. The effects of temperature on emulsion stability of DTAB with ZnO

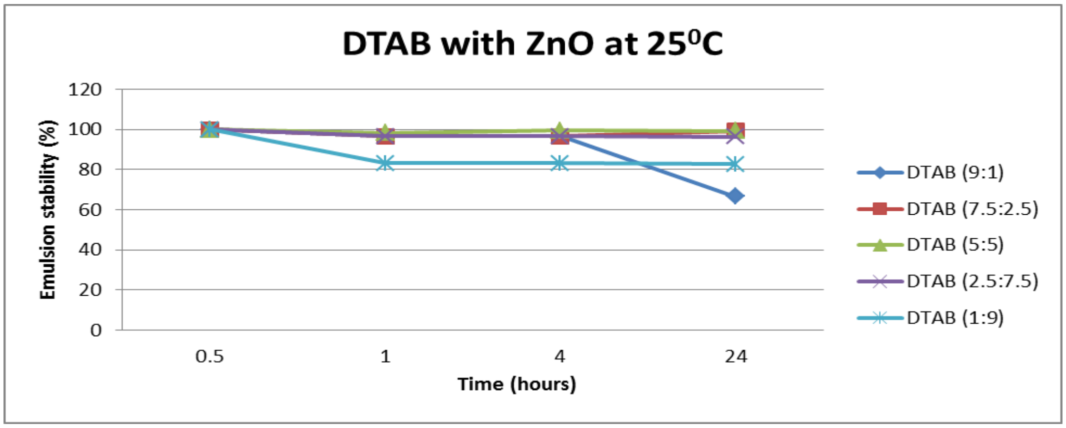


Figure 4.7. Stability of DTAB with ZnO at 25^0C over 24hours

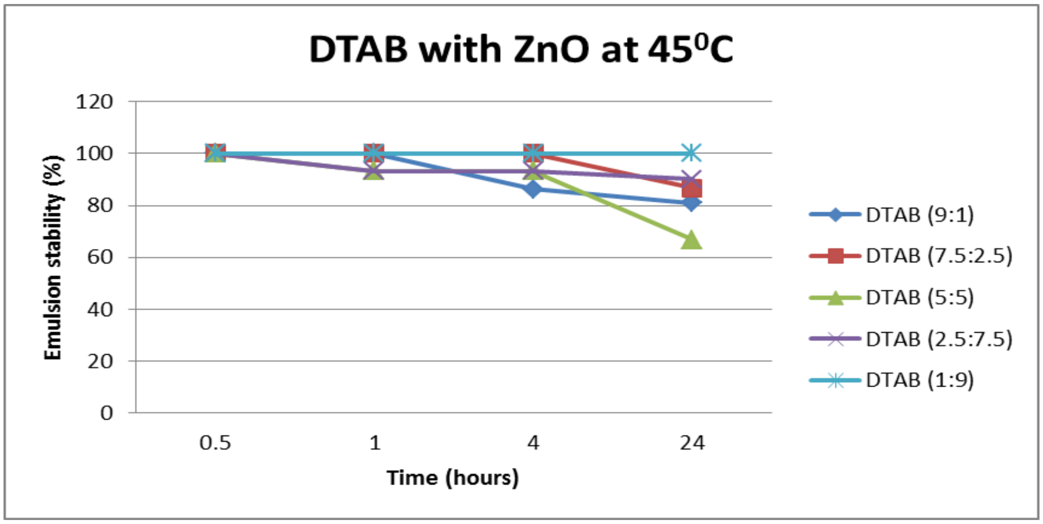


Figure 4.8. Stability of DTAB with ZnO at 45^0C over 24hours

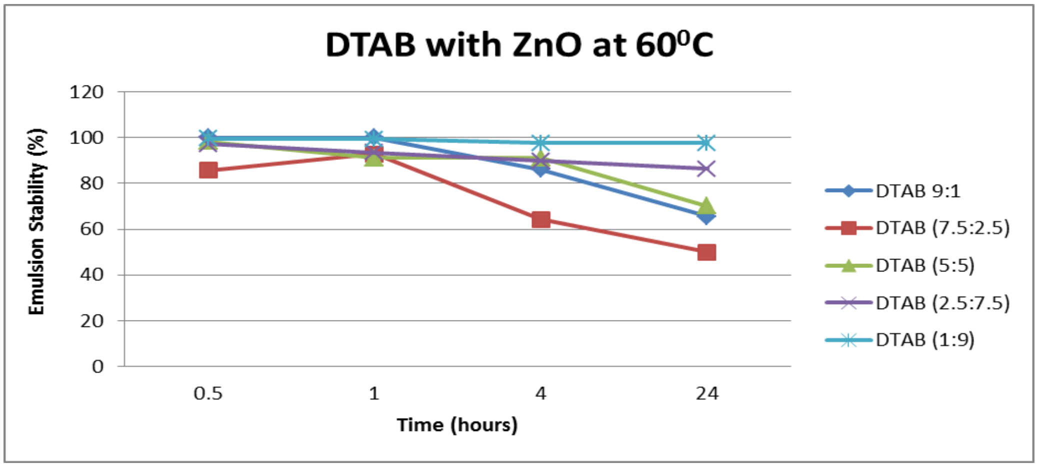


Figure 4.9. Stability of DTAB with ZnO at 60^0C over 24hours

The sample with water-to-oil ratio of 5:5 was more stable with the addition of ZnO nanoparticle, an average of 93% emulsion stability was reached under all temperature conditions and with the emulsion stability remaining constant for 24hours at 25^0C (figure 4.10). At 45^0C and 60^0C the stability decreases to 66% and 70% respectively, this is still more stable than when solution mixture was surfactant only.

No change in stability is seen for 1:9 under 45^0C and 60^0C, see figure 4.8 and 4.9 above, where emulsion stability remained 100% with the addition of ZnO. However, under 25^0C (see figure 4.10), there was phase separation and only 96% emulsion stability was reached. The ZnO settled at the bottom creating the instability. This was a different case for sample with water-to-oil ratio of 9:1, the emulsion under 25^0C was stable and constant for 4 hours (100%) and thereafter phase separation occurred dropping stability to 66%, the same is observed under 60^0C but instability occurred earlier. Under temperatures of 45^0C instability is also just after an hour reaching a constant emulsion stability of 81% thereafter.

When the water to oil ratio was 7.5:2.5 and 2.5:7.5, only 96% emulsion stability was reached at 25^0C, however, under higher temperatures both samples were less stable with 7.5:2.5 reaching emulsion stability of 65%. For a summary of these results please refer to Table 4.2.

4.2.2. The effects of <u>temperature</u> on emulsion stability of Triton® X-100 with ZnO

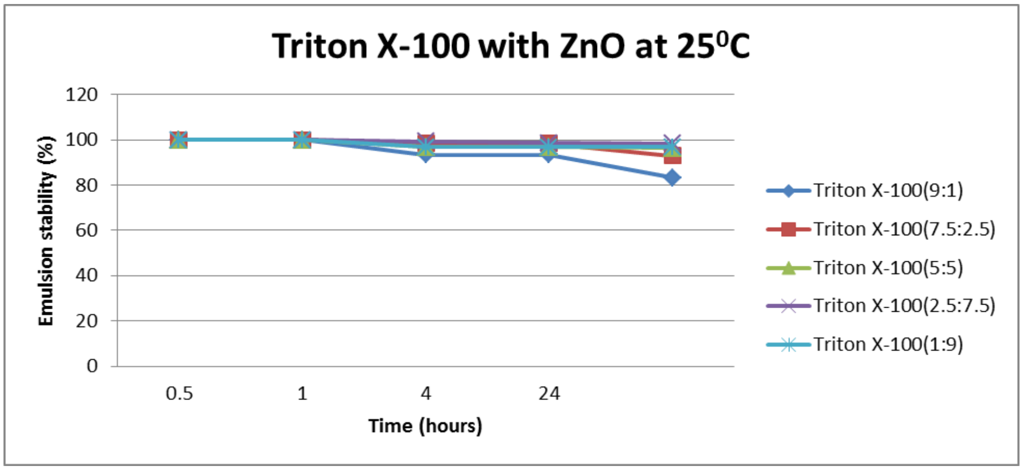


Figure 4.10. Stability of Triton® X-100 with ZnO at 25^0C over 24hours

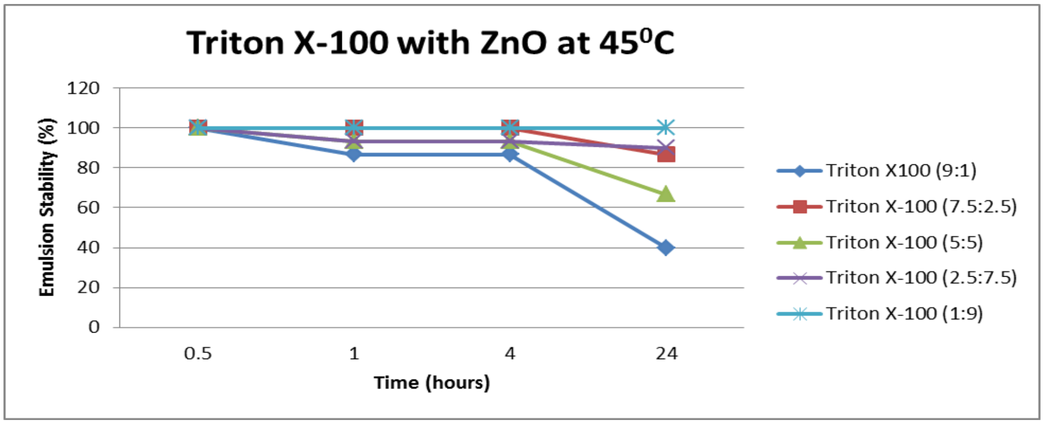


Figure 4.11. Stability of Triton® X-100 with ZnO at 45^{0}C over 24hours

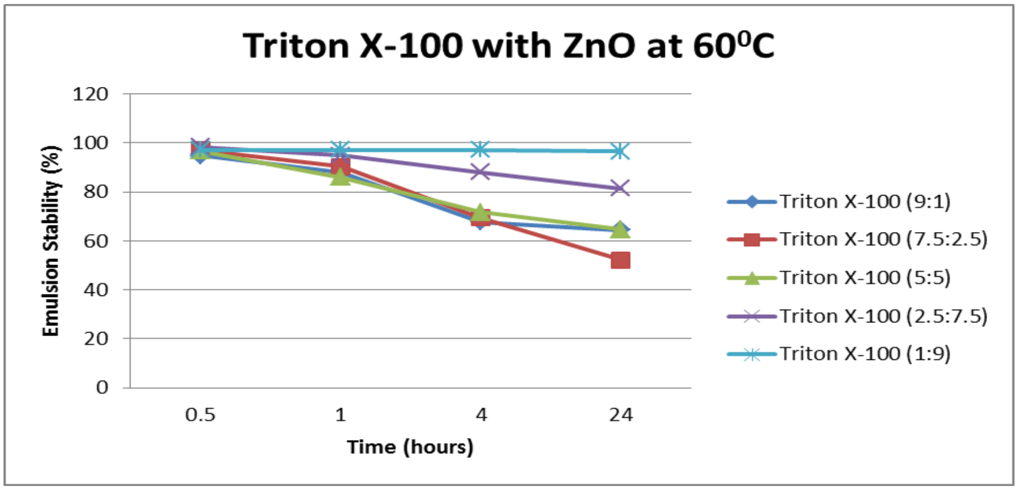


Figure 4.12. Stability of Triton® X-100 with ZnO at 60^{0}C over 24hours

Looking at the non-ionic surfactant, Triton® X-100, when ZnO is added to the samples with water-to-oil ratio of 7.5:2.5 and 2.5:7.5 behave similar to DTAB when mixed ZnO as discussed above. These samples are more stable at 25^{0}C (see figure 4.10) but decreases drastically under higher temperatures (figure 4.12); 7.5:2.5 reached emulsion stability of 64% and 2.5:7.5 reaches 98%.

Sample 5:5 also proves to be more stable with the addition of ZnO as stability reaches 96% under 25^{0}C and remains constant for 24hours. This is a much better stability than with Triton® X-100 only which saw stability of only 40% after 24hours. However, after a week the emulsion stability with ZnO dropped again.

4.3. Effects of <u>phase ratios</u> on Emulsion Stability

4.3.1. The effects on DTAB emulsion stability

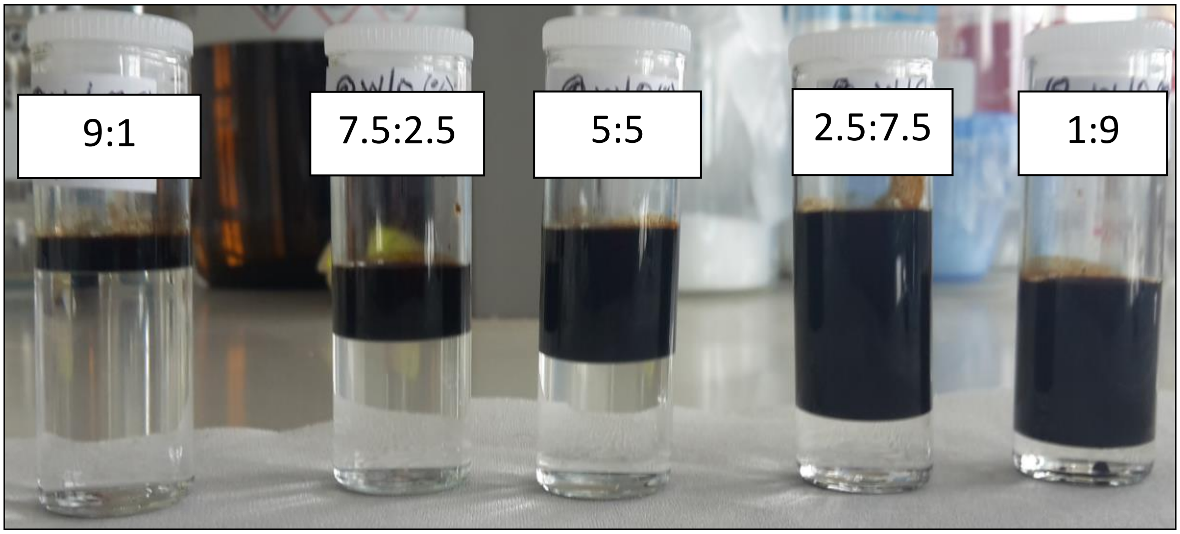


Figure 4.13. Water-Oil ratio of DTAB, brine solution and crude oil. Before mixing

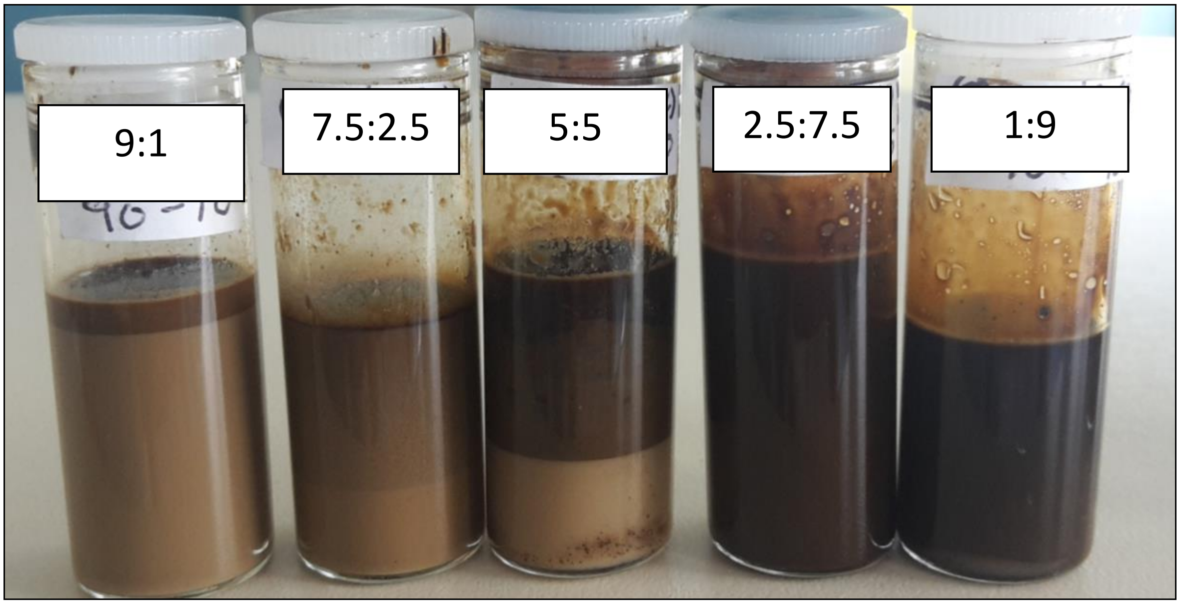


Figure 4.14. Water-Oil ratio of DTAB, brine solution and crude oil after mixing

The different water-to-oil ratios had a great influence on the stability of the emulsion formed. Samples with 9:1 and 7.5:2.5 formed a more stable emulsion. These samples are aqueous (water) continuous and the aquoeus phases was more brown in colour, therefore they must have contained oil droplets. Same applies to samples with water-to-oil ratio of 2.5:7.5 and 1:9 which are oil continuous but these samples have no clear phase separation. The darker colour of the emulsion formed indicates oil in water(o/w) emulsion.

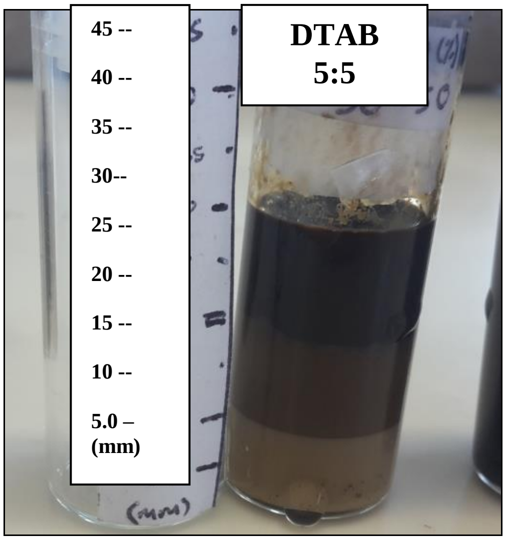


Figure 4.15. Three layers formed for sample with water-to-oil ration 5:5

The sample with ratio of 5:5 in figure 4.15 show phase separation in an almost equal percentage, at higher temperatures three layers had formed (see figure 4.14). After an hour these three layers started coalescing to form only two phases, this explains the slight decrease in emulsion stability seen in figure 4.3 when the phases converted into two layers (this can also be attributed to higher temperatures).

4.3.2. The effects on Triton® X-100 emulsion stability

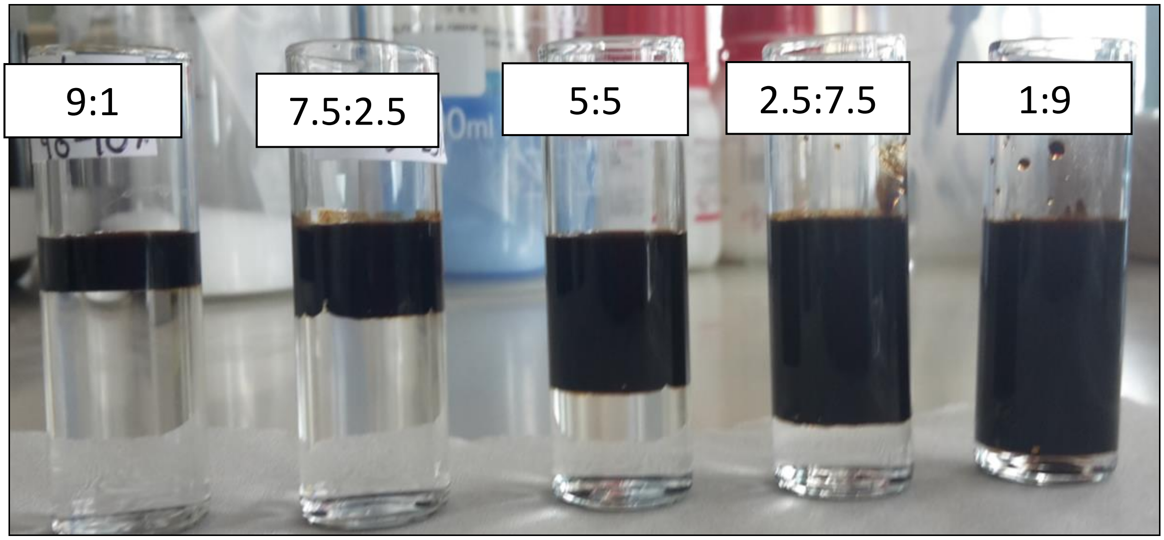


Figure 4.16. Water-Oil ratio of Triton® X-100, brine solution and crude oil. Before mixing

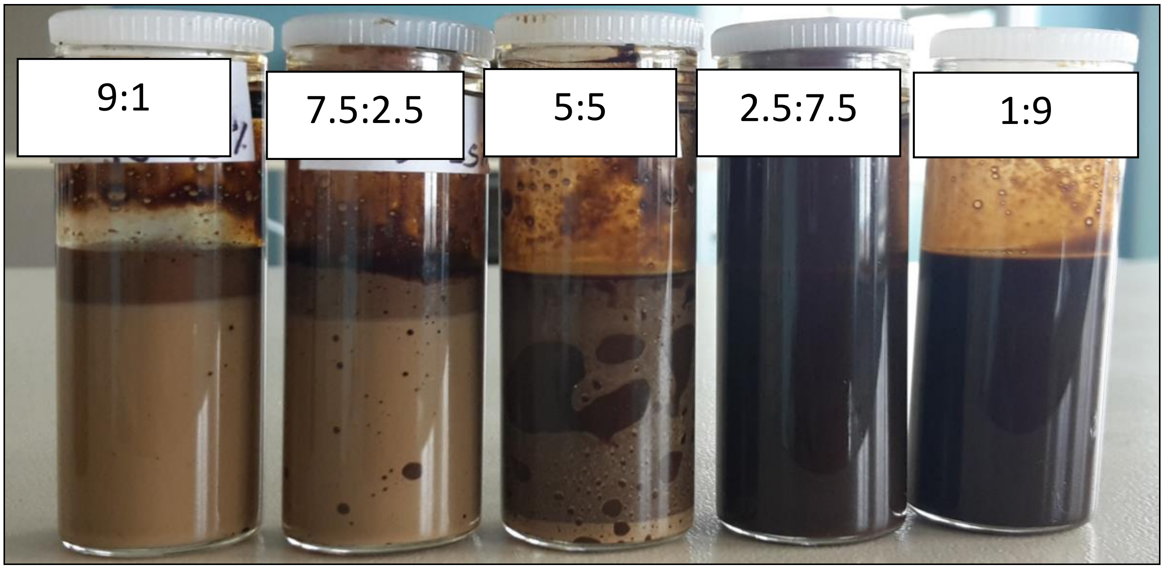


Figure 4.17. Water-Oil ratio of Triton® X-100, brine solution and crude oil after mixing

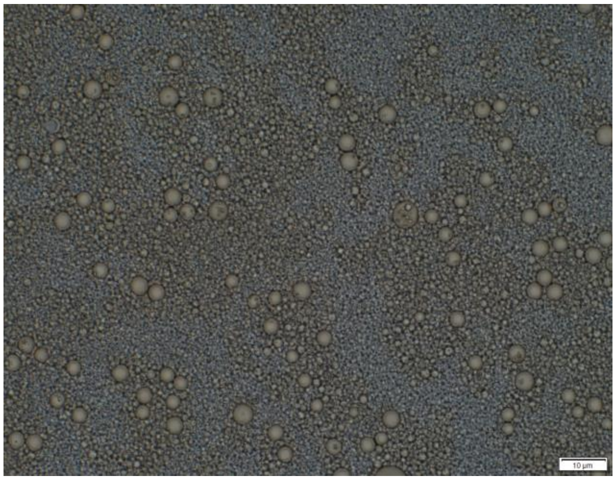
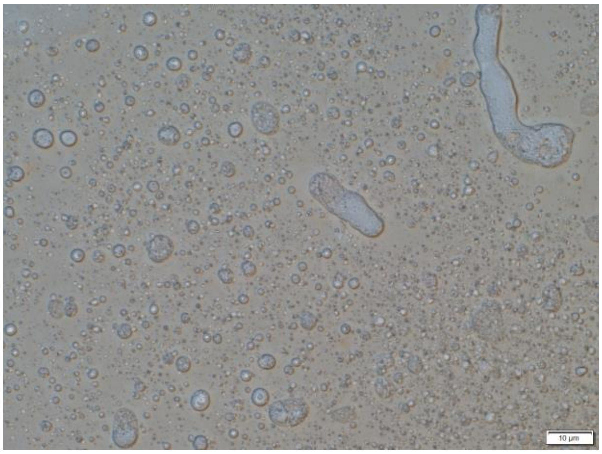
Emulsions formed were unstable for 9:1, 7.5:2.5 and 5:5 as phase separation occurred. Here, the viscous property of Triton® X-100 gives less phase separation over time. The continous aqueous phase is brown in colour for 7.5:2.5 suggesting an oil-in-water(O/W) emulsion had formed as seen by the oil droplets in the aqueous phase (see figure 4.9). Higher speed was required to mix sample 5:5 and the continous phase showed O/W emulsion, the dark brown colour supports this and also the droplets of oil stuck along the side walls of the test tube.

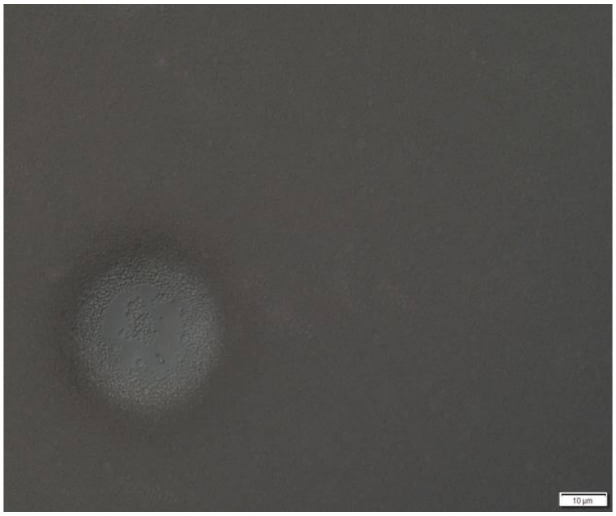
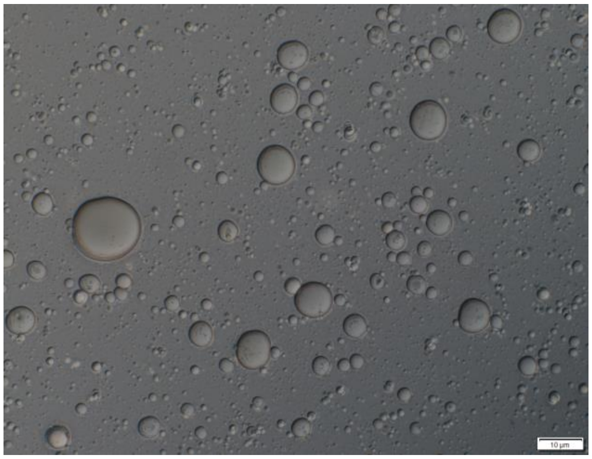
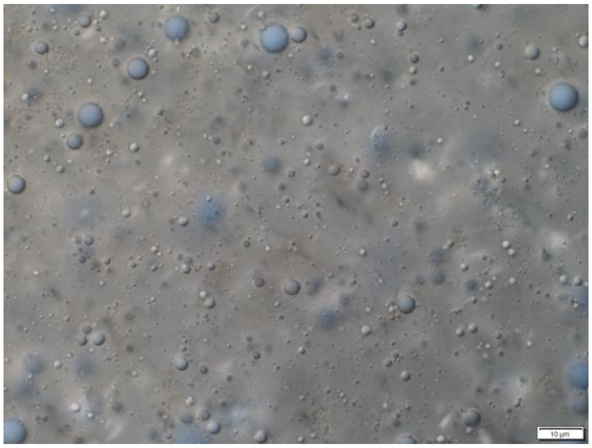
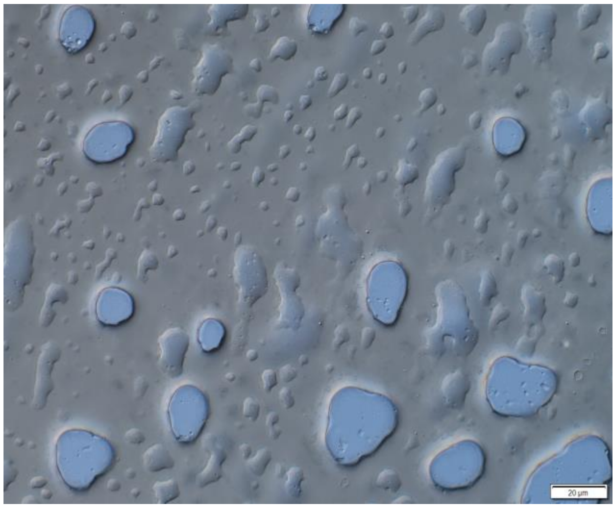
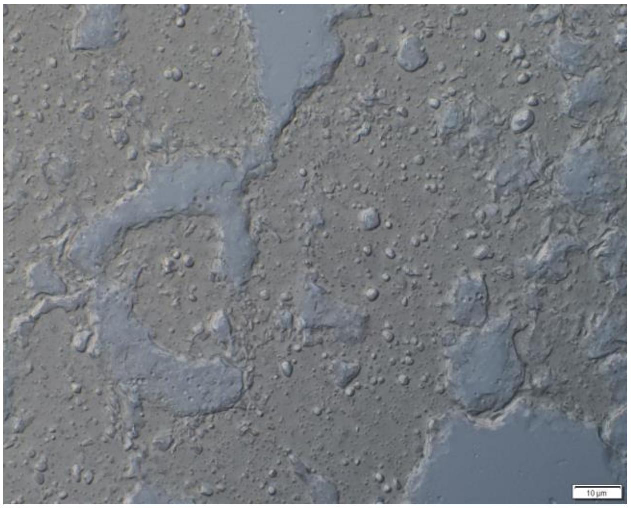
The oil continuous phases of sample 2.5:7.5 and 1:9 had no clear visible separation, the continuous phase was slightly less darker (almost dark brown). Visual observations gave evidence of droplet coalesce; that is, free water (aqueous) was observed.

4.4. Droplet size distribution of emulsions formed

The samples were analysed using a microscope to determine if the emulsions are Oil-in-Water (O/W) or Water-in-Oil (W/O) emulsions. As it is commonly known, emulsions look dark and less bright when they have large diameter droplets (low total interfacial surface area). It is therefore expected for experimental samples with W: O ratios of 2.5:7.5 and 1:9 to have large diameter droplets because emulsions formed are darker in colour (figure 4.13 and figure 4.15). For samples with W: O ratios of 9:1 and 7.5:2.5 diameter droplets formed are expected to be smaller because of the light brown colour of the emulsion. As a rule of thumb, the smaller the average size of the dispersed water droplets, the tighter the emulsion.

4.4.1. The effects of surfactant type on size and distribution of droplets

DTAB (9:1)	**Triton® X-100 (9:1)**
	
DTAB (7.2:2.5)	**Triton® X-100 (7.5:2.5)**

	
DTAB (5:5)	**Triton® X-100 (5:5)**
	
DTAB (2.5:7.5)	**Triton® X-100 (2.5:7.5)**
	
DTAB (1:9)	**Triton® X-100 (1:9)**

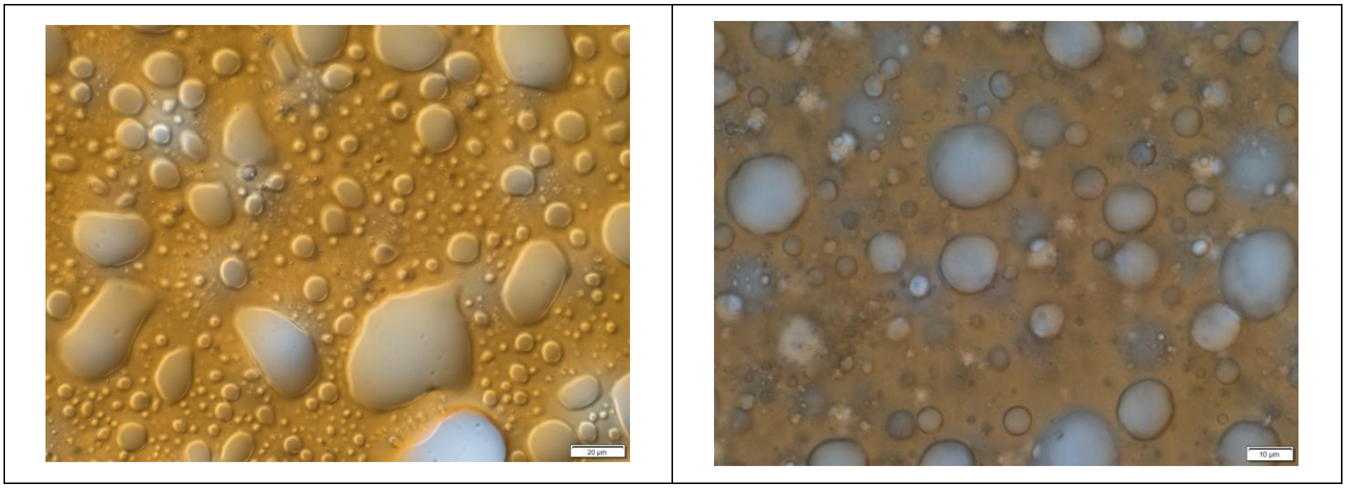


Figure 4.18. Microphotographs (100X) of surfactants DTAB (left) and Triton® X-100 (right) at 25^0C

Emulsions that have smaller size droplets (≤10 micron) will generally be more stable. The droplet size distribution affects emulsion viscosity because it is higher when droplets are smaller Since emulsion stability depends on droplet size, droplet size distribution and formation of interfacial films (known to decrease ITF and as a result increases emulsion stability), figure 4.18 compares droplet sizes formed and its effect on emulsion stability for the two surfactants (dodecyl trimethyl; ammonium bromide (DTAB) and Triton® X-100)

For samples with water to oil ration 9:1, the DTAB formed interfacial films more than Triton® X-100, however, for 1:9 the Triton® X-100 show smaller droplets and more interfacial films formed than DTAB as seen in Figure 4.18. Looking at the temperature graphs in figures 4.1 and 4.4 this finding is supported because it is seen that at 25^0C samples 9:1 for DTAB show 80% emulsion stability just after 30 minutes and Triton® X-100 show 70%.

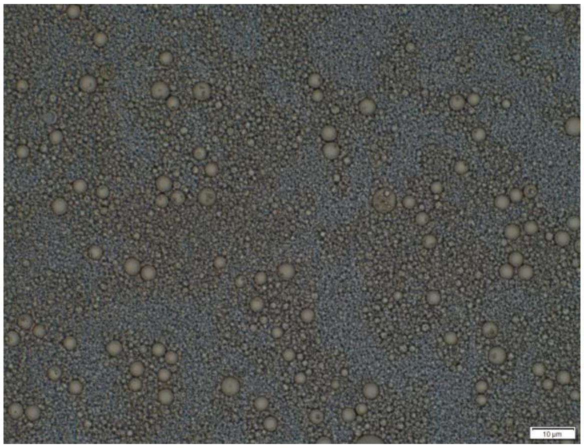
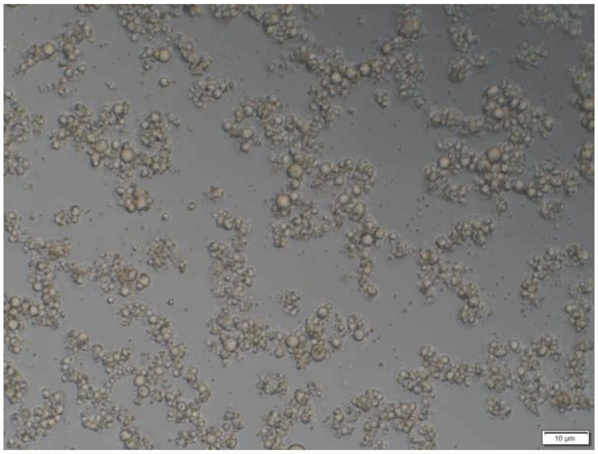
Samples with ratios 7.5:2.5 show random larger droplets with the majority of the sample made up of smaller droplets. For DTAB the random large droplets are far smaller than those formed in Triton® X-100. In contrast, for samples 2.5:7.5, the DTAB have regular shaped droplets in comparison to Triton X-100. Here, the droplets of DTAB show presence of interfacial film whereas for the Triton there is no clear observation-the droplets appear to be more cemented and irregular in shape.

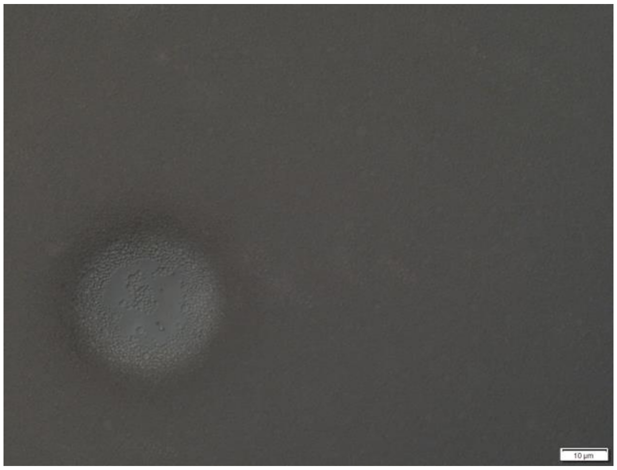
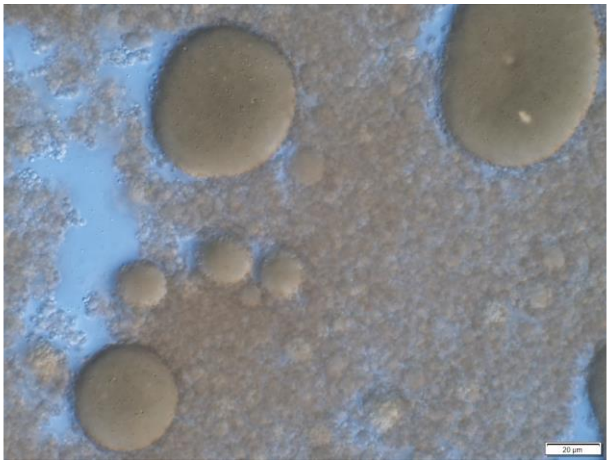
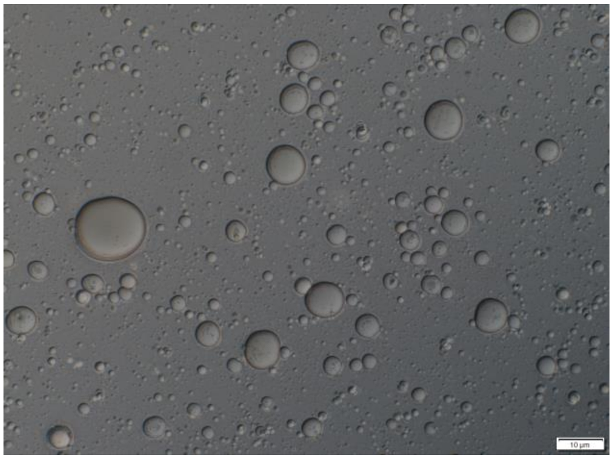
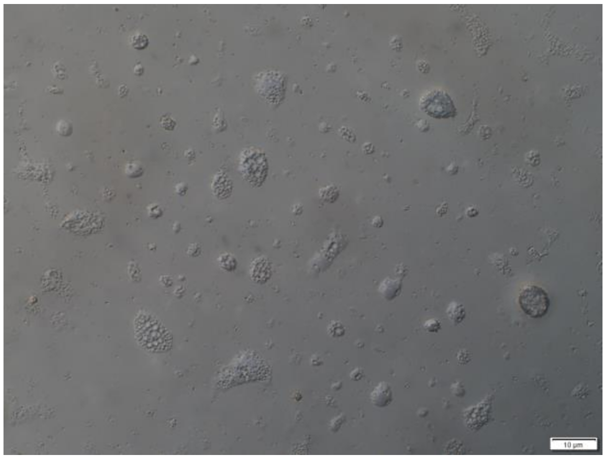
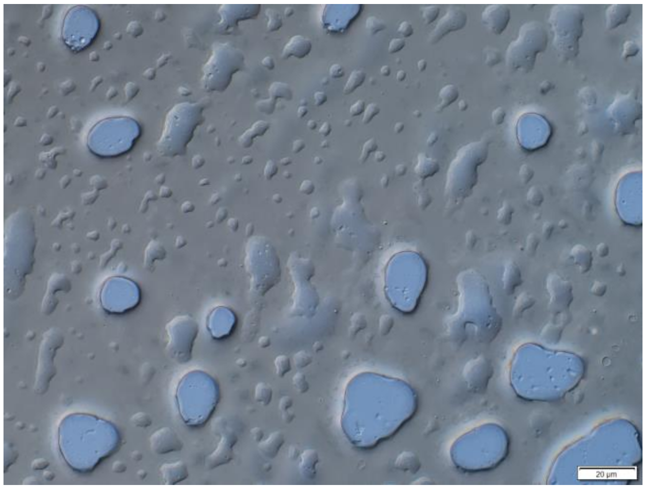
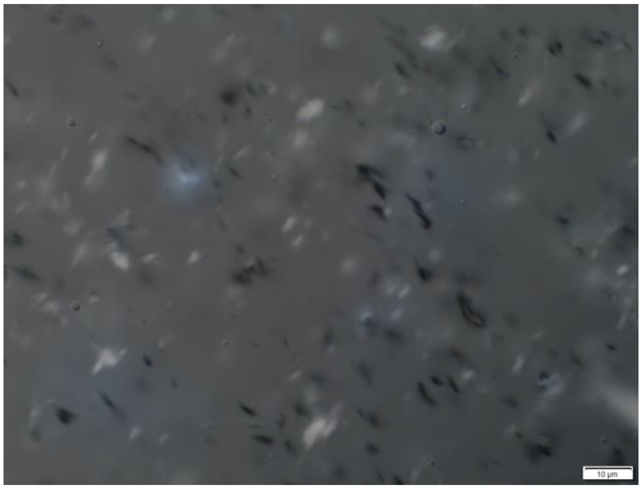
When looking at the samples with water to ratio of 5:5, the droplets formed for Triton® X-100 is much smaller in size compared to DTAB. For both samples interfacial film did form, for this phase ratio, DTAB is less stable than Triton® X-100 because of the larger droplet sizes that formed. This is further supported by the temperature graphs of the two surfactants at 25^0C where DTAB emulsion stability was just above 40% after 24 hours and Triton® X-100 was at 93% (figure 4.1 and 4.4 above).

4.4.2. The effects of nanoparticle (ZnO) on size and distribution of droplets

I. Dodecyl Trimethyl Ammonium Bromide (DTAB) with ZnO

The droplet size distribution for DTAB is different for the different W:O ratios. For samples that are water continuous i.e. samples 9:1 and 7.5:2.5 the droplet sizes are smaller, when looking at higher magnification (100X) the droplet sizes for 7.5:2.5 are not as clear, they are less than 10 square micron (μm^2), the droplets were continuously in motion during observation (see figure 4.17). For sample 9:1; the droplets formed here had formed an interfacial film around the droplets indicating a decrease/lowering of interfacial tension (IFT). These samples formed O/W emulsions whereas samples 2.5:7.5 and 1:9 (oil continuous phases) have formed W/O emulsions. This is due to having more oil in the poly vials and the water droplets being smaller than the oil droplets.

DTAB (9:1)	**DTAB + ZnO (9:1)**
	
DTAB (7.2:2.5)	**DTAB + ZnO (7.5:2.5)**

	
DTAB (5:5)	**DTAB + ZnO (5:5)**
	
DTAB (2.5:7.5)	**DTAB + ZnO (2.5:7.5)**
	
DTAB (1:9)	**DTAB + ZnO (1:9)**

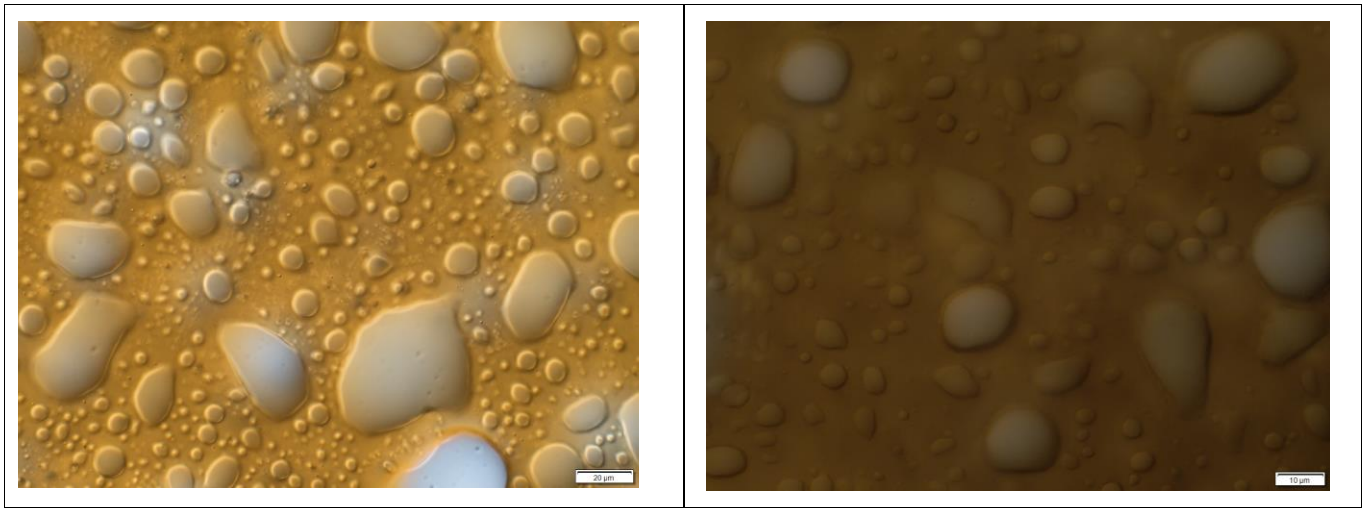


Figure 4.19. Microphotographs (100X) of surfactants DTAB (left) and DTAB with ZnO (right) at 25^0C

The sample with W:O ratio of 5:5 has formed more random big oil droplets with evidence of coalescence .

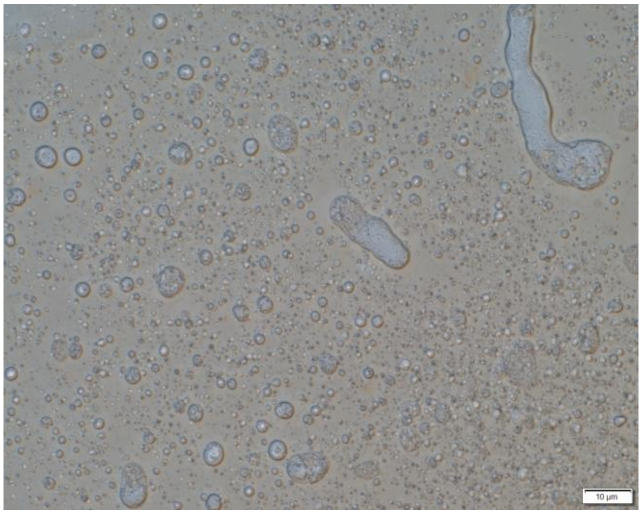
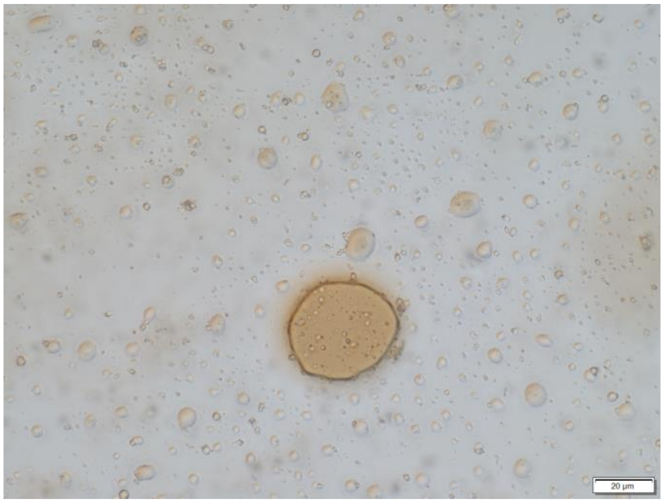
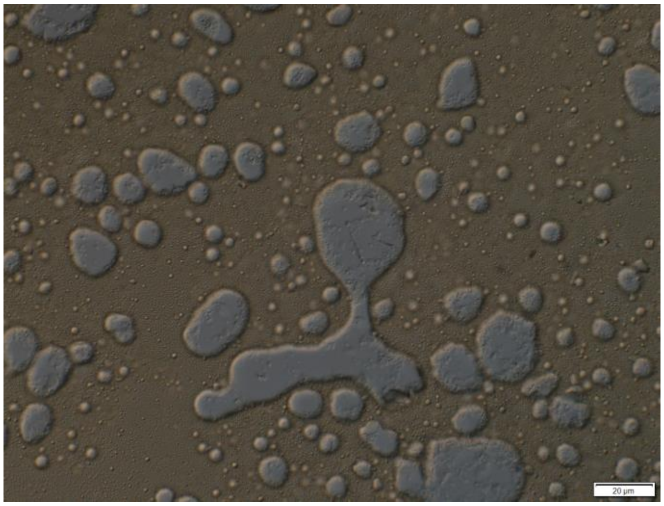
When nanoparticle ZnO was added, much smaller droplets were formed for samples 9:1 and 5:5. The ZnO nanoparticle decreased the oil droplet sizes; for 5:5, the droplet sizes look more cemented with traces of what looks like ZnO nanoparticles inside the droplets formed. On the other hand, sample 7.5:2.5 show more random big droplets with a concentration of ZnO. For oil continuous samples, 1:9, the droplet sizes formed weren’t as significantly different from samples with surfactant only.

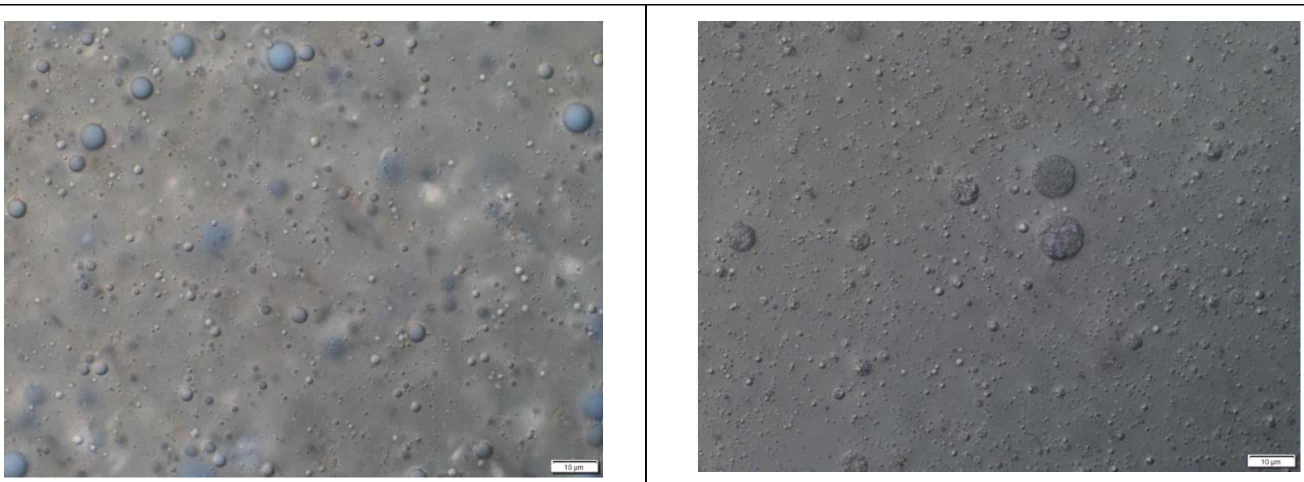
The emulsion stability formed with surfactant DTAB only was less stable, addition of ZnO helped increase emulsion stability especially for sample 5:5.

II. Triton® X-100 with ZnO

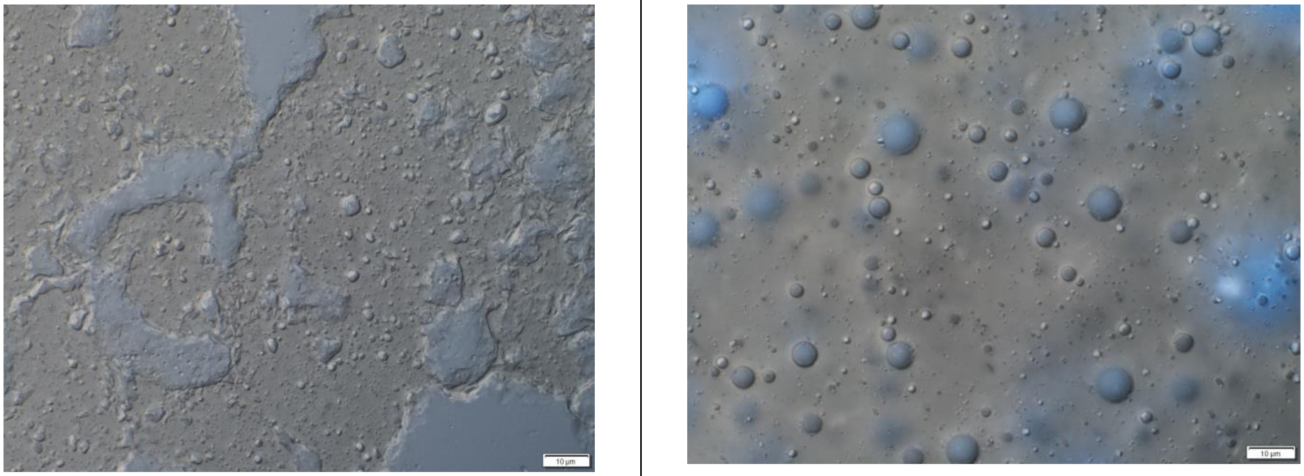
The figure 4.18 below show the droplet size of emulsions formed for Triton® X-100 and when Zinc Oxide nanoparticle is added to Triton® X-100. The different droplet sizes formed are observed and their effect on stability of emulsion formed.

This non-ionic surfactant resulted in droplet sizes that are much smaller than with cationic dodecyl trimethyl ammonium bromide (DTAB). The droplet size distribution was not as spread out for sample having water to oil ratio of 9:1, random irregular shaped droplets formed, this could be as a result of merging of droplets. This is however different when ZnO particle is added, the random bigger droplets that formed are more round and the smaller droplets that formed are less than those formed with surfactant only. With 7.5:2.5 the oil droplets formed are smaller than those under nanoparticle ZnO (figure 4.18) this is the opposite of what was expected.

Triton® X-100 (9:1)	**Triton® X-100 + ZnO (9:1)**
	
Triton® X-100 (7.2:2.5)	**Triton® X-100+ ZnO (7.5:2.5)**
	
Triton® X-100 (5:5)	**Triton® X-100+ ZnO (5:5)**



Triton® X-100 (2.5:7.5) | **Triton® X-100+ ZnO (2.5:7.5)**



Triton® X-100 (1:9) | **Triton® X-100+ ZnO (1:9)**

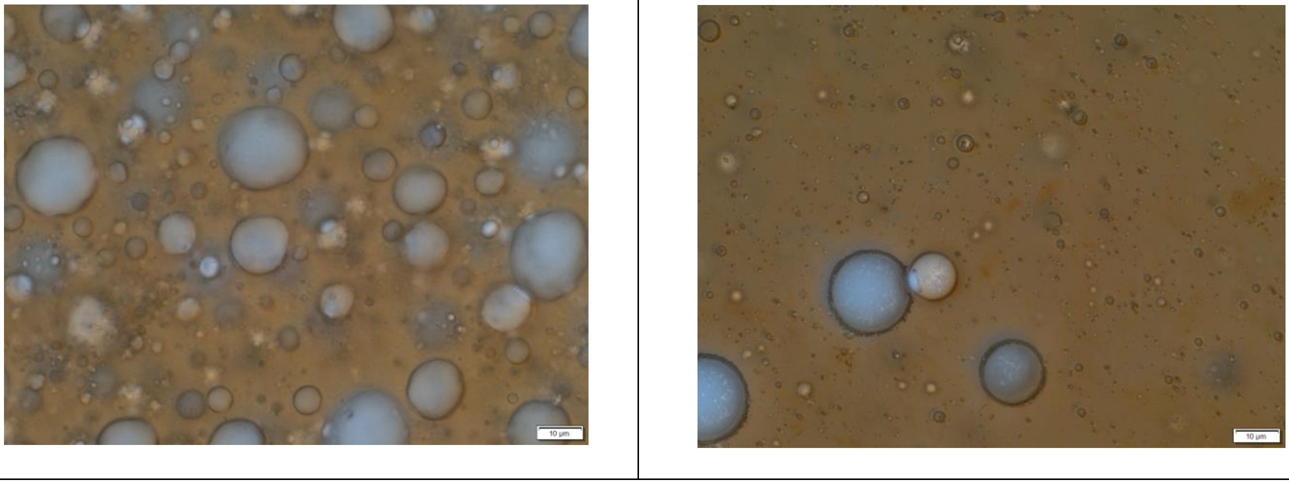


Figure 4.20. Microphotographs of surfactant Triton® X and Triton® X-100 with ZnO at 25^{0}C

When the oil and aqueous phases are in equal ratios (5:5) the droplet sizes formed are more regular and round with the average grain size being small, random sizes are more medium in size than large. An addition of nanoparticle ZnO created a more cemented droplet sizes with the average grain sizes being smaller than when emulsion contained only the surfactant.

Sample 2.5:7.5 formed droplet sizes that are irregular in shape and appear to be more cemented (figure 4.12), with addition of ZnO the droplet sizes appear more round in shape with a dark film formed around them. This supports the increase in emulsion stability with an addition of nanoparticle. When looking at sample containing water to oil ratio of 1:9 , the water droplets that formed are round and bigger when the sample contains only surfactant, when ZnO is added, the water droplet formed are much smaller with other random medium sized droplets forming. These medium droplets have a solid black interfacial film around them, this decreases any interfacial tension formed and thus increasing emulsion stability. Similar interfacial film is observed in 2.5:7.5 and 7.5:2.5. Table 4.4 summarises the effects of phase ratio on droplet size.

4.5. Summary of results

Table 4.1: Stability results of Surfactant

Water to Oil ratio (W:O)	Cationic DTAB	Non-ionic Triton® X-100
9:1	• Unstable at 25^0C Figure 4.1	• Unstable at 25^0C Figure 4.4
7.5:2.5	• Unstable at 25^0C Figure 4.1	• Unstable at all temperatures Figures 4.4-4.6
5:5	• Unstable at 25^0C Figure 4.1	• Unstable at all temperatures Figures 4.4-4.6
2.5:7.5	• Stable Figure 4.1	• Stable at 25^0C Figure 4.4
1:9	• Stable only at 25^0C Figure 4.1	• Stable at 25^0C and 45^0C Figure 4.4 and 4.5

Table 4.2: Stability of Surfactant & ZnO

Water to Oil ratio (W:O)	DTAB + ZnO	Triton® X-100+ ZnO
9:1	• Unstable at 25^0C • Figure 4.7	• Unstable at 25^0C Figure 4.10
7.5:2.5	• Unstable at 25^0C	• Unstable at 25^0C Figure 4.10
5:5	• More stable at 25^0C • Three layers formed at 45^0C Figure 4.7 and Figure 4.8	• Unstable at 25^0C Figure 4.10
2.5:7.5	• Unstable at 25^0C • Stable at 45^0C Figure 4.8	• Stable at 25^0C Figure 4.10
1:9	• Stable at 25^0C and 45^0C Figure 4.7-4.9 • Unstable at 60^0C	• Unstable at 60^0C Figure 4.12 • Stable at 25^0C and 45^0C

Emulsion formed of cationic DTAB surfactant with brine and crude oil is more stable under room temperature (25^0C) than at 60^0C . Looking at non-ionic surfactant emulsion stability, we see more stability at all temperatures much better than that seen with cationic surfactant.

When nanoparticle is added to the solution, the emulsion is more stable at higher temperatures but not for long. This is seen for both cationic surfactants.

Table 4.3: Expectations of Chemicals added and results

Chemicals	Expectations	Results
DTAB	• O/W stable due to charge effect • Not temperature sensitive	• O/W unstable emulsion • Sensitive to high temperature
Triton® X-100	• Stable due to its viscosity	• Unstable • High temperature sensitive
DTAB + ZnO	• Stable at 25^0C and 45^0C •	• Unstable • ZnO settled to the bottom
Triton® X-100 + ZnO	• Stable • Hydrophilic	• Unstable • Temperature sensitive

The results of emulsion stability of non-ionic surfactant with brine and oil solution vs adding nanoparticle was not what was expected.

Table 4.4: Effects of Phase Ratios on drop and size

Water to Oil ratio (W:O)	Expectations	Results
9:1	- Smaller droplet size formation due to the light brown emulsion	- Loose emulsion - unstable
7.5:2.5	- Smaller droplet sizes formation due to the light brown colour - Stable and tight emulsion	- Small and random medium to large sized droplets formed - Figure 4.17-4.18
5:5	- Medium oil droplets to form due to the darker brown colour - Figure 4.17-4.18	- Smaller droplets formed for non-ionic - Medium droplets formed for cationic surfactant
2.5:7.5	- Large droplets to form due to the darker brown colour of the w/o emulsion formed - Loose and unstable emulsion	- Smaller-medium droplets formed for cationic - Medium to large droplets formed for non-ionic surfactant
1:9	- Large droplets to form due to the darker brown colour formed - Loose and unstable - Figure 4.17-4.18	- Smaller-medium droplets formed for non-ionic - Medium to large droplets formed for cationic surfactant - Stable

When surfactant was the continuous phase loose emulsions formed and this was seen in the light brown colour that formed. It was expected that the emulsion formed would be stable but this was not the case. When oil was the continuous phase, it was expected for the emulsion formed to be unstable, however this was the opposite and more stability was seen and smaller to medium droplet sizes seen indicating a tighter emulsion.

5. CONCLUSION AND RECOMMENDATION

From the experimental work conducted it is evident that surfactants dodecyl trimethyl ammonium bromide (DTAB) and Triton® X-100 (1 wt%) are good candidates for forming stable emulsions with real crude oil systems. Triton® X-100 provided a much better emulsion stability due to its viscosity and critical micellar concentration (CMC) being greater than DTAB. Higher concentrations (2wt% or more) are recommended to be used in future.

By changing the ratios of oil-to-water, we found that when the continuous phase is oil (1:9 and 7.2:2.5), emulsion formed were more stable for both surfactants. When aqueous solution and oil were in equal ratios (5:5) the solution separated when the continuous phase was aqueous the emulsion was less stable. An oil-to-water ratio affects emulsion stability therefore the amount of surfactant injected is critical.

Addition of nanoparticle ZnO provided an increase in stability of emulsions formed, reaching close to 100% for samples that are oil continuous. A mixture of surfactant and nanoparticle provides a better emulsion stability than when surfactant is used alone. Since some of the ZnO solid nanoparticles settled at the bottom, a recommendation is that ZnO nanorods (NRs) be used in future as they display better physical properties compared to ZnO nanoparticles. Further investigation is however required.

By increasing the temperature we found that the emulsions were more stable at room temperatures (25^0C) than at 45^0C and 60^0C; emulsion stability lasted longer, however, when temperatures were higher the stability didn't last as long. It was expected for emulsion stability to be greater at temperatures above 25^0C since the crude oil viscosity decreases at higher temperatures. However, at higher temperatures the kinetic barrier to drop coalescence still exists and the existence of divalent cations present from the brine solution created ($CaCl_2$ + NaCl+ distilled water) contributed to emulsion instability. Divalent cations such as Ca^{2+} contribute to the properties of water that cause it to be hard therefore preventing coalescence. At room temperatures, pH of water is not affected and remains neutral(7); however at greater temperatures the pH of water decreases slightly because water molecules have the tendency to separate or break down into their elements (hydrogen and oxygen) as temperature increases. This can explain why the instability of emulsions at temperatures > 25^0C.

A mixture of nanoparticle and surfactants with crude oil was far less stable at 60^{0}C than when surfactant alone, this suggests nanoparticle to be more sensitive to higher temperatures.

It is unfortunate that during the period of this research the nuclear magnetic resonance (NMR) spectroscopy was not available to conduct the droplet size distribution analysis. Droplet size distribution information is required to back-up the observation made from microscopic analysis for the droplets formed, therefore it is recommended that a NMR analysis be done in future to obtain the average droplet size distribution information. Also, a pH analysis of samples is required to investigate the effects of temperature on pH and the resulting effect on emulsion stability.

Further investigation is required to look into the demulsification processes that are economical to separate the brine solution from the crude oil in preparation for distillation unit column.

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