Use of Surfactants for Crude Oil-in-Water Emulsions Demulsification

By

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DECLARATION

I, **Edith Laure Yonguep Ngoupeyou** declare that the contents of this thesis represent my own unaided work and that the thesis has not previously been submitted for academic examination towards any qualification. Furthermore, it represents my own opinions and not necessarily those of the Cape Peninsula University of Technology.

Signed	**Date**
Edith Yonguep	29 April 2020

ABSTRACT

Enhanced oil recovery (EOR), known as tertiary crude oil recovery, is an important technique applied by the petroleum industries to improve crude oil recovery. Over 30 to 60% of the original oil in place (OOIP) is improved by this technique as compared to primary and secondary techniques. However, the EOR technique results in the formation of stable water-in-oil and oil-in-water emulsions. Emulsions are undesirable in the petroleum industry as these add to the overall production cost and also to the loss of valuable amounts of crude oil. It is therefore essential for economic and environmental reasons to demulsify these emulsions in order to separate the oil from water. Chemical demulsification (use of demulsifiers to separate oil from water) is the most commonly practiced method to treat these emulsions. Nevertheless, no studies have been reported on the use of response surface methodology (RSM) to optimize the demulsification efficiency of crude oil-in-water emulsions resulting from the EOR technique.

This study aims to investigate the effectiveness of two demulsifiers, namely cetyl trimethylammonium bromide (CTAB), and trimethyl-tetradecyl ammonium chloride (TTAC) on the demulsification efficiency of crude oil-in-water emulsions resulting from EOR techniques using response surface methodology (RSM). In order to achieve this aim, synthetic oil-in-water emulsions containing various oil to water ratios (15:85, 25:75, 35:65 and 45:55) were simulated with diesel as the oil phase. The emulsion stability index (ESI) of the simulated oil-in-water emulsions was investigated based on the emulsifier concentration, homogenization speed, brine salinity and oil to water ratio. The result showed that an increase in the homogenization speed and surfactant concentration helped to achieve better ESI. It was also observed that high brine salinity led to poor emulsion stability for this case study. In addition, the oil to water ratio did not have much influence on the emulsions' stability index as long as the homogenization speed was as high as 24000 rpm. In this study, 2% surfactant concentration, 24000 rpm homogenization speed and 1000 ppm NaCl were the optimal conditions to formulate the emulsions. At this condition, the ESI of 15:85, 25:75, 35:65 and 45:55 was found to be 99.3, 92.5, 91.2, and 90% respectively.

Central composite design (CCD) and response surface methodology (RSM) was used to design and optimize the settling time, demulsifier concentration and the oil to water ratio on the demulsification efficiency of CTAB and TTAC. The results showed that the settling time, demulsifiers concentration, oil to water ratio as well as the interaction between the demulsifiers concentration and oil to water ratio had significantly impacted the response (demulsification efficiency) because of their p-values < 0.0001.

The quadratic model obtained was proven to be significant with the F-value of 16.03 and 16.63 for CTAB and TTAC demulsifiers respectively. The coefficient of determination (R^2) was found to be 0.944 and 0.863 for CTAB and TTAC demulsifiers respectively. These high values validated the accuracy of the model. The results revealed that a maximum demulsification efficiency of 82.6% and 80% was achieved by adding 850 ppm of CTAB and TTAC demulsifier and settling for 10 h with 15 and 25% diesel in water (D/W) emulsions respectively. These were proven to be the optimum conditions for maximum oil recovery for this case study.

It was also found that ageing the emulsion could greatly influence the performance of the demulsifier. This study showed ageing of the emulsions decreased the demulsification efficiency of CTAB from 86.66 for fresh emulsions to 50% after ageing the emulsions for 60 days.

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DEDICATION

To my caring brother Dr Semegni Jean Yves and my loving parents Mr Jouemo Ngoupeyou Thomas and Mrs Kondjio Elizabeth, I am forever grateful to you for your many sacrifices, love, and prayers.

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GLOSSARY

Terms/ abbreviation	**Definition/explanation**
ANOVA	Analysis of variance
CCD	Central composite design
CMC	Critical micelle concentration
CTAB	Cetyl-trimethylammonium bromide
DoE	Design of experiments
EOR	Enhanced oil recovery
ESI	Emulsions stability index
GDP	Gross domestic products
HLB	Hydrophilic lipophilic balance
IFT	Interfacial tension
OOIP	Original oil in place
PW	Produced water
RSM	Response surface methodology
TTAC	Trimethyl-tetradecylammonium chloride

CLASSIFICATION OF TERMS

Coalescence	The spontaneous joining of small droplets of an emulsion to for larger ones
Creaming	The natural tendency of a droplet of an emulsion to rise due to gravitational force
CMC	Critical micelle concentration
Crude oil	Naturally occurring liquid found from in geological formation from beneath the earth surface
Demulsification	Process of separating water from oil using chemical demulsifiers
Demulsifier	A chemical compound with the ability to destabilize emulsions
Emulsion	A mixture of two immiscible liquids in the presence of an emulsifying agent
Enhanced Oil Recovery	Advanced process technology of Oil and Gas recovery
Flocculation	Phase at which the distance between the droplets of an emulsion diminishes due to the weakening of the net attractive force between them
Hydrophilic Lipophilic number	The number ranged from 0 to 20 which determine the nature of the emulsion
Interfacial Tension	The adhesive force between two phases (e.g oil and water) in emulsion
PW: Produced Water Emulsions	Wastewater recovered at the surface of the well along with Oil and Gas during petroleum extraction
Surfactant	Surface acting compound responsible formation of the emulsion

CHAPTER 1: ENHANCED OIL RECOVERY

1.1. Chapter summary

This chapter provides an introduction and general background of petroleum recovery processes and petroleum produced emulsions known as oilfield emulsions, while emphasizing enhanced oil recovery (EOR) processes. It also outlines the problem statement, the aim, objectives, and motivation of the research. The research hypothesis and research scope are also viewed.

1.2. Introduction

Crude oil is one of the main sources of energy and its exploration and production are considered one of the most active industries of the twenty-first century (Igunnu & Chen, 2014). According to BP's statistical report of 2017, crude oil accounts for about a third of global energy consumption; it also supplies approximately 95% of the energy used for global transportation. Similarly, in South Africa, almost all (97%) of the energy needed in the transport system depends on crude oil, with more than 80% made up of petrol and diesel (Department of Energy Republic of South Africa, 2016; Cooper, 2007).

Since the 1850s the demand for crude derivatives has not stopped rising. According to Igunnu and Chen (2014), the world's daily demand for fuel consumption increased to 85 million barrels in 2006 and is estimated to rise up to 106.6 million barrels by 2030. Crude oil contributes to the economic growth of many countries such as the United State of America (USA), Saudi Arabia, South Africa, and many others. America's Oil and Natural Gas industry, (2016), projected that the production of crude oil in the USA will contribute about 300 000 jobs and will increase the gross domestic product (GDP) by $38.1 billion dollars by 2020. In South Africa, the petroleum industry provides about 692 706 jobs and adds to about R324 billon to the national gross domestic product (GDP) (Viljoen, 2017).

Crude oil, also known as petroleum, comes from the remains of animals and plants subjected to heat and pressure for millions of years over time. It accumulates in oil fields, between layers of impermeable rock (Allen *et al.,* 2011). Crude oil is recovered from underground wells through several recovery methods (primary, secondary and tertiary, also known as enhanced oil recovery) as shown in **Figure 1.1**. Initially, the trapped oil is brought to the surface under reservoir natural pressure (known as primary recovery). As the pressure is depleted the reservoir is pressurized with water or steam to maintain the flow of petroleum to the surface (secondary recovery). Primary and secondary recovery methods on the average produce less than one-third of the original oil in place (OOIP), therefore chemicals and energy in the form of heat are injected into the reservoir to alter the properties of the reservoir rock and to promote crude oil recovery (tertiary recovery or enhanced oil recovery) (Alagorni *et al*., 2015; Swearingen, 2000). It has been reposted that enhanced oil recovery (EOR) processes can achieve about 30 to 60% or more of the OOIP compared to primary and secondary processes which can only result in about 20 to 40% (Sino Australia Oil & Gas Pty Ltd 2013).

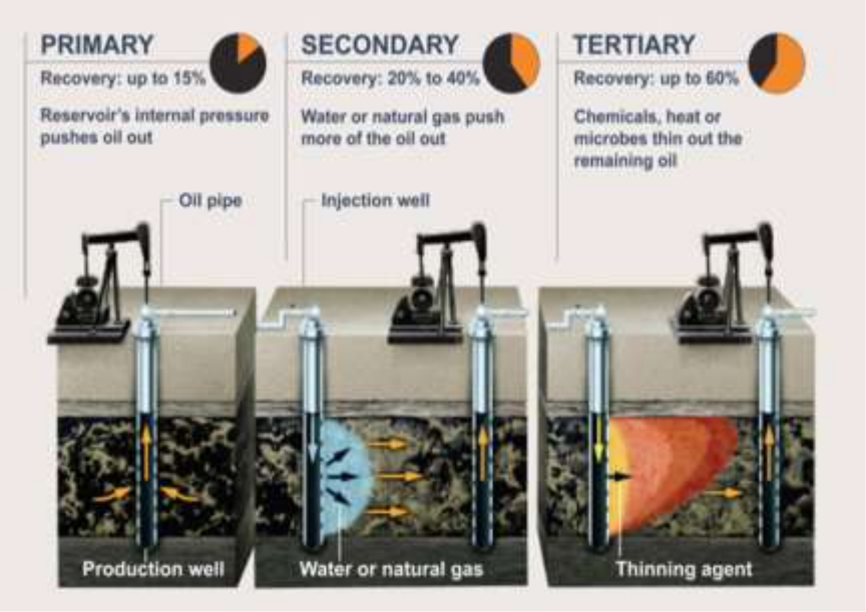


Figure 1:1: Stages of crude oil recovery (Tzimas & Georgakaki, 2005)

Enhanced oil recovery (EOR) techniques consist of injecting various chemicals such as surfactants, polymers, and alkali or their combination to help recover the remaining oil in the reservoir (Romero-Zerón, 2010). The production of crude oil by EOR techniques has drawn great attention in the petroleum industry because of its high recovery efficiency (over 60% of oil recovery) (Arash & Amir, 2014; Nguyen *et al*., 2011; Zolfaghari *et al*., 2016). However, the residue of this type of production is usually a mixture of crude oil, water, and sediments in their pure phases or different phases but mostly in the form of emulsions (water-in-oil and oil-in-water) called oilfield emulsions or produced emulsions (Nemer *et al*., 2013; Nguyen *et al*., 2012; Goldszal & Bourrel, 2000). Emulsions are formed when oil and water come into contact in the pipeline while being transported from the oil well to the surface, during drilling and processing of crude oil or at the refinery while cleaning up the plant (Kokal & Aramco, 2005). Oil field emulsion is often placed in open air pools known as production pitch in direct contact with the soil (Arash & Amir, 2014), and with time, these emulsions form very stable systems, extremely difficult to break or demulsify (Nguyen *et al*., 2012).

The oil and gas industry is among the largest liquid waste generators in the world, producing roughly three times as much water as crude oil, equivalent to an annual production of approximately 15 billion m^3 of produced emulsions (Allen *et al*., 2011). This volume is expected to increase as the daily demand for petroleum derivatives increases. Oilfield emulsions have become a great concern to the petroleum industry, as it leads to numerous operational problems such as increasing pumping cost, corrosion of pipelines during transportation and environmental problems such as soil contamination, and underground and surface water pollution (Nguyen *et al.*, 2012). It has also been reported that re-injecting these waters into the oil well as a way to enforce recovery is directly linked to seismic activities (Bakke *et al*., 2013). With the current strict environmental regulations, many countries such as the USA, China and the United Kingdom (UK) have limited their average discharge of oil and grease to about 30 ppm (Yishu Li, 2017). Also, due to the rising demand for petroleum derivatives, petroleum producers are obliged to look into alternative methods to separate these emulsions. Moreover, the prospect of improving oil recovery has also driven researchers to look into alternative ways to demulsify oilfield emulsions (Ma *et al.*, 2017). In addition, most of the areas used by onshore oil and gas industries are arid, making water a valuable commodity. This has led to the capability to partially treat oilfield emulsions for other beneficial purposes such as irrigation, watering of livestock and road maintenance, as well as to increase oil recovery and to maximize overall profitability.

Current conventional oilfield emulsion demulsification methods involve the application of mechanical, thermal, electrical, and chemical processes or their combination (Fakhru'l-Razi *et al.,* 2009). However, the chemical method, also known as chemical demulsification, is the most common method used in industries because of its high efficiency (more than 90%) as compared to other techniques mentioned above (Issaka *et al*., 2015). This method consists of adding a small quantity of surface-active compounds called demulsifiers capable of disrupting the interfacial tension between the oil and water in order to separate them into individual components. Hence, this study focused on the design and optimization of existing process parameters in order to improve the demulsification process of oilfield emulsions.

1.3. Problem statement

The demulsification of oilfield emulsions has been previously done by mechanical, thermal, electrical and chemical methods (Hadjiev *et al*., 1997; Martínez-Palou *et al*., 2013; Hao *et al.,* 2013a; El-Ashtoukhy & Fouad*,* 2014). Although the chemical method has been effectively applied for this purpose (Hirasaki et al., 2011; Al-Sabagh et al., 2009; Abdurahman & Nuraini, 2010; B.M. Hanapi, A. Samasuri, W. A. Rahman, 2006; Oseghale et al., 2012), none of the above researchers provided clear information regarding the ideal process conditions for efficient demulsification of these emulsions. This study seeks to optimize some existing process parameters in order to maximize the demulsification efficiency of oilfield emulsions using response surface methodology and central composite design.

1.4. Research aim and objectives

This research aims at investigating the capability of two types of chemical demulsifiers, cetyl trimethylammonium bromide (CTAB) and trimethyl-tetradecyl ammonium chloride (TTAC) on the destabilization process of oil-in-water emulsions existing during enhanced oil recovery (EOR) using response surface methodology. In order to determine the optimum conditions for maximum destabilization efficiency, the following objectives were defined:

a) To simulate stable synthetic oil field emulsions at different oil ratios and study the effect of controlling factors such as oil ratio, surfactant concentration, homogenization speed and salinity on the stability of the formulated emulsions.
b) To design and optimize the process parameters, namely demulsifier types and concentration, settling time and oil to water ratio using a central composite design and response surface methodology, and to investigate the influence of the aforementioned parameters on the demulsification efficiency.
c) To study the ageing effect of the emulsions on the effectiveness of the demulsifiers.

1.5. Research questions

Investigating the above-mentioned objectives will provide answers to the following questions.

a) What are the factors that contribute to the stability of oilfield emulsions?
b) What chemical demulsifiers are the most effective in destabilizing oilfield emulsions?
c) What are the optimum operating conditions for which maximum demulsification efficiency would be achieved?
d) How will ageing affect the performance of the demulsifiers?

1.6. Scope of the research

This research seeks to optimize the efficiency of demulsification of oil-in-water emulsions from matured reservoirs subjected to enhanced oil recovery (EOR) using cetyl trimethylammonium bromide (CTAB) and trimethyl-tetradecyl ammonium chloride (TTAC). This study will focus on simulating stable oil-in-water emulsions at different oil ratios and investigate the factors (oil to water ratio, emulsifier concentration, homogenization speed, salinity, and droplet size) that could affect the stability of the emulsion. Factors such as demulsification time, demulsifier concentration, and oil ratio will be investigated via response surface methodology with central composite design to determine the optimum operating conditions for maximum demulsification efficiency.

1.7. Research outline

This study is divided into two parts; the first part consists of simulating stable synthetic oilfield oil-in-water emulsions containing different oil ratios. The second part consists of optimizing some existing parameters in order to maximize the demulsification efficiency of the simulated emulsions using statistical modeling. Chapter 1 serves as an introduction to the thesis. Chapter 2 is a presentation of the relevant literature pertaining to the study. It covers relevant literature on petroleum emulsion formation and stability and emulsion destabilization mechanism. Chapter 3 provides a comprehensive description of the methods of experimentation, and procedures used in the analysis of the results. Chapters 4 and 5 present an overview of the findings and discussion pertaining to the experiments conducted throughout the research. Chapter 6 presents the conclusion drawn from the experimental results and recommendations for further studies.

CHAPTER 2: LITERATURE REVIEW

2. Chapter summary

This chapter provides a brief account of literature and previous research work related to this study. It presents an overview of crude oil recovery as well as how oilfield emulsions are generated. The chapter is divided into three sections.

The first section gives a review of the different stages of petroleum recovery, as well as the origin and oilfield emulsions formation. It also provides detailed literature on the composition and characteristics of oilfield emulsions.

The second section outlines some general concepts of petroleum emulsion while focusing on the different types of emulsions encountered during enhanced oil recovery (EOR) processes. It describes the main compounds responsible for the stabilization of oilfield emulsions, the mechanism of stabilization, and the impact on the environment.

The third section describes some methods of oilfield emulsion demulsification by emphasizing the chemical method which is the focus in this study.

2.1. Crude oil

Crude oil, also known as petroleum, is a natural product derived from remains of dead animals and vegetation that sedimented below the surface of the earth millions of years ago (Walters & Walters, 2015). Crude oil is formed and trapped in porous rocks due to the high pressure of the sedimented materials, the high temperature beneath the earth and the actions of bacteria. Crude oil is a mixture of sand, salt, water, and natural gas; it is usually a thick and smelly oily liquid comprised primarily of hydrogen and carbon compounds and other compounds such as sulphur, oxygen, and nitrogen. The colour varies from black, brown to greenish depending on the location of the oilfield (Zhang *et al.,* 2014). Crude oil is recovered in three different stages; primary, secondary and tertiary recovery. The latter is known as enhanced oil recovery (EOR), depending on the production life of the reservoir.

2.2. Crude oil recovery

2.2.1. Primary oil recovery

Primary recovery is the extraction of crude oil from underground by the means of natural energy present or pressure of the reservoirs (Oseghale *et al*., 2012). The pressure difference within the reservoir causes the oil to flow from the zone of high pressure to the zone of low pressure (surface). When the natural pressure within the reservoir is not strong enough to push the oil out, artificial energy, such as pumping systems and gas lift is used to increase the pressure of the reservoir and to maintain the production rate (Alagorni *et al.,* 2015). The recovery efficiency at this stage varies from less than 10% to slightly above 30% of the initial oil in place depending on the oil flown (Alagorni *et al*., 2015; Swearingen, 2000). This usually leads to the implementation of the secondary oil recovery.

2.2.2. Secondary oil recovery

Secondary recovery is the first step in improving primary recovery when the natural pressure in the reservoir has decreased considerably. According to Pashakolaie *et al.,* (2015) using secondary oil recovery can increase oil recovery by up to 50%. Secondary recovery is accomplished by injecting external fluids such as water and gas into the reservoir to maintain the reservoir pressure and to improve crude oil recovery (Alagorni *et al.,* 2015).

2.2.2.1. Water flooding

Water flooding is the process in which water is injected into the oil reservoir to boost production. The purpose of water flooding is to supplement and maintain the reservoir's pressure (Alagorni *et al.,* 2015). This is the most common method used in industries because of its availability, its low capital investment and operating cost (Alagorni *et al.*, 2015; Swearingen, 2000). The performance of water flooding depends on the permeability and porosity of the reservoir rock. It is most efficient in highly permeable reservoirs. Most of the time a significant percentage of oil is left in the reservoir after water flooding has reached its economic limits hence gas is used as a fluid, known as gas flooding.

2.2.2.2. Gas flooding

Gas flooding is the term used when gases are injected into the reservoir for pressure maintenance (Romero-Zerón, 2010). Gases used in this process include CO_2, natural gas (methane) or nitrogen (Alagorni *et al.,* 2015). These gases reduce the viscosity of the oil and provide good displacement from the reservoir to the surface. CO_2 is the most common gas used for this process because it is cheaper compared to any other gas. Nitrogen is often used as a substitute for CO_2 flooding because of its efficiency (Alagorni *et al.,* 2015). The efficiency of gas flooding depends on the temperature, pressure of the reservoir and the crude oil composition (Sino Australia Oil & Gas Pty Limited, 2013).

However, the combination of primary and secondary recovery methods on average produce no more than one-third of the OOIP (Alagorni *et al.,* 2015), hence tertiary recovery or enhanced oil recovery is generally implemented to recover remaining petroleum underground.

2.2.3. Tertiary oil recovery or enhanced oil recovery (EOR)

Tertiary oil recovery, also known as the enhanced oil recovery (EOR) process, is the third phase of crude oil extraction. It is usually done by injecting steam, chemicals, and microbes in the reservoir to enhance crude oil production (Pashakolaie *et al.,* 2015). These elements provide favourable conditions (the reservoir rock becomes more wettable, reduces the interfacial tension (IFT) between oil and water and the oil becomes less viscous) for high oil recovery (Aladasani & Bai, 2010). When steam is the fluid injected the process is called steam flooding or thermal recovery; when chemicals are injected the process is called chemical flooding; when microbes or bacteria are used, the process is called microbial recovery (Aladasani & Bai, 2010; Romero-Zerón, 2010). According to Zolfaghari *et al.* (2016) this technique can increase the overall production rate up to 80% or more as compared to primary and secondary recovery.

2.2.3.1. Steam flooding or thermal recovery

Steam flooding or thermal recovery refers to the injection of heat in the form of steam into the reservoir to improve crude oil recovery. Steam reduces oil viscosity and increases the mobility of the oil (Romero-Zerón, 2010). When heat is increased, the interfacial tension between the oil and water becomes smaller, which causes the crude oil to become more permeable and flow more easily from the reservoir rocks to the surface (Oseghale *et al.*, 2012).

2.2.3.2. Chemical flooding

In chemical flooding, chemicals such as surfactants, polymers, micellar-polymers, and alkaline are added to a fluid (mostly water) (Romero-Zerón, 2010) before it is injected into the reservoir. These chemicals react such as to increase the viscosity of the displacing fluid (water), decrease its relative permeability and consequently increase the relative permeability of the oil (Romero-Zerón, 2010). Surfactants improve the displacement efficiency of the droplets through the reservoir by lowering the interfacial tension (IFT) between the oil and water, and cause the water and oil to form emulsions which can easily flow (Romero-Zerón, 2010). Alkali such as sodium hydroxide, sodium silicate, and sodium carbonate reacts with the organic acid present in the oil to minimize the surface adsorption, to adjust the pH and salinity of the oil. Polymers such as polyacrylamide and polysaccharide are used as mobility control agents (Swearingen, 2000). Their role is to diminish the mobility ratio of water and oil by increasing the viscosity of water, thus improving the volumetric sweep efficiency, and consequently increasing oil recovery (Zolfaghari *et al*., 2016).

2.2.3.3. Microbial flooding

Microbial recovery is a process in which microorganisms or bacteria are injected into underground reservoirs to boost oil recovery (Oseghale *et al*., 2012). It includes cyclic microbial recovery and microbial flooding. These microorganisms produce substances such as acids, surfactants, and gases such as carbon dioxide and hydrogen, which act as agents to enhance recovery.

The crude oil extracted from the tertiary or enhanced oil recovery methods is usually found in the form of a stable mixture of oil and water called oilfield emulsions or produced emulsions, which are difficult to demulsify. This constitutes the main focus of this research work.

2.3. Oil field emulsions

The petroleum industry is a combination of three industries, namely coal-bed methane, oil and conventional gas producers. The effluents from these industries are known as emulsions (Lynn *et al.,* 2003). Emulsions consist of a mixture of three phases: the dispersed phase, the continuous phase which keeps the dispersed phase in suspension, and the interphase which is the emulsifier or stabilizer that binds the dispersed and the continuous phase together, preventing them from separating (Udonne, 2012). The appearance of crude oil emulsions varies widely depending on the phase volume ratio (the percentage of water to oil or oil to water) and the characteristics of oil and water. Oilfield emulsions are often dark reddish, dark brown, grey or blackish brown. The colour mostly depends on the oilfield location. Generally, emulsions look muddy and opaque because of the light that is scattered at the oil-water interface (Sunil & Kokal, 2006).

Oilfield emulsion is the largest waste stream associated with crude oil production. In a study conducted by Igunnu & Chen (2014), it was found that during the EOR processes, for every barrel of crude oil produced 3 barrels of water are generated, giving an oil to water ratio of 1:3. Emulsions account for approximately 90 to 95% of the total waste generated during exploration and production (Çakmakc *et al.,* 2008; Altare *et al.,* 2007; Igunnu *et al.,* 2014).

The water originates from within the hydrocarbon zone as shown in **Figure 2.1** then becomes emulsions when it comes into contact with the hydrocarbon-bearing rocks and is brought together to the surface of the well (Lynn *et al.,* 2003).

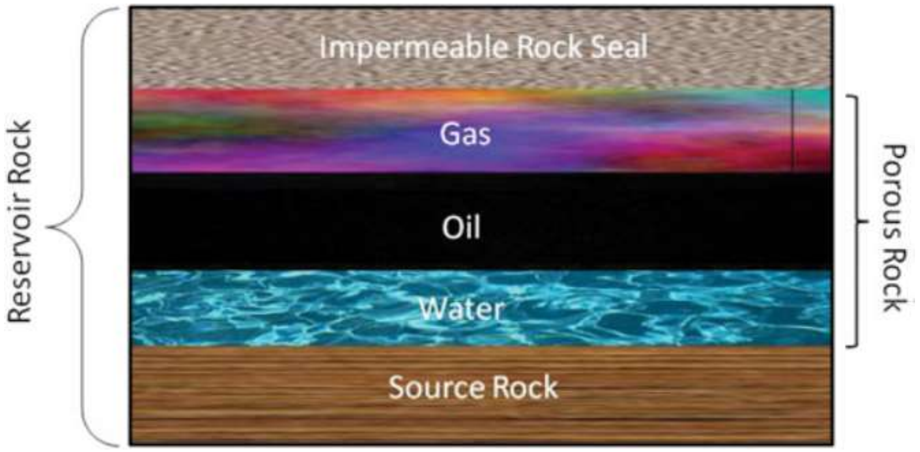


Figure 2:1: Typical crude oil reservoir (Igunnu & Chen, 2014)

2.3.1. Oil field emulsion formation

Emulsions form through the process of emulsification during which sufficient energy in the form of agitation is needed to deform, break and disperse the phases into one another (Wong *et al.,* 2015; Fingas, 1995; Förster, 2017). During emulsification the dispersed phase is broken up into fine droplets, and the emulsifier molecules are adsorbed onto the newly formed droplets causing the interfaces to stabilize to form a homogeneous system (Pichot, 2010). Emulsification can either be achieved by shaking, mixing with a rotor-stator system, by injecting a liquid (mostly water) through porous membranes, or high-pressure homogenization (Abdurahman & Nuraini, 2010). **Figure 2.2** illustrates the process of deformation and breakup of emulsion droplets. For the emulsion to form, three conditions are necessary, namely: the two liquids should be immiscible; energy must be present in the form of shearing or agitation; and a surface-active compound must be present.

Figure 2:2: Droplet breakup during emulsification (Akbari & Nour, 2018)

Oilfield emulsions form during petroleum recovery, in pipelines while being transported from the reservoir to the surface, during drilling and processing, and at the refinery while cleaning (Kokal & Aramco, 2005). During drilling, emulsions form in the valves, pump cylinders and the elevating pipes from the reciprocating movement of the pump bars. During crude oil extraction, pressure rising over the chokes and valves generates sufficiently high shear forces to disperse water as droplets in the oil phase and vice versa, and cause the emulsion to form (Othman, 2009). **Figure 2.3** shows how emulsions are formed during petroleum processing.

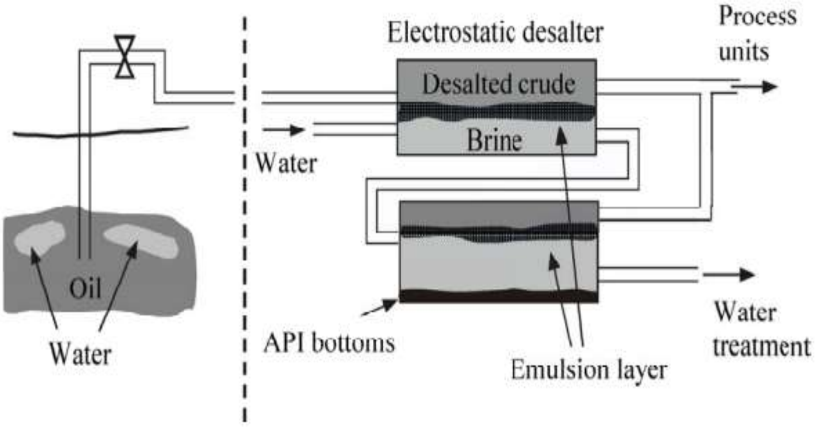


Figure 2:3: Petroleum recovery process and emulsion formation (Raleigh, 2001)

Oilfield emulsions vary from reservoir to reservoir depending on the geographic location, the geology of the formation, the type of hydrocarbons being produced as well as the method of production (Bakke *et al*., 2013). For example, the water generated during EOR processes consists mainly of chemical additives such as surfactants, alkali, and polymers, and other chemicals such as biocides, friction breaker, gelling agents and gel breakers (Rosenblum *et al*., 2017; ERM, 2014).

2.3.2. Characteristics of oilfield emulsions

The characteristics of oilfield emulsions vary depending on the type of reservoir in production, the geology of the rock and the location of the oilfield (Gazali *et al.,* 2017). In general, oilfield emulsions possess the characteristics of the rocks with which it has been in contact. It comprises mostly a mixture of natural organic and inorganic compounds as well as chemicals added during EOR processes (Papakostas, 2017). The organic compounds are oil and grease components such as benzene, toluene, ethyl-benzene and xylene (BTEX) (Ahmadun *et al.*, 2009; Igunnu & Chen, 2014) usually present in the form of small droplets (0.5 to 200µm) dissolved in water (Ahmadun *et al.,* 2009). The inorganic compounds are the total dissolved solids (TDS) and total suspended solids (TSS) (Clark, 2009; Igunnu & Chen, 2014) found in the form of anions such as Cl^-, SO_4^2-, CO_3^2-, HCO_3 and cations such as Na^+, K^+, Ca^2+, Mg^2+ Ba^2+ Sr^2+ Fe^2+ (Papakostas, 2017). Some naturally occurring radioactive material (NORM) such as radium ^{226}R and ^{228}R isotopes are also present (Igunnu & Chen, 2014). The Heavy metals are mostly cadmium, chromium, copper, lead, mercury, nickel, silver, and zinc. **Table 2.1** shows the physicochemical characteristics of a typical oilfield emulsion.

Table 2:1. Characteristics of oil field emulsions (Ahmadun et al., 2009)

Parameters	values (mg/L)	Heavy metals	values (mg/L)
Density	1014 - 1140	Calcium	13 - 25 800
Conductivity	4200 - 58 600	Sodium	132 - 97 000
Surface tension	43 – 78	Potassium	23 - 4300
pH	4.3 – 10	Magnesium	8 - 6000
TOC	0 – 1500	Iron	<0.1 - 100
COD	0 – 1220	Aluminium	310 - 410
TSS	1.2 - 1000	Boron	5 - 95
Total oil	2 – 565	Barium	1.3 - 650
Volatile (BTEX)	0.39 – 35	Cadmium	<0.005 - 0.2
Base neutrals	0 - <140	Copper	<0.02 - 1.5
Total non-volatile (μg/L)	0 – 275	Chromium	0.02 - 1.1
Chloride	80 - 200 000	Lithium	3 - 50
Bicarbonates	77 – 3990	Manganese	0.004 - 175
Sulphate	<2 – 1650	Lead	0.002 - 8.8
Ammoniacal nitrogen	10 – 300	Strontium	0.02 - 1000
Sulphite	0 – 10	Titanium	<0.01 - 0.7
Total polar	9.7 – 600	Zinc	0.01 - 35
Higher acids	<1 – 63	Arsenic	<0.005 - 0.3
Phenols	0.009 - 23	Mercury	<0.005 - 0.3
Volatile fatty acids	2 – 4900	Silver	<0.001 - 0.15

2.3.3. Oilfield Emulsion classification

Emulsions are classified depending on the nature (be water or oil) of the dispersed phase as well as the volume of the dispersed phase (Fakultät *et al.*, 2009; Papakostas, 2017). The most common types of emulsions encountered in the oilfield are water-in-oil and oil-in-water emulsions as shown in **Figure 2.4.** Oil-in-water (O/W) emulsions consist of oil droplets dispersed in water and water-in-oil (W/O) emulsions are those in which water droplets are dispersed oil (Silset, 2008). Other types such as water-in-oil-in-water and oil-in-water-in-oil types may also be found (Fields et al., 2009); these are more complex and stable, consisting of small droplets of the internal phase (which can be oil or water) that are dispersed in a continuous phase (which can be either oil or water as well).

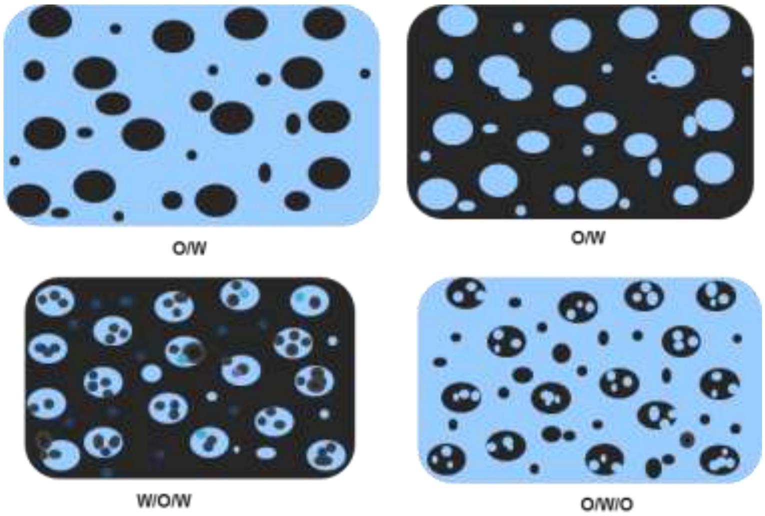


Figure 2:4: Oilfield emulsion types (Akbari & Nour, 2018)

The types of emulsions formed depend on many factors including the phase ratio: meaning that in an emulsion, the phase that has the smallest ratio is considered to be the dispersed phase (Sunil & Kokal, 2006).

According to Hamadi & Mahmood (2009), emulsion can also be classified according to the degree of stability which can be qualified as unstable, meso-stable and stable. Unstable emulsions are those which decompose into their original phases immediately after homogenization; meso-stable emulsions have properties between unstable and stable emulsions, but will eventually break down after days or weeks (Hamadi & Mahmood, 2009).
Emulsions are thermodynamically unstable systems due to their natural tendency to separate, however some emulsions present kinetic stability behaviour, meaning they can remain stable over a long period (Hanapi *et al.,* 2006 & Othman, 2009).

In this work, stable emulsions were considered and were classified according to phase volume ratio.

2.3.4. Oilfield emulsion stability

Emulsion stability is defined as the resistance of an emulsion to separate or its ability to maintain its physicochemical properties for a long period (Hanapi *et al*., 2006). Emulsions are stable because there exists an interfacial barrier (usually a thin and rigid film) between oil and water that prevents the droplets of the dispersed phase from assembling and coalescing (Hamadi & Mahmood, 2009). The thin rigid interfacial film is stabilized by a surface-active compound known as an emulsifier.

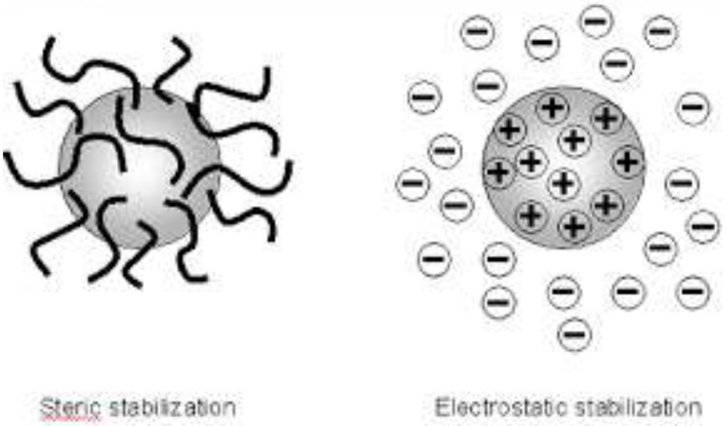
Oilfield emulsions are stabilized by natural emulsifiers, namely asphaltene, resins, waxes, inorganic solids, organic acids, and chemicals initially present or added in the reservoir (Nasser & Khamis, 2014). Organic compounds such as sodium hydroxide react with the fatty acid present in the crude oil to form a strong and elastic interfacial film, thus causing the emulsions to stabilize (Zhang *et al.,* 2011). This film performs two functions: it reduces the interfacial tension which consequently increases the interfacial area of the two liquids; and decreases the rate of aggregation and coalescence of the dispersed droplets by forming mechanical steric and electrical barriers around them (Oluwatosin, 2016). The steric and electric barriers prevent the droplets from approaching each other (Fingas, 2005). The degree of stability of the emulsions depends on the strength of the interfacial film (Feng & Behles, 2015). The most stable emulsion occurs when the contact angle at the film interface is close to 90º (Auflem, 2002).

2.3.4.1. Emulsion stability mechanism

Four mechanisms are involved in the stabilization of emulsions namely:

i) Electrostatic repulsion: this is the interacting force that exists between the electrically charged layers around the droplets in the emulsion, preventing them from coming into contact. This occurs when the emulsion is stabilized by anionic emulsifier (Malakasiotis & Androutsopoulos, 2010). This charged layer is made up of ionic surfactants and is neutralized by counterions in the continuous phase; this kind of stabilization leads to the formation of oil-in-water emulsions (Malakasiotis & Androutsopoulos, 2010).

ii) Steric repulsion occurs when the emulsion is stabilized by a non-ionic surfactant and polymers (Zhang, 2013) **Figure 2.6**. This process occurs when the dispersed droplets are covered by a non-ionic surfactant to prevent the droplets from coming close to each other (Akbari & Nour, 2018). This kind of stabilization often results in the formation of water-in-oil emulsions.



Steric stabilization Electrostatic stabilization

Figure 2:5: Steric and electrostatic stabilization of emulsions (Akbari & Nour, 2018)

iii) The Marangoni Gibbs effect prevents the drainage of the continuous phase between two opposite dispersed droplets that promote the stability of the system. This occurs because of the deformation of the droplet's surface area as they draw closer to each other, forming a parallel plane between the films as seen in **Figure 2.7**.

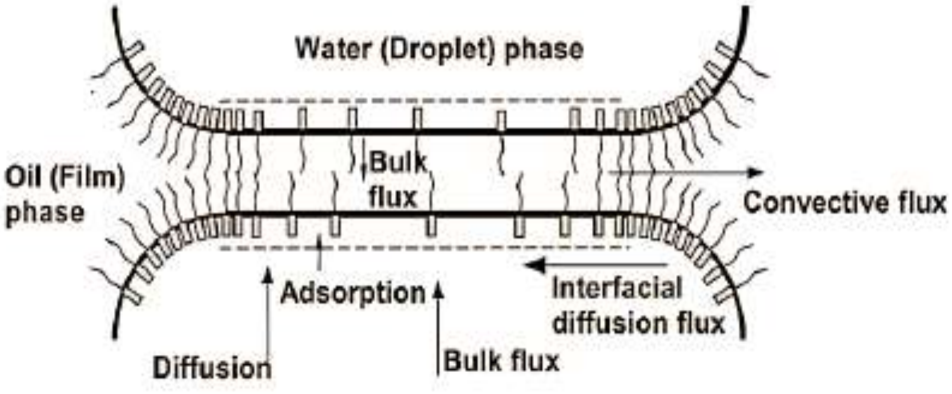


Figure 2:6: The Marangoni Gibbs effect of emulsions stabilization (Raleigh, 2001)

iv) Thin-film stabilization: during this process, a rigid and viscoelastic film is formed around the dispersed droplets preventing them from coming into contact with each other and coalescing. This process mostly depends on the ability to dissolve and the kinetics of diffusion and adsorption of the surfactant present in the emulsion (Raleigh, 2001).

2.4. Factors determining the stability of oilfield emulsions

Generally, the stability of oilfield emulsions is influenced by the natural surfactants (asphaltenes, waxes, and resins) initially present in the reservoir, brine water composition and the interfacial film between the droplets, emulsion droplet size, and the homogenization speed.

2.4.1. Asphaltenes

Asphaltenes are a fraction of crude oil that possesses the highest number of aromatic rings, higher molecular weight in the range of 500-1500 g/mole, a high atomic ratio of carbon/hydrogen and high aromaticity (Abdel-raouf, 2012). The asphaltene fractions are the most polar molecules, insoluble in aliphatic hydrocarbons such as n-heptane and soluble in aromatic hydrocarbons such as toluene (Savvidou, 2017). They consist of a mixture of heterogeneous molecules containing aromatic, naphthenic rings, aliphatic chains and other heteroatoms such as sulphur, nitrogen, oxygen in the form of carboxylic acids, amides, amine, and alcohols. Other metals such as vanadium, nickel, and iron are also present as represented in **Figure 2.8.** These molecules aggregate at the oil-water interface to form a viscoelastic and physical cross-linked network preventing the dispersed droplets from coalescing (Politova *et al.,* 2017). A review done by Politova *et al.* (2017) showed that the stability of emulsions by asphaltene films is attributed to their specific ability to assemble 3D networks inside of the emulsion and their acidic and basic behaviour. **Figure 2.9** shows the mechanism of asphaltene stabilization.

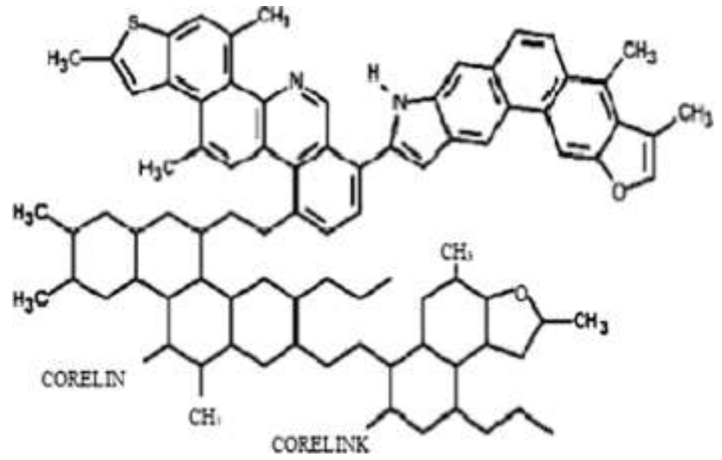


Figure 2:7: Structure of asphaltene compounds (Abdulredha *et al.,* 2018)

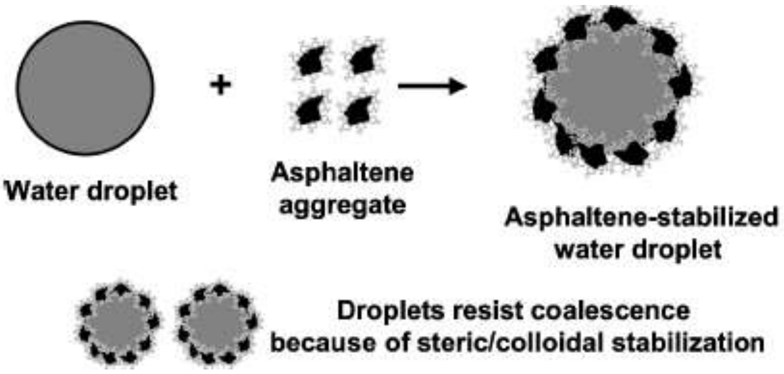


Figure 2:8: Mechanism of emulsion stabilization by asphaltene compounds (Oluwatosin, 2016)

2.4.2. Resins

Resins are the compounds of crude oil that contain heteroatoms such as nitrogen, oxygen or sulphur (Olajire, 2014) as seen in **Figure 2.10**. Resins are characterized by their higher H/C ratio; they are structurally similar to asphaltenes but have smaller molecular weight. They are fractions of crude oil that are insoluble in propane and ethyl acetate and soluble in n-pentane and n-heptane (Savvidou, 2017). The resin molecules play the role of surfactants in stabilizing the colloidal particles of asphaltenes in crude oil (Abdel-Raouf, 2012).

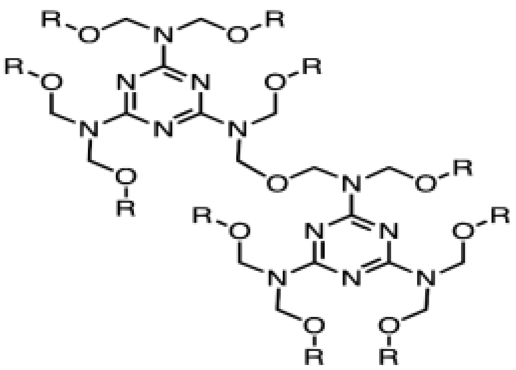


Figure 2:9: Structure of resin compound (Savvidou, 2017)

2.4.3. Interfacial tension of emulsions

Oilfield emulsions are stabilized by the interfacial tension (IFT) that forms around the dispersed phase droplets of the emulsions. Emulsion IFT is the thin layer that separates two immiscible fluids when they are in contact with one another (Malakasiotis & Androutsopoulos, 2010). The IFT is described by Kristian & Greenway (2017) as the work needed to keep two immiscible fluids apart at constant temperature (T), pressure (P), and a constant number of moles (n), as described by **Equation 2.1**.

$$\sigma = \left(\frac{\partial G}{\sigma A}\right) P, T, n \qquad \mathbf{2.1}$$

Where G is the Gibbs free energy, A is the area of the interface between the immiscible fluids and σ is the interfacial tension.

The characteristics of the interfacial film depends on the crude oil type (asphaltic or paraffinic), composition and pH of the brine water, ageing time, and the concentration of the polar molecule in the crude oil (Kokal & Aramco, 2005). The strength of this film is dependent on the surfactant adsorption-desorption kinetics, the solubility of the surfactant, and the interfacial rheological properties such as elasticity, interfacial tension gradient and interfacial viscosity (Krawczyk *et al.*, 1991).

2.4.4. Surfactants or surface-active agents

Surfactants are amphiphilic polymer molecules that have the ability to partially dissolve in water and oil. Surfactant molecules have the ability to minimize the energy needed for the formation of emulsions by reducing the interfacial tension (IFT) between the two immiscible liquids (Katepalli, 2014). These molecules possess a hydrophilic part or polar head with the ability to dissolve in water and the lipophilic or hydrophobic part or non-polar tail with the ability to dissolve in oil (Abdulredha *et al.,* 2018). **Figure 2.11** represents the structure of a surfactant and its orientation in water and oil.

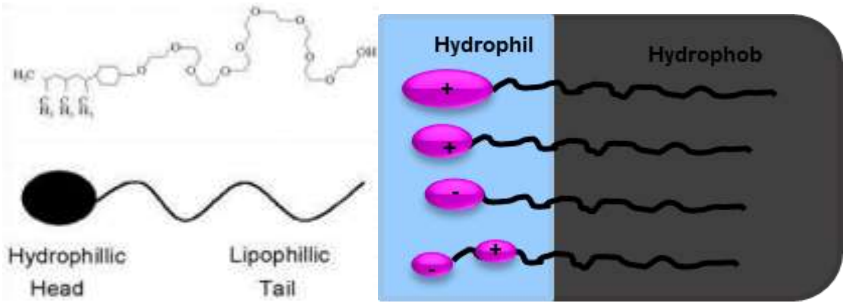


Figure 2:10: Structure of surfactant and orientation in emulsions (Marzzacco, 2016; Pichot, 2010)

Two phenomena take place when surfactant molecules are in solution, namely desorption and adsorption. Desorption refers to the transfer of surfactant molecules to the phases (oil and water) while adsorption refers to the passing of the surfactants from the phases to the interface with a specific orientation (Fakultät *et al.,* 2009). As the surfactants are added to the system, individual molecules called monomers aggregate together to form micelles (Savvidou, 2017) as represented in **Figure 2.12**. The concentration above which micelles are formed is called critical micelle concentration (CMC) (Marzzacco, 2016). Beyond this concentration, any further addition of surfactant will not affect the interfacial tension and stability of emulsions (Kristian & Greenway, 2017).

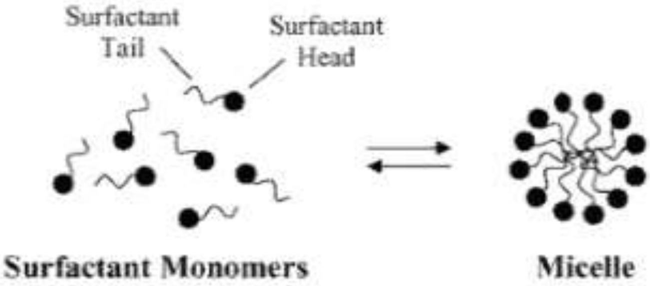


Figure 2:11: Aggregation of surfactant monomers into micelles (Dave & Joshi, 2017)

The affinity of surfactants for water or oil is defined by their hydrophilic-lipophilic balance (HLB) number (Farn, 2006; Kanicky *et al*., 2001). The hydrophobic-lipophilic balance is a number raged from 0-20; the HLB number >10 is attracted to water (hydrophilic), whereas HLB number <10 is attracted to oil (Udonne, 2012).

2.4.4.1. Types of surfactants

Surfactants are classified based on the charge present on their structure. They can be anionic, cationic, non-anionic, and amphoteric or zwitterions (Savvidou, 2017& Azarmi & Ashjaran, 2015).

2.4.4.1.1. Anionic surfactants

Anionic: Anionic surfactants are negatively charged; they are also known as hydrophobic which means water-fearing surfactants. Anionic surfactants are the most widely used type of surfactants as part of the EOR. This is because of their negative charged head, their ability to achieve ultra-low IFT, their relative stability, and low adsorption properties which make them suitable in almost all types of reservoirs (Jean-Louis, 2002). Some examples of anionic surfactants are sodium dodecyl sulphate (SDS) and ammonium lauryl sulphate (ALS) as shown in **Figure 2.13**.

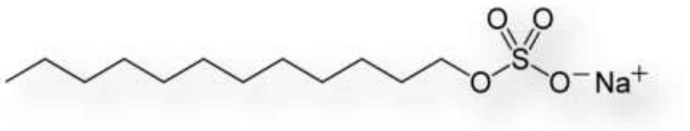


Figure 2:12: Structure of an anionic surfactant (SDS) (Marzzacco, 2016)

2.4.4.1.2. Cationic surfactants

Cationic surfactants possess a positive charge on their head group, making them difficult to be adsorbed onto sandstone rocks. They therefore cannot be used in this type of reservoir, but they are suitable in carbonate reservoirs (Kanicky *et al*., 2001). However, they dissociate in water to form amphiphilic cations and anions, normally a halide (Cl- and Br-). Examples of this type are RNH_3+Cl, salts of a long chain amine and cetyltrimethylammonium bromide (CTAB) represented in **Figure 2.14**.

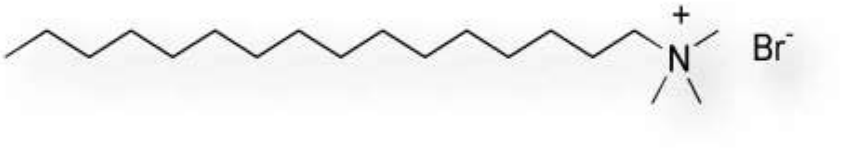


Figure 2:13: Structure of an anionic surfactant (CTAB) (Marzzacco, 2016)

2.4.4.1.3. Non-ionic surfactants

Non-ionic surfactants do not dissociate in water; the hydrophilic head has a neutral charge as seen in **Figure 2.15**. Non-ionic surfactants frequently serve as surfactants to improve system behaviour (Azarmi & Ashjaran, 2015).

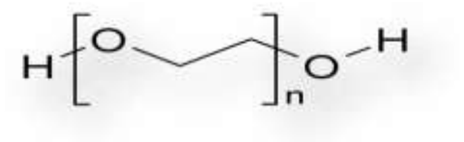


Figure 2:14: Structure of a non-ionic surfactant (Polyethylene glycol) (Marzzacco, 2016)

2.4.4.1.4. Amphoteric surfactants

Amphoteric surfactants display both anionic and cationic behaviour; they have both anionic and cationic centres attached to the same molecule (Alabdulmohsen, 2015). An example of amphoteric surfactants is represented in **Figure 2.16**. The nature of amphiphilic surfactants causes the molecule to adsorb at the interface of oil and water; in doing so it reduces the energy difference created at the interface of water and oil and thus stabilizes the emulsion (Shosa & Schramm, 2001).

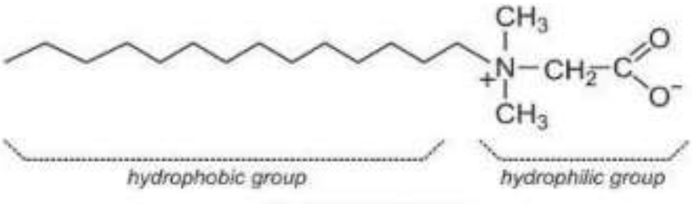


Figure 2:15: Structure of an amphoteric surfactant (Marzzacco, 2016)

2.4.5. Investigation of the factors that influence the stability of the emulsions (laboratory work)

In this research work, the factors considered to determine the stability of the emulsion were the emulsifier type and concentration, homogenization speed, brine salinity, oil to water ratio and average droplet size.

2.4.5.1. Effect of surfactant on the emulsion stability

The most important task in formulating emulsions is the choice of suitable surfactants that can emulsify and keep the emulsions stable for a long period of time. Some surfactants have the ability to either stabilize oil-in-water or water-in-oil emulsions and some can stabilize both types of emulsion. This is because surfactants are different in chemical properties such as the hydrophilic-lipophilic balance (HLB) and solubility in water. For example, surfactants that are oil-soluble have more affinity to oil than water; therefore, they will likely stabilize water-in-oil emulsion. Whereas water-soluble surfactants have more affinity to water and will stabilize oil-in-water emulsions (Farn, 2006; Kanicky *et al*., 2001). Surfactants are also selected based on their environmental friendliness.

Ahmed *et al.* (1999) investigated the effect of anionic and non-ionic surfactant stability of oil-in-water emulsions; the stability of the emulsions was characterized through the measurement of the mean droplet size. They observed that anionic surfactants processed smaller droplet size, which resulted in higher stability compared to non-anionic surfactants. They concluded that anionic surfactants have a greater ability to decrease the interfacial tension and to stabilize oil-in-water emulsions as compared to non-anionic ones.

Dong *et al. (*2010) investigated the influence of non-ionic and anionic surfactants on the stability of oil-in-water emulsions and water-in-oil emulsions. The stability study was done by measuring the interfacial tensions of the emulsions. The results showed that both surfactants were able to decrease the interfacial tension between the oil and the water which consequently enhanced the stability of the emulsions. They concluded that the stability of the emulsions was more dependent on the surfactant concentration than the surfactant types.

Daaou & Bendedouch (2012) studied the effect of cationic, anionic and non-ionic surfactants on the stability of Algerian crude oil-in-water emulsions. The stability test was performed by observing the water separated in the emulsions over a period of 24 h. It was found that the maximum stability was observed for emulsions containing the non-ionic surfactants, whereas the ionic and cationic exhibited lesser emulsion stability. Less water was separated (18%) from the oil (considered the most stable emulsion because only a little water was separated) with non-ionic as compared to cationic (82%) and anionic (85%).

In this research work, a non-ionic surfactant (Span 20) was used to formulate the oil-in-water emulsions.

2.4.5.2. Effect of surfactant concentration on the stability of oil-in-water emulsions

Another factor that influences the stability of the emulsions is the surfactant concentration. The stability of crude oil emulsions depends on the smallness of the interfacial film between the water and the oil in the emulsions which usually occurs when the surfactant is at high concentration. The ability of the surfactants to diminish this interfacial film is usually due to the number of surfactants present in the emulsion. Bakke *et al.* (2013) investigated the influence of surfactant concentration on the stability of water-in-oil emulsions (diesel was used as the oil phase). The emulsions were prepared at different surfactant concentrations (2, 4 and 6 vol%, based on the total volume of emulsions to be prepared) and the stability of the emulsions was measured based on the time taken for complete separation of the emulsions. The reported results showed that the emulsion that was prepared with 2 vol% surfactant separated completely after 12 min, the 4 vol% separated after 22 min and the 6 vol% separated after 109 minutes, representing an 89% increase in the separation time as the surfactant concentration increased from 2 to 6 vol%.

The influence of surfactant concentration on the stability of the emulsions was also studied by Tcholakova *et al.* (2004). In their study, the stability of the emulsions was characterized by the mean droplet size (as a rule of thumb, emulsions with smaller mean droplets are more stable than those with larger ones). The emulsions were prepared in the presence of 0.01 to 1 wt% surfactant concentration. They observed that the mean droplet size decreased from 30 to 12 µm when the surfactant concentration increased from 0.02 to 0.1 wt%, and further decreased to about 7.5 µm when the concentration was increased to 0.2 wt%. Emulsions containing high surfactant concentration have smaller droplet size as compared to those with low concentration, and therefore are considered to be more stable.

Kumar & Mahto (2017a) focused on the stability of an Indian crude oil-in-water emulsion prepared by varying the emulsifier concentration from 1 to 3 wt%, the oil concentration from 40 to 60% and the temperature from 15 to 35°C. They found that an increase in the oil content and surfactant concentration resulted in an increase in the stability of the emulsions, and the emulsions kept at lower temperature were more stable than those kept at high temperature. The emulsion stability was improved from 51.7 to 85% when the oil content increased from 40 to 60% at 35°C and 2 wt% emulsifier concentration. Also, emulsions with high oil content were found to be more stable at low temperatures than those with low oil content. At 15°C, the stability of 40% oil content was 83.3% whereas those above 40% was 100%.

High stability of emulsions is achieved with high surfactant concentration because more molecules of surfactant are adsorbed at the interface of the oil and water, consequently diminishing the interfacial film between the droplets, retarding the droplet coalescence and enhancing the stability of the emulsions. When the temperature is low, the internal energy of the dispersed molecules decreases, thus reducing the rate of coalescence and inducing the stability of the emulsions (Kumar & Mahto, 2017a).

2.4.5.3. Effect of homogenization speed

The homogenization speed plays a very important part in the stabilization of emulsions. Homogenization provides the energy needed to break up bigger droplets into smaller ones and to form emulsions (Selim, 2014). Stirring is needed to transfer the phases of the emulsion into one another, also to generate small droplet sizes which keeps the emulsions stable. The degree of emulsion stability depends on the intensity of the homogenization that is applied.

Patil *et al.* (2015) reported that by increasing the homogenization speed from 3000 to 5000 rpm the stability of 30:70 diesel-in-water emulsion prepared in the presence of 5% surfactant concentration increased from 2 h to 5 h. They observed that there was not much difference in the emulsion stability when the mixing increased from 5000 to 8000 rpm even when the time increased from 20 to 30 minutes. Similar results were found by many other researchers (Peralta-Martínez *et al.,* 2004; Kundu *et al.,* 2019; Tolosa *et al.,* 2006). It takes more time and more surfactant to produce emulsions with low homogenization speed.

A study by Abdurahman *et al.* (2015) revealed that the surfactant concentration can be reduced to about 0.9% if the homogenization speed is as high as 15000 rpm to produce an emulsion that is 100% stable (without any phase separation). Selim (2014) reported that emulsions with high water content will require high homogenization energy in order to stabilize. Emulsions were prepared with 30:70 and 40:60 diesel-in-water. Both emulsions were prepared at the same condition (0.25% surfactant concentration, homogenization speed 20000 rpm). It was observed that the emulsion with high oil content (40:60) was stable for 1 h and that with low oil content (30:70) was stable for 1 week.

2.4.5.4. Effect of brine salinity

The composition of oilfield brine has a very important effect on the stability of oilfield emulsions. The ions present in the brine influence the interfacial film behaviour and result in stabilizing the emulsion (Kokal, 2006). Brine water or formation water contains ions including $NaCl^+$, Ca+ Mg+ at high concentrations; these ions react with the emulsion to form insoluble salts that affect the interfacial tension (IFT) of the emulsion (Kokal, 2006). The concentration of salts may vary from 100 to about 300 000mg/L depending on the characteristics of the reservoir (Ahmadun *et al.,* 2009). According to Manning & Thompson (1995). Freshwater or low salt concentration favours stable emulsions whereas high salt concentration favours loose or unstable emulsions.

Maaref & Ayatollahi (2018) investigated the effect of NaCl concentration on the stability of water-in-oil emulsion by analyzing the evolution of the emulsion droplet size distribution throughout 12 h. They found that the droplet size distribution of the emulsion increased from 2 to 60 µm when the NaCl concentration was increased from 60 to 220 g/L, resulting in poor emulsion stability at an increased salt concentration in the emulsion.

On the other hand, Alves *et al. (*2014) in their study found that at a high NaCl concentration of 250 g/L there was no phase separation in the emulsions after 16 h of testing, resulting in high emulsion stability. They concluded that the presence of salt in the emulsion resulted in the formation of a rigid interfacial film between the emulsion droplets, therefore preventing the droplets from coming closer to form bigger droplets.

Another study by Aman *et al.* (2017) showed that the stability of emulsions increased as the NaCl concentration increased from 0 to 10%. The same test was conducted with emulsions containing 2% of natural surfactant and they observed that only 0.1 % NaCl was required to stabilize the emulsions for a period of 4 days, while a further increase in NaCl resulted in poor emulsion stability. They concluded from their findings that crude oil containing natural surfactants are more stable at low NaCl concentration compared to those without natural surfactant.

In this research work, the effect of salinity on emulsion stability will be investigated at various concentrations of NaCl varying from 1000 ppm to 4000 ppm.

2.4.5.5. Effect of droplet size on the stability of the missions

The droplet size of emulsions produced in the oilfield vary from 0.1 to 100 µm or larger (Kokal & Aramco, 2005). **Figure 2.17** represents the size distribution of a typical oilfield emulsion. The droplet size of emulsions depends on several factors, namely oil to water ratio, homogenization speed, the nature and amount of the emulsifying agents, the solid content and the properties of the phases (Kokal & Aramco, 2005; Kokal, 2006). According to literature the IFT between bigger droplets is higher compared to that of smaller droplets (Peng *et al.,* 2011). The droplet size distribution of the dispersed phase to a certain extent determines the emulsion stability. It is considered that the smaller the droplet size of the dispersed phase, the more stable the emulsion becomes and requires longer separation time or would not separate at all.

Kumar & Mahto (2017b) studied the effect of surfactant concentration and oil content on the droplet size distribution of crude oil-in-water emulsion. Their research revealed that emulsions with high oil content (60% oil content) had smaller oil droplet size distribution (in the range of 164 – 396 nm) and were more stable and more viscous as compared to those with low oil content (40% content), in which the droplet size was distributed in the range of 292 – 615 nm. This could be attributed to the fact that when the oil content is high in the emulsion, smaller droplets are produced, leading to the formation of a larger interfacial area, and thus increasing the stability of the emulsions. They also observed that the droplet size distribution of the emulsions with high surfactants concentration (2 w%) was smaller (in the range of 122 – 295 nm) than those with low surfactant concentrations (0.5 w%), which was in the range of (396 – 825 nm). Surfactants work to reduce the interfacial tension between the oil droplets and lead to the formation of smaller droplets with less energy, and thus enhance emulsion stability.

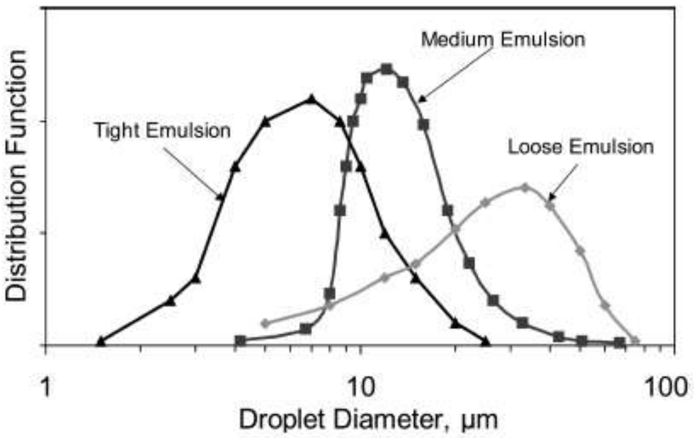


Figure 2:16: Droplet size distribution of oilfield emulsions (Kokal & Aramco, 2005)

2.5. Oilfield emulsion volume

Li (2017) estimated a global average of 25 billion barrels of emulsion are generated daily. Clark & Veil (2015) also reported that about 15 to 21 billion barrels of emulsions are generated in the United State of America per year. The volume of water produced does not remain constant throughout the lifetime of a well; the water to hydrocarbon ratio increases as the production time increases. At the early stage of a well, little or no water and more oil is produced. As the well matures more water and less oil is produced. **Figure 2.18** shows the production profile of a typical oil well. Emulsions have become one of the major concerns around petroleum produced because of the volume. This therefore requires proper treatment methods, which can be very costly.

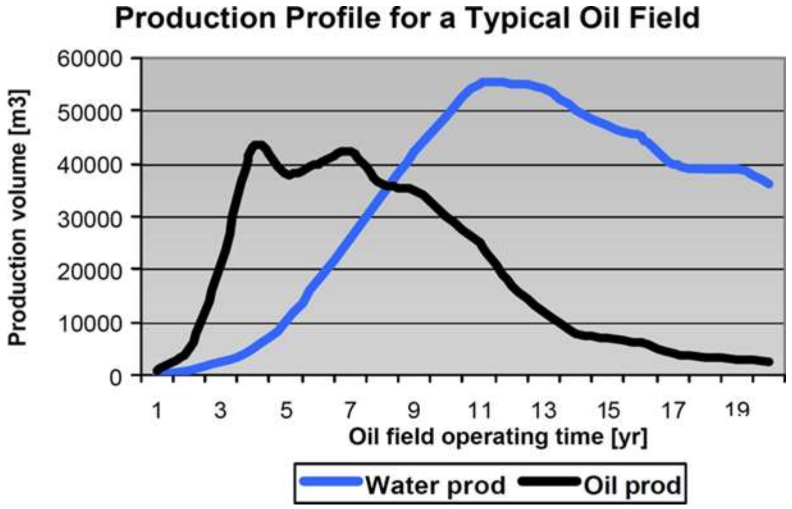


Figure 2:17: Oilfield production profile (Igunnu & Chen, 2014)

2.6. Environmental impact of oilfield emulsions

Oilfield emulsions have become one of the major challenges to petroleum producers due to the huge volume. Generally, part of the oilfield emulsions is reinjected into the reservoir to enhance recovery, these emulsions usually end up in aquifers and underground water. The other part is disposed of in the deep sea, which has adverse consequences on the marine environment and soils as illustrated in **Figure 2.19**. According to Gazali *et al. (*2017), about one billion barrels of emulsions are discharged into the environment per year in Nigeria. This water can affect species diversity up to 100m from the discharge point, as reported by Kumar *et al.* (2013). The dark colour of oilfield water prevents sunlight from penetrating into the water and consequently affects marine life. The heavy metals and other pollutants present in the produced emulsions affect the fertility of aquatic species (Bakke *et al.,* 2013). Hydrocarbons such as Benzene, Toluene, Ethylbenzene and Xylenes (BTEX) are carcinogenic; dissolved Polycyclic Aromatic Hydrocarbons (PAHs) and alkyl phenol fractions are contaminants of most concern in terms of acute and chronic environmental toxicity (Igunnu & Chen, 2014; Zheng *et al.,* 2016). Produced emulsions contain a high concentration of salts as high as 30000 ppm that can affect the quality of fresh water as well as the quality of the soil. High soil salinity can lead to the loss of the soil structure. This can limit plant growth and the yield of crops (Iwan *et al.,* 2017). Gaseous compounds such as CO_2, H_2, and O_2 contribute to greenhouse gas emission. Commercial oilfield waste disposal facilities are made of open pits used to store emulsions. These pits usually contain visible sheens of oil on the surface which pose significant risks to migratory birds and wildlife.

Figure 2:18: Impact of oilfield emulsions on the environment (Guan *et al.*, 2019)

Researchers have found several demulsification methods to alleviate the environmental problem caused by the oilfield emulsions. Demulsification is a technique used to separate oil from water in the emulsions. The demulsification methods that have been used before are discussed in the next section.

2.7. Oilfield emulsion demulsification methods

There are several conventional methods of oilfield emulsion demulsification which include mechanical, electrochemical, thermal and chemical methods (Fakhru'l-Razi *et al.,* 2009). Other methods such as membrane filtration, flotation, flocculation and biodegradation can also be used (Ekott & Akpabio, 2010). This study focuses on the chemical method of demulsification.

2.7.1. Physical or mechanical demulsification

Mechanical demulsification is a method in which emulsions are separated by means of mechanical equipment such as two- and three-phase centrifugal separators, cyclones and settling tanks (Kokal & Aramco, 2002). The above-mentioned equipment provides sufficient mechanical forces to breakdown the interfacial barrier that exists between the water and the oil in order to separate the two phases. The separation efficiency of this technique is mostly influenced by the velocity at which the oil is separated (Saad *et al.*, 2019).

Hao *et al. (*2013) investigated the effects of rotor speed, inlet flow rate, water temperature, oil content and the crude oil density on the separation efficiency of a centrifugal contractor, with the goal of treating the over-standard oil content in electric desalting wastewater. They found that the oil removal efficiency increased with decrease in the inlet flow rate, increase in oil concentration and decrease in oil density, and proposed that this method was highly efficient as the oil concentration in emulsions ranging from 4000 mg/L to 60000 mg/L was reduced to below 200 mg/L.

However, this method has not been widely used due to its high capital cost and low capacity (Abed *et al.,* 2019). Another disadvantage of this technique is that the devices are often difficult to operate; they are small in capacity resulting in increased storage cost; and it is limited to emulsions containing high oil content (above 90%) (Hao et al., 2013b).

2.7.2. Electrochemical demulsification

Electrochemical demulsification is a process in which oil is separated from the emulsion by means of electrodes through oxidation-reduction reactions (Nonato *et al.,* 2018). This process occurs when an electric current is applied causing an imbalance of electric potential in the emulsion (Nonato *et al.,* 2018). When an electric field is applied, the water droplets move rapidly and collide with each other and coalesce. The electric field weakens the interfacial film between the phases (water and oil) thereby enhancing coalescence and separation (Hanapi *et al.*, 2006 and Kokal & Aramco, 2005). The electric system consists of a transformer and electrodes which provide high voltage current to the system; the electrodes are placed in such a way as to provide an electric field that is perpendicular to the direction of flow. This will break the energy barrier between the droplets, and the water molecules will immediately be hydrolyzed into hydrogen and oxygen gas molecules (Issaka, 2015).

Körbahti & Artut (2010) used an electrochemical batch reactor to investigate the influence of current density and reaction temperature on the efficiency of removal of oil and grease in synthetic bilge water. They found that oil removal efficiency was influenced by the current density and the reaction temperature. 96.8% oil was removed when the current density was 12 mA/m^2 and 32°C. A similar result was obtained by other researchers (El-Ashtoukhy & Fouad, 2014; Xu, 2017).

2.7.3. Thermal demulsification

Thermal treatment is referred to as the use of temperature to break petroleum emulsions (Igunnu & Chen, 2014). Thermal demulsification encompasses microwave demulsification and conventional thermal heating (hotplate). Heating enhances the breaking of the interfacial film between oil and water and increases the settling rate and the coalescence frequency of the phases (Issaka, 2015). The higher the thermal energy, the higher the collision rate between the dispersed droplets, thus the separation of phases is enhanced.

Nour (2012) conducted a comparative study on the effectiveness of microwave irradiation and conventional heating on the demulsification of water-in-crude oil emulsion encountered in refinery industries. They found that microwave irradiation efficiently enhanced the demulsification as compared to conventional heating. They reported that demulsification efficiency was affected by the microwave power and the demulsification time.

Another study was conducted by Akbari *et al. (*2016) to compare the demulsification efficiency of microwave irradiation and conventional heating. They reported that with microwave irradiation a separation efficiency of 100% was achieved, whereas 96% water separation efficiency was achieved by conventional heating. The maximum separation efficiency was obtained at an irradiation time of 3 minutes, microwave power of 360 W and demulsifier concentration of 2.5 vol% for the microwave.

In as much as thermal heating can be effectively used to demulsify oilfield emulsions, this technique is usually associated with high operating costs as well as potential corrosion of the treatment vessels (Akbari *et al.,* 2016). Another disadvantage includes the use of poor conductors in the heating vessel; therefore, it takes time for the heat to be transferred into the sample. Thermal demulsification often results in the loss of light ends of the crude oil due to heating which has a negative effect on the gravity settling (Saad *et al.*, 2019).

2.7.4. Chemical demulsification

Chemical demulsification is the process of adding chemicals called demulsifiers to accelerate the rate of coalescence of the dispersed phase of the emulsion (Issaka *et al.*, 2015). These chemicals are designed to neutralize the effect of the surfactant that stabilized the emulsion and displace them from the interfacial film surrounding the emulsion droplets, thus enhancing destabilization (Issaka *et al.*, 2015).

2.7.4.1. Chemical demulsifiers

Demulsifiers are classes of surfactants used to destabilize or break the emulsion stability (Shosa & Schramm, 2001). Demulsifiers are surfactant polymers including ethylene and propylene oxide, alkyl phenol-formaldehyde resins, ethoxylated or propoxylated phenol-formaldehyde resins, ethoxylated phenol, nonylphenols, alcohol and amines, polyhydric alcohols and sulphonic acid salts containing high molecular weight compared to natural surfactants (Kokal & Aramco, 2005; Wang *et al.,* 2015). These compounds are known by their ability to counteract and neutralize the stability effect of the emulsifying agent in an emulsion which promotes coalescence. Demulsifiers are classified according to the structure of their hydrophilic group and their application. **Figure 2.20** shows the basic structure of a demulsifier.

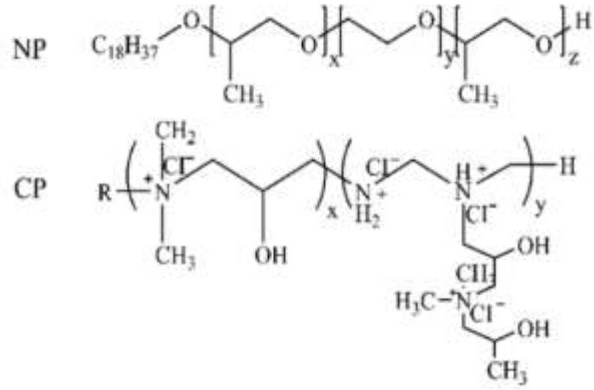


Figure 2:19: Basic structure of demulsifiers: NP and CP are nonionic and cationic groups and R is the alkyl group (Chen et al., 2018).

The performance of the demulsifiers depends on the demulsifier type and concentration.

2.7.4.1.1. Demulsifier selection

The selection of the right demulsifier is crucial for emulsion breaking as emulsions differ in types and properties. Generally, demulsifiers are specific for a given emulsion and can be completely ineffective for other types of emulsions. Demulsifiers are commonly selected in accordance with the type of emulsion that is being dealt with (oil-in-water or water-in-oil) (Zhang *et al*., 2011; Wu *et al.*, 2003) as listed in **Table 2.2.** This is because the polarity of the functional group, which is also known as the HLB, is different for each demulsifier (Nour, 2011). For example, the hydrophobic (non-polar groups or water-fearing) demulsifiers are suitable for water-in-oil emulsions while the hydrophilic (polar group or water-loving) are suitable for oil-in-water emulsions.

Nour, (2011) studied the effect of different HLB number of demulsifiers on the demulsification of water-in-oil emulsion and found that an amine demulsifier group with HLB below 9 exhibited the highest efficiency to break water-in-oil emulsions compared to polyhydric, alcohol and natural group (with HLB above 9). Demulsifiers are also selected based on their equal partitioning between the oil and water phases (partially soluble in oil as well as in water) (Ekott & Akpabio, 2010).

Balsamo et al. (2017) in their work reported that the performance of a demulsifier can also be affected by its molecular weight; they found that the greater the molecular weight and the more hydrophobic the demulsifier is, the faster the coalescence of the water droplets, thus the higher the demulsification efficiency of water-in-oil emulsion.

Table 2:2. Demulsifier types and functions

Name	**Charge**	**Type**	**Function**	**References**
Diallyl dimethyl ammonium chloride polymer	cationic	O/W	Flocculants	(Fink, 2015; Nasiri *et al.,* 2017)
Poly(sodium acrylate)	Anionic	-	Scale inhibitor and reverse emulsion breakers	(Nasiri *et al.,* 2017)
Oxalkylated poly(alkylene) poly(amine)s	Cationic	O/W	Flocculants	(Nasiri *et al.,* 2017)
PAM (polyacrylamide)	Cationic	-	Drag reducing agents	(Wang *et al.,* 2015)
acryloxyethyltrimethylammonium chloride) copolymer	Cationic	O/W	-	(Fink, 2015)

Polyamines	Cationic	-	Emulsion breakers and corrosion inhibitors	(Nasiri *et al.,* 2017)
Poly (vinylsulfonic acid) potassium salt	Anionic	O/W		(Fink, 2015)
Polyoxyethylene and polypropylene co-polymer	Non-ionic	-	Coagulants	(Fink, 2015)
Cethyltrimetilammonium bromide	Cationic	O/w or W/O	Reverse emulsion breakers	(Nasiri *et al.,* 2017)
AM/MAPTAC (acrylamide/ methacrylamidopropyltrimethyl ammonium chloride) copolymer	Cationic	-	Dewatering agents	(Nasiri *et al.,* 2017)
Oxalkylated poly(alkylene) poly(amine)s	Cationic	W/O	-	(Fink, 2015)
Phenol-formaldehyde resins	-	W/O and O/W	-	(Wang *et al.,* 2015)

2.7.4.2. Mechanism of demulsification

Demulsification is the process of breaking crude oil emulsions into individual oil and water phases. The process of demulsification does not occur spontaneously. Several forces and processes are involved including gravitational forces and surfactant interchange with the emulsion phases (Fingas, 2008). **Figure 2.21** illustrates the steps involved in the demulsification of crude.

Creaming or sedimentation according to Fingas (2008) is the natural tendency of a droplet to rise or to sink due to gravity or density differences. The creaming process depends on many factors such as the size of the droplets (bigger droplets will rise if their density is lower than that of the continuous phase or remain at the bottom if their density is higher). Creaming and sedimentation are influenced by the rheology of the continuous phase, the hydro-dynamic and colloidal interaction between droplets, the electrical charge on the droplets and the nature of the interfacial membrane or film (Jones *et al.,* 1978).

Flocculation is the phase in which the distance between droplets of the dispersed is diminished due to the weakening of the net attraction force (van der Waals force) between them, causing the droplets to clump together without any ruptured (Abdurahman & Nuraini, 2010). The rate of flocculation depends on the water cut, temperature, oil viscosity and the density difference between the oil and water (Alabdulmohsen, 2015).

Coalescence is the process whereby smaller droplets come together to form bigger ones (Jones *et al*., 1978). This process involves the elimination of thin interfacial films that separate the dispersed droplets, leading to their reduction in number and enabling complete demulsification. Coalescence is enhanced by a high rate of flocculation, the absence of strong films, high interfacial tension, low viscosity, high water cut and high temperature.

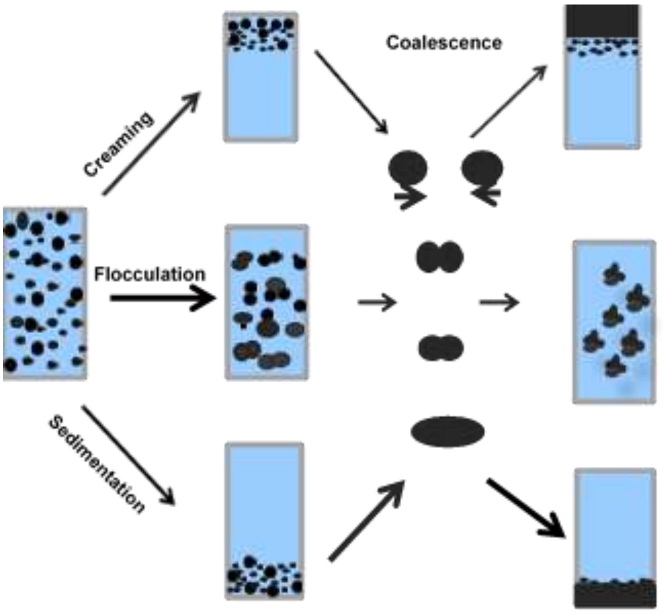


Figure 2:20: Demulsification mechanism (Srisan, 2016)

The process of demulsification is governed by Stoke's law (Equation 2); the chemical demulsifier acts directly on the film that separates the oil and water phases to produce larger dispersed droplets and allowing the thermal velocity to increase and speed up coalescence (Vin *et al.,* 2005). The process of demulsification is affected by the residence time, temperature, phase volume ratio, demulsifier dosage, crude oil properties and age of the emulsions.

2.7.4.3. Factors affecting demulsification

2.7.4.3.1. Effect of temperature

As explained by Zolfaghari *et al.* (2016), temperature affects the physical properties of oil-water interfacial films by increasing the thermal energy of the droplets, hence increasing the frequency of drop collisions. Increase in temperature weakens the interfacial film between the oil and the water droplets, lowers the oil viscosity, and increases the mobility and settling rate of the water droplets. This reduces the interfacial viscosity, resulting in a faster film drainage rate and enhancing drop coalescence (Kokal *et al.,* 2000).

In their work Oliveira *et al. (*2007) studied the effect of temperature on the performance of demulsifiers. They observed a straight relationship between demulsification efficiency and temperature; the highest demulsification efficiency was observed at the highest temperature.

The influence of temperature on the demulsification efficiency of water-in-oil emulsion was investigated by Balsamo *et al. (*2017). A demulsification test was performed at various temperatures (30, 45 and 60 ºC). The demulsifier used was an ionic liquid and the concentration was $2.9\text{x}10^{-2}$ mol. L^{-1}. The model emulsion was a mixture of toluene and water (70:30 toluene-in-water emulsion). They observed faster droplet collision frequency (high rate coalescence of droplets) at high temperatures. The highest demulsification efficiency (74%) was observed when the temperature was 30℃.

Hajivand & Vaziri (2015) conducted a bottle test on the separation of water-in-oil emulsion at different temperatures (10, 20, 50, 60 70 and 80 ºC) at constant pH of 5.5 for 72 h and 10 ppm demulsifier concentration. They found that high temperature improved water separation. The separated water was increased from 15 to 59% when the temperature was raised from 10 to 50 ºC. When the temperature increased to 70 ºC the efficiency increased to 57%, but when the temperature was 80 ºC the separation efficiency was 59% (only 2% increment). From this result it can be concluded that temperature can only affect separation efficiency to a certain extent; above 70 ºC the impact on water separation is minor, and increases in temperature at this stage would only add to operational cost.

2.7.4.3.2. Water and oil content

The phase volume ratio is one of the principal parameters that affect the efficiency of demulsification. According to Zolfaghari *et al.* (2016) oilfield emulsions with high water content promote the efficiency of demulsification while decreasing the demulsifier dose and the time needed for the phases to separate, provided that the water content is in the range of 30 to 70% of volumetric fraction. In other words, emulsions with high water content are more readily separated as compared to those with lower water content. Generally, emulsions are likely to separate faster when the volume of the dispersed phase is increased as the distance between the droplets is reduced.

Zaki (1997) reported that decreasing the oil content from 90 to 60 vol% in a surfactant-stabilized oil-in-water emulsion in the absence of demulsifier resulted in less water separation and observed a better separation when the oil content was reduced to 50%. It was concluded that an increase of the oil content (60% and above) in an oil-in-water emulsion may result in shifting the system to a water-in-oil emulsion, which happens to be more viscous and more stable due to the level of oil content.

2.7.4.3.3. Retention or settling time

Retention time is the period of time taken by the emulsion to separate completely into individual phases. According to Abdulkadir (2010), increasing the retention time aids the diffusion of the demulsifier through the interface of oil and water and promotes gravity settling, and consequently increases demulsification efficiency. Although the retention time has an important effect on demulsification efficiency, it is also important to take note that it comes at the expense of high separator equipment costs; therefore, it is important to evaluate the optimum retention time to avoid wasting time and money.

Kokal (2006) reported that for typical crude oil emulsions, the retention time varies between 10 to 30 minutes, and may be much longer for tight (highly stable) emulsions. The influence of retention time on the destabilization of oilfield emulsion was studied by Abdulkadir (2010); the results from a bottle test showed an increase in water separated as the retention time increased from 10 to 20 minutes and from 20 to 30 minutes. It was observed however that the demulsification efficiency only increases by 0.12% after 30 minutes, and from 40 to 60 minutes deviation from the expected result was observed because only 0.1% efficiency could be achieved. It was concluded however that retention time might also have a negative effect on the demulsification efficiency as it can lead to re-emulsification, which would reduce the efficiency of demulsification.

Many authors (Hirasaki *et al.,* 2011; Oseghale & Akpabio, 2014; Huang *et al.,* 2019; Al-Otaibi *et al.,* 2003) have investigated the influence of time on the demulsification efficiency of oilfield emulsions, and have all observed a decrease in oil concentration of the emulsion (after treatment) with an increased settling time. This resulted in increased efficiency of demulsification; the maximum efficiency was obtained after 4 hours of settling time.

2.7.4.3.4. Demulsifier concentration

The separation rate of emulsions is greatly influenced by the quantity of chemicals used, the degree of stability of the emulsions as well as the type of emulsions. Usually, in practical operation, demulsifiers are applied by trial and error; the operator injects a certain quantity of chemical, sees the effect on efficiency and adjusts the quantity injected accordingly (Al-Otaibi *et al.,* 2003). Nevertheless, emulsions with a high concentration of emulsifiers would require a high concentration of demulsifiers for separation.

Zolfaghari *et al. (*2016) mentioned that emulsions formed during EOR process require higher demulsifier concentration than those formed from first and secondary recovery processes; usually hundreds of ppm or even more are used in extreme conditions. Overdosing demulsifiers can result in the restabilization of the emulsions. The hydrophilicity or lipophilicity and molecular weight of demulsifiers are determining factors in identifying the optimum dosage for efficient demulsification.

Studies have been done by many researchers (Al-Sabagh *et al.,* 2009; Hamadi 2010; Hajivand & Vaziri, 2015) on the effect of demulsifier concentration on demulsification efficiency and they have all observed that high doses of demulsifier increase the number of demulsifier molecules per unit area on the interface layer, causing the droplets to coalesce with one another and thus enhance demulsification.

Hanapi *et al. (*2006) observed an increase from 6.4% to 94% of water separated after adjusting the demulsifier concentration from 10 to 100 ppm. A similar result was obtained by Rajak *et al. (*2016) who also obtained more than 98% efficiency of oil separated after an increase of demulsifier to an optimum dosage of 100 ppm. Al-Otaibi *et al. (*2003) however pointed out that excessive use of demulsifiers can further reduce the surface tension between phases and create a more stable emulsion or could lead to the formation of other types of emulsions.

2.7.5. The ageing effect in the destabilization of emulsions

Emulsions tend to change depending on the time of formation; the ease of separating crude oil emulsions depends on the ageing of the emulsion (Lucas, *et al.*, 2012). For example; aged emulsions are more difficult to separate compared to fresh samples. This is mainly because oil contains many types of absorbable materials whose effects can only be seen after some time, or when the emulsion is subjected to change in the environmental condition (Lucas, *et al.*, 2012). The ageing effect on emulsion separation was investigated by Lucas, *et al.* (2012). A demulsification test was performed on the first day of preparation and every 15 days for 30 days. It was found that demulsification efficiency decreased from 72.7% on the first day to 0% (no phase separation) on the 30th day of ageing. They were not able to improve demulsification efficiency even by increasing the demulsifier concentration 40 times the initial concentration. Based on their study it can be said that even the most effective demulsifier can become ineffective in demulsifying aged emulsions which is of great concern to crude oil treatment.

According to Manning & Thompson (1995), time allows the natural surfactants to accumulate at the interface of the droplets in the emulsions, resulting in the formation of a thicker and stronger film which can become difficult to break.

To the best of this researcher's knowledge, not much research has been done to study the effect of ageing on demulsification, therefore it was worth the investigation.

2.8. Response surface methodology

Response surface methodology (RSM) is a collection of mathematical and practical methods that are used to design, develop, improve and optimize a process (Trinh & Kang, 2010). This technique was first introduced by Box and Wilson in 1951 to optimize particular situations where several input variables may potentially influence the quality of the expected response or the performance of a particular process (Afizal, 2015). RSM also helps to evaluate the effect of factors individually and the effect of factors on each other, and to search for the optimum conditions for the modeling and analysis of the response (Chauhan et al., 2013). The response can be optimized either by minimization, maximization or within the range of targeted value (Olawoye, 2016). The predicted model is usually given in the form of an equation as presented in **Equation 2.5** and in the form of a 3D surface plot whereby for each value of the variables there is a corresponding response as a surface lying above the 3D plane. RSM is implemented in three different steps: (1) design of experiments which can be done using Box Behnken or Central Composite Design (CCD); (2) statistical modeling and regression analysis to develop model equations that represent the response surface modeling; and (3) variable optimization carried out through model equations (Afizal, 2015).

$$\mathrm{Y} = \beta_0 + \sum_{i=1}^{k} \beta_i x_i + \sum_{i=1}^{k} \beta_{ii} x^2 + \sum_{i=}^{k-1} \sum_{j-2}^{k} \beta_{ij} x_i x_j + \varepsilon \qquad \mathbf{2.5}$$

Where β_0, β_i, β_{ii}, and β_{ij} are the regression coefficients for the intercept, linear, quadratic and interaction terms respectively while x_i and x_j are the interdependent variable. Y is the response and e is the statistical error (Mäkelä, 2017; Afizal, 2015; Roshan et al., 2018a).

2.8.1. Design of experiments (DoE)

All scientific research requires the formulation of certain hypotheses whose validity is examined through the data generated from experiments conducted. Thus the design of an experiment becomes an indispensable component for this process. DoE consists of planning and conducting experiments, and analyzing and interpreting results (Badr, 2011). It also helps to evaluate the effect of multiple input variables and determine individual effect or their interaction on the response variable. The DoE can be performed using methods such as Box Behnken or Central Composite Design (CCD) and Doehlert Design. CCD, according to Roshan *et al. (*2018), is the most effective RSM design to model and analyze a process because it reduces the number of experimental runs and saves time. For the purpose of this study, CCD was used to design the experiments.

2.8.1.1. Central composite design (CCD)

CCD is useful in RSM for fitting a second-order response or quadratic surface model. It is composed of a factorial design that forms a cube with sides that are two coded unit lengths containing the centre points and the star or axial points (Anderson-Cook, 2009). The axial or star point is usually denoted by (α); the centre point is denoted as (0, 0) and the level of the factors are as given by minus (-) for low, plus (+) for high levels (Myers *et al.,* 2009). The factorial design can either be full or fractional factorial. A full factorial designed experiment consists of all possible combinations of all levels for all the studied variables. The simplest design has only two factors and two levels (low and high level), denoted as 2^2 factorial design (Badr, 2012). In a fractional factorial design, only the parameters that have the most effect on the response variable are used. **Figure 2.24** is a diagram of the factorial design for 2 and 3 factors.

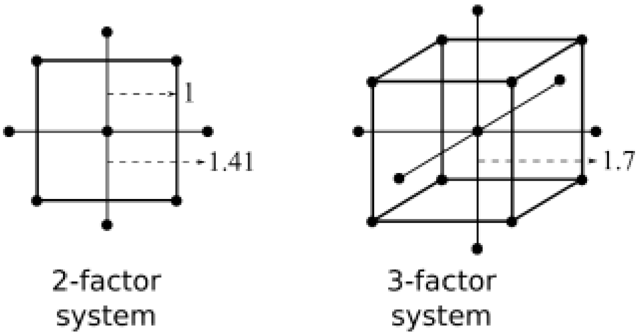


Figure 2:21: 2 and 3 factors factorial design diagram (Badr, 2012)

The two variables experiments will have the corners in the square while the three variable designs will have the corners in a cube (Myers *et al.,* 2009). The CCD for k factors is denoted 2^k and the fractional design will have 2k experiments. The number of experiment obtained by each factor is given by the formula:

$$N = 2^k + 2k + n \qquad \mathbf{2.6}$$

Where N is the total number of experimental run, k is the number of factors and n is the number of centre points or replicates the designer desires, which can be set between 2 to 6. For example for k = 4 the factorial design will have $2^4 + 2*4 + 6 = 30$ experimental runs if the centre point is 6.

The axial or start point can be calculated as follow: $\alpha = 2^{\frac{k}{4}}$, for example for k = 4 $\alpha = 2^{\frac{4}{4}} = 2$ (Myers *et al.,* 2009).

2.8.2. Statistical modelling and regression analysis

Statistical modeling is the method used to analyze the data obtained from an experiment. Statistical modeling is done by fitting a mathematical equation that describes the relationship between the experimental variables and the response into a model (Tirta *et al.,* 2017). The equation generated is usually solved using the method of least square (MLS). MLS is a multiple regression technique that is used to fit a mathematical model as a set of experimental data to generate the lowest residual possible (Almeida *et al.,* 2008). The quality and accuracy of the predicted regression model are evaluated by the application of the analysis of variance (ANOVA). The ANOVA is used to confirm the adequacy of the model, by comparing the variation due to the change in the combination of variables and the variation due to random errors that could occur during measurements of the responses (Aanchal *et al.,* 2016). The significance of the regression model is evaluated using the Fisher distribution test (F-test), the lack of fit test, the *p*-value, and the coefficient of determination R^2 (Aanchal *et al.,* 2016).

The significance of the regression is calculated by the ratio of the media of the square regression (MSreg) and the media of the square residual (MSres) (see **Equation 2.7**); the values are compared using the F-test. A large value of F indicates that the difference in the output caused by the source is greater than the difference caused by noise, meaning that the model fits well the experimental data (Mäkelä, 2017; Aanchal *et al.,* 2016)

$$F_{vreg,vres} = \frac{MS_{reg}}{MS_{res}} \qquad \mathbf{2.7}$$

The lack of fit compares the residual error with the pure error from the replicated design points (Aanchal *et al.,* 2016). A probability value (Prob>F) less than 0.05 indicates the significance of the model, while greater than 0.10 indicates the insignificance of the model (Aanchal *et al.,* 2016). If the *p*-value is less than the confidence level (p<0.05) it is considered to have a significant effect on the output response (Afizal, 2015). Another way to verify the adequacy of the model is by checking the values of the coefficient of determination (R^2), the adjusted (Adj R^2), the predicted (Pred R^2) and the adequate precision. The closer the R^2 is to 1 the better the fit, the adjusted R^2 is the value that is adjusted for the number of parameters in the given model. Predicted R^2 is a measure of how well the model predicts the observations. For a good model, the difference between the predicted and the adjusted R^2 should be less than 0.2 (Myers *et al.,* 2009). The adequate precision measures the signal to noise ratio and a ratio greater than 4 is desirable (Myers *et al.,* 2009). A model will be well fitted to the experimental data if it presents a significant regression and a non-significant lack of fit. Another way of validating the model is through the diagnostics plots such as the normal probability plot, the residuals versus predicted.

2.8.2.1. Residual analysis and diagnostics plots

2.8.2.1.1. Normal probability plots

The normal probability plot indicates whether the difference between the observed and the predicted values are normally distributed. The assumption made in this test is that the residual error should follow a straight line (Mäkelä, 2018). There are two types of normal probability plots namely externally studentized residuals and internal studentized residuals. The external studentized residual is the more recommended because it is highly sensitive to finding problems with the analysis; in this research work the external studentized residual will be used to evaluate the model. **Figure 2.23** shows an example of the normal probability plot graph.

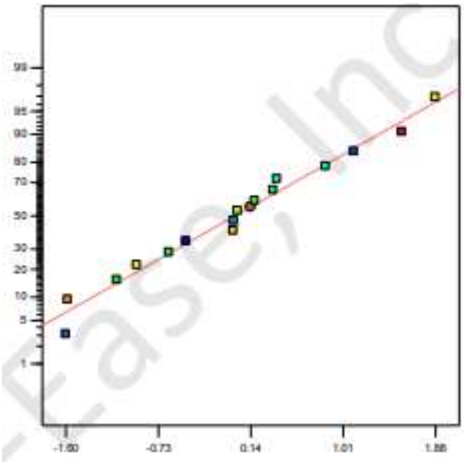


Figure 2:22: Normal probability plot graph (Mäkelä, 2018)

2.8.2.1.2. Residuals versus predicted

Residual estimates of errors obtained during the experiment. Residuals are found by subtracting the observed responses from the predicted responses. This test is one of the key parts of all statistical modeling because it tells whether the assumptions made are reasonable and the choice of the model is appropriate (Myers *et al.,* 2009). A good model is obtained when the data points are randomly scattered across the graph showing a constant variance of the data points. There should also not be any pattern on this graph, and the data points should not exceed the interval [-3, 3]. An example is shown in **Figure 2.26**. The types of residual plots include the residual versus predicted and residual versus the run numbers.

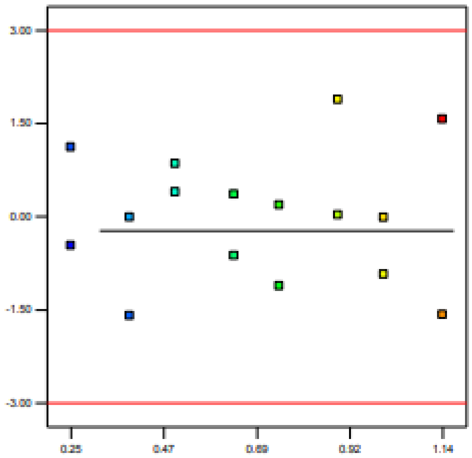


Figure 2:23: Graph of the residuals versus predicted (Myers *et al.,* 2009)

2.8.3. Summary of previous studies on crude oil demulsification using RSM

Biniaz *et al.* (2016) investigated the effect of temperature (50 to 80°C), demulsifier concentration (1000 to 2000ppm), pH of water (5 to 9) and water content (3 to 10%) on the demulsification efficiency of crude oil-in-water emulsions. Trioctylmethylammonium chloride, trioctylmethylammonium bromide and 1-hexadecyltrimethylammonium bromide were used as demulsifiers. The experiments were designed based on the central composite design method (CCD). The model was developed based on the statistical testing of the variables by the analysis of variance (ANOVA) to predict the demulsification efficiency. Response surface methodology (RSM) was used to find the optimum conditions for the input variable for maximum demulsification efficiency. Their results showed that temperature, pH and demulsifier concentration were two main parameters that affected the demulsification process and the maximum efficiency of 100% was attained at a neutral value of pH of 7.09, maximum temperature of 78.49°C, demulsifier concentration of 1039.22 ppm, and the best demulsifier was found to be trioctylmethylammonium chloride.

Roshan *et al. (*2018a) used response surface methodology (RSM) based on central composite design (CCD) to design and model the influence of temperature, demulsifier concentration, water content and pH on the demulsification efficiency of four surface-active compounds, namely poly(ethylene glycol)distearate, N,N-dimethyl-dodecyl amine N–oxide solution, polyoxyethylenetridecyl ether, and polyethylene glycol sorbitan monooleate, as demulsifier agents. The significance of the parameters on the efficiency was determined using ANOVA. It was found that N,N-dimethyldodecylamine N–oxide solution agent achieved the highest demulsification efficiency and the optimum values of temperature, concentration, water content, and pH were 78.62, 595.42 mg/L, 19.16%, and 8.98 respectively.

Tetteh *et al.* (2017) used RSM based on Box-Behnken design (BBD) to optimize the separation of oily wastewater using the coagulation flotation method process. The factors studied were pH, coagulant dosage and flotation time. ANOVA was used to test the fitness of the response models as well as the effects of their interactions. The model was selected based on the highest coefficient of determination R^2, adjusted R^2, the predicted R^2 values, and the lowest standard deviation and the lowest *p*-value. Their results suggested that coagulant dosage, pH, the interaction of pH and coagulant dosage showed a significant effect on oil removal efficiency.

2.9. Chapter outcome

In this chapter, literature on the formation and stability of oilfield emulsions as well as the conventional methods for oilfield demulsification was discussed. When natural reservoir water comes in contact with hydrocarbon-bearing rocks, emulsions are formed. These emulsions are stabilized by natural surfactant compounds such as asphalt, resin, naphthalene and another organic acids present in the reservoir. The literature has shown that the demulsification of these emulsions is one of the major environmental and economic concerns for petroleum producers. Various conventional methods of demulsification of oilfields were reviewed. Although these methods are claimed to be favourable from an environmental and economic point of view it was observed from the literature that they also present some drawbacks and disadvantages of which one was low oil recovery yield and high cost. The chemical destabilization method which according to the literature is the most effective demulsification method consists of adding surface-active compounds to enhance the separation of oil and water. In this chapter, the mechanism of demulsification was discussed in detail and factors such as retention time, temperature, and demulsifier type and dosage and phase volume ratio were identified to be the main factors affecting this process. Although chemical demulsification is currently the most commonly applied, to the best of the researcher’s knowledge there have only been few studies done to optimize this process using RSM. This study aims at optimizing the chemical destabilization of oil-in-water emulsions using RSM. This study will also evaluate the effect of different types and concentrations of demulsifiers, retention time and the oil to water ratio on demulsification efficiency.

CHAPTER 3. EXPERIMENTAL METHODOLOGY

3. Chapter summary

The equipment, chemicals, and procedures used in this study are described in this chapter. The first section of this chapter focuses precisely on the formulation of simulated oilfield (oil-in-water) emulsions. Diesel was the oil used for this study. Preliminary evaluation of the simulated oil field emulsion was carried out and the method used for the measurement of emulsion droplet size distribution as well as the stability of the prepared emulsions are reported.

The second section describes the method used to demulsify the simulated oil-in-water emulsions. Response surface methodology (RSM) with central composite design (CCD) was used for the optimization of the demulsification efficiency of the emulsions in this section.

3.1. Materials and methods

The oil phase used in the preparation of the synthetic oil-in-water emulsion is diesel, a typically saturated hydrocarbon and common petroleum product purchased from a local Caltex pumping station in Parow, Cape Town, South Africa.

3.1.1. Equipment

The following equipment was used: Labotec overhead stirrer (LAB01/03232/18, Heidolph Germany) operating between 0 - 2500rpm, pH meter, thermometer, electric balance, stopwatch, Discovery hybrid rheometer (TA20), and Turbiscan Lab Expert (MA 2000, France). Scilogex D500 homogenizer operating between 10000 - 50000rpm purchased from United Scientific. Zetersizer S90 particle size analyzer available at CPUT Chemistry Laboratory.

3.1.2. Chemicals

The following chemicals were used: sodium carbonate (Na_2CO_3), sodium chloride (NaCl), calcium chloride hexahydrate ($CaCl_2.6H_2O$), magnesium chloride hexahydrate ($MgCl_2.6H_2O$), sodium hydrogen carbonate ($NaHCO_3$), isobutyl alcohol. All these chemicals were purchased from Sigma Aldrich and were available in the Cape Peninsula University of Technology (CPUT) Chemical Engineering laboratory. The non-ionic surfactant used for this study is sorbian monolaurate (Span20), cetyl-trimethylammonium bromide

($CH_3(CH_2)_{15}N^+(CH_3)_3Br^-$), trimethyl-tetradecyl-ammonium chloride ($C_{12}H_{25}N^+(CH_3)_3Cl^-$), purchased at Sigma Aldrich. All chemicals were used as received without any further purification.

3.2. Brine preparation

Synthetic brine was prepared based on the method described by Nguyen *et al.* (2012). The composition of the brine solution is shown in **Table 3.1**. The synthetic brine composition was prepared in 2L of deionized water at room temperature; the mixture was stirred using an overhead stirrer at 300rpm for 10 minutes. The brine solution was stored in two 1000mL transparent Schott bottles and stored at room temperature as seen in **Figure 3.1**.

Table 3:1. Composition of synthetic brine (Nguyen *et al.,* 2012)

Parameters	Amount (mg/L)
Na_2CO_3	1000
NaCl	1000
$CaCl_2.6H_2O$	150
$MgCl_2.6H_2O$	139
$NaHCO_3$	430
Polymer	150
Isobutyl alcohol	750

Figure 3:1: Brine solution

3.3. Screening of parameters for the simulation of synthetic oil-in-water emulsions

The parameters studied for the formulation of stable oil-in-water emulsions were emulsifier concentration, homogenization speed, and brine salinity. These parameters were selected because they have shown greater effect on the stability index of the emulsions (ESI) based on the preliminary experiments conducted. The emulsifier concentration varied from 1–2.5% at 0.5% interval settings based on the total volume of the emulsions prepared. The homogenization speed was set as 1000, 14000, 19000 and 24000 rpm. The purpose of this test was to find the optimum parameter values in order to formulate 15%, 25%, 35% and 45% diesel water (D/W) emulsions with maximum emulsion stability index (ESI). According to the literature investigated, the salinity of a typical oilfield reservoir is about 30 mg/L (Oruwori & Ikiensikimama, 2010). Therefore, the salinity was adjusted by varying the NaCl concentration (1000, 2000 L, 3000 and 4000 mg/L). This concentration was selected in order to suit the experimental conditions for this case study. The trial experiment was carried out by fixing one parameter constant and varying the others, while the average droplet size of the emulsions and ESI were measured. The graphs of the studied parameter against the average droplet size of the emulsions and ESI were plotted. The parameter levels were chosen base on previously reported literature.

3.4. Emulsion preparation

The flowchart of the experimental steps for the simulation of oil-in-water emulsions is shown in **Figure 3.2**. This procedure involves two stages, namely the pre-emulsification and the emulsification stage (Alves *et al.,* 2014). During the pre-emulsification stage, a known amount of the brine solution (continuous phase) was added in a 250ml beaker followed by the emulsifying agent (Span20) and then mixed. The mixture was agitated using an overhead stirrer at 250 rpm for 2 minutes to allow the emulsifier to completely incorporate with the brine, after which a known amount of oil (diesel) was subsequently added and the mixture (brine + Span20 + diesel) was homogenized at high speed for a duration of 5 minutes (Kumar & Mahto, 2017b). (All the emulsions were prepared at room temperature and constant pH of 9.8). The homogenization was carried for this short amount of time to avoid foaming. The total volume of each emulsion sample was 100 ml; the concentration of emulsifier in the aqueous phase was measured based on the total volume of each emulsion sample prepared. All prepared emulsion samples were tested to determine the type of emulsion (water-in-oil or oil-in-water) by drop test. A drop of the emulsion was dropped into a beaker containing water; if the emulsion sprayed immediately into the water the emulsion was oil-in-water emulsion; if not it was water-in-oil emulsion (Liu *et al.,* 2018). Only oil-in-water emulsion types were observed. The emulsions were characterized by measuring the average droplet size and the emulsion stability index.

The first step in the formulation of the emulsions was to optimize the emulsifier concentration that could achieve maximum stability of the emulsions. This was done by varying the emulsifier concentration from 1.0 to 2.5% v/v-(volume percentage), based on the total volume of the emulsion) and keeping other parameters constant, namely mixing speed and brine salinity (NaCl) constant at 10000 rpm and 1000 mg/L respectively. The emulsion stability index (ESI) of the emulsions was investigated by monitoring oil separation as a function of emulsifier concentration for a period of 2 weeks at 2 day intervals.

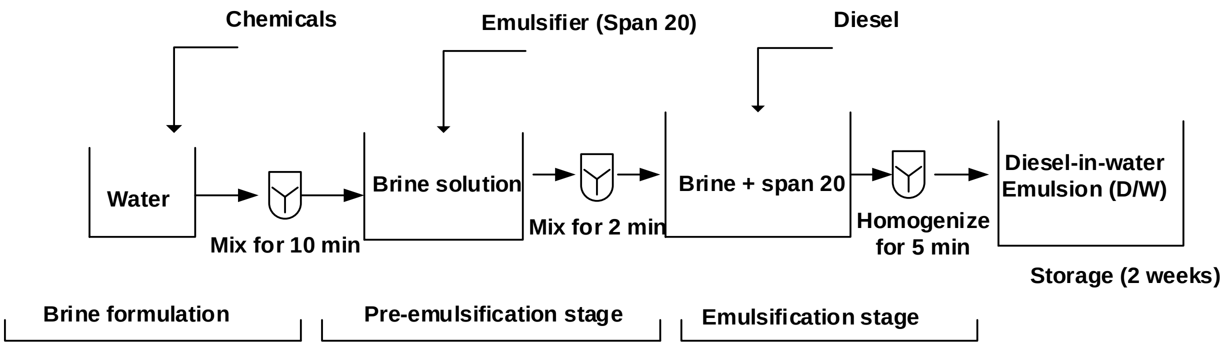


Figure 3:2: Illustration of the experimental steps

3.5. Emulsions characterization

3.5.1. Measurement of the stability index of the emulsions

The stability of the prepared emulsions was assessed through the bottle test at ambient temperature. The emulsions were kept in 45 mL calibrated centrifuge bottles and placed on the laboratory bench to settle through gravity for 2 weeks. The samples were observed and the amount of oil separated was recorded at the end of the 14th day. The amounts of the separated oil from the samples were recorded and the ESI was calculated using **Equation 3.1**. The experiment was performed in duplicate to ensure repeatability.

$$\text{ESI} = 1-\frac{\text{the oil separated (\%)}}{\text{total oil content (\%)}}\times 100 \qquad \textbf{(3.1)}$$

(Kumar & Mahto, 2017b)

Experiments were carried out and the value of the parameter which exhibited the highest ESI was considered to be the optimum condition for the formulation of oil-in-water emulsions. Therefore, these conditions were used to simulate the emulsions for the rest of this study.

The formulated emulsions were again tested for their stability using multiple light scattering techniques, and the average droplet size was also measured. This test was done in order to check the results obtained from the bottle test measurements in section 3.5.1.

3.5.2. Measurement of emulsion stability index using Turbiscan

The stability of emulsions was studied using the Turbiscan Classic MA 2000 Lab Expert Stability Analyzer (Formulation Company, France) based on the principle of multiple light scattering techniques. Turbiscan MA 2000 is a recently developed tool used for optical characterization of emulsions. This equipment enables the study of systems containing dispersed phases ranging from 0.1 up to 1000 microns in all kinds of dispersing media such as water, alcohol and organic solvents (Ruiquan *et al.*, 2006). The Turbiscan consists of a reading head that moves along a flat-bottomed cylindrical glass cell. The working principle is illustrated in **Figure 3.3**. The Turbiscan detects the change in the size of the dispersed particles as they migrate along the tube in order to quantify the phase separation of emulsions as a function of time. The reading head is equipped with a pulsed near-infrared light source (λ = 880 nm) and two synchronous optical detectors which determine the intensity of light received and emitted by the sample through the phenomenon known as transmission (T) and backscattering (BS). The transmitter (T) detector receives the light which goes through the sample at 0° while the backscattering detector receives the light backscattered by the sample at an angle of 135°, acquiring data while moving along the cell length (Umar *et al.,* 2018). The Turbiscan scans the samples at various programmed times and overlaps the profiles on one graph to show the destabilization evolution of the emulsions. A stable emulsion has all the profiles overplayed on one graph. The backscattering profile intensity along the sample height gives a quantitative indication of the particle size and concentration.

Fresh emulsion was added to the testing tube till full and the sample was inserted into the Turbiscan probe at room temperature; the auto-scan was set with 72 acquisitions every 10 minutes which made a total testing period of 12 h. The measurements were performed in duplicate.

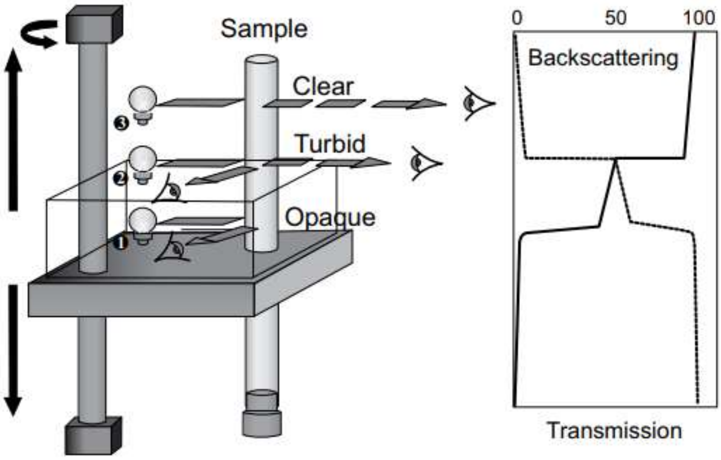


Figure 3:3: Transmission and backscattering (Tian et al., 2019)

3.5.3. Emulsion droplet size measurement

The droplet size of the emulsions was measured immediately after homogenization using a Malvern Zetasizer (**Figure 3.4**). This instrument uses dynamic light scattering at an angle of 90° to measure the size of particles in the emulsions. The technique analyses the diffusion and the random collision of particles as they constantly move (Brownian motion) within the liquid in which they are dispersed. It does so by measuring the intensity of the light scattered within the emulsion and converts it into droplet sized distribution using the Stokes-Einstein relationship. This instrument provides a measurement of three fundamental emulsion parameters such as particle size distribution, zeta potential, and molecular weight. This study focuses only on the measurement of emulsion particle size distribution. A known amount (0.5 mL) of the emulsion sample was added to the disposable capillary cuvette and inserted into the cuvette holder. Parameters such as the temperature, the dispersion media (water in this case) and the dispersed phase (diesel in this case) were set and the measurements were carried out. The calibration time was set to 20 seconds and the test was run 3 times for repeatability. The emulsion samples were run without dilution because they were optically clear enough.

Figure 3:4: Zetasizer nanoparticles

3.6. Emulsion demulsification

The demulsification of emulsions was done using the bottle test or gravity separation method (Schramm, 2005; Trinh & Kang, 2010). This test consisted of placing the emulsion samples in a graduated cylindrical tube and allowing the phases to separate due to the difference in density (**Figure 3.5**). The emulsions consisted of 15:85, 25:75, 35:65, and 45:55 diesel to water ratios respectively. Fresh emulsions were introduced in a 250 mL beaker and the demulsifiers were added and stirred by hand for 1 minute to enhance the transfer of the demulsifier into the emulsion. The mixture was then poured into a 100mL graduated measuring cylinder and was placed in a water bath at 30°C. Upon reaching the desired temperature (30°C) the samples were stirred to allow homogeneous heat transfer in the emulsions and were returned to the water bath. The samples were then allowed to settle through gravity while monitoring and recording the amount (mL) of the oil separated over the time interval of 2-12 h. The amount of diesel separated as a function of demulsifier concentration, settling time and diesel to water ratio was then converted into demulsification efficiency using **Equation 3.2**.

The demulsifiers used in this study were cetyl-trimethylammonium bromide (CTAB) and trimethyl-dodecyl ammonium chloride (TTAC) (Hirasaki *et al.*, 2011). Their molecular structures are represented in **Figure 3. 6**. These chemicals were selected based on the fact that they are cheap and they are environmentally friendly. Additionally, they are cationic demulsifiers which are a type of surfactants commonly used for crude oil demulsification.

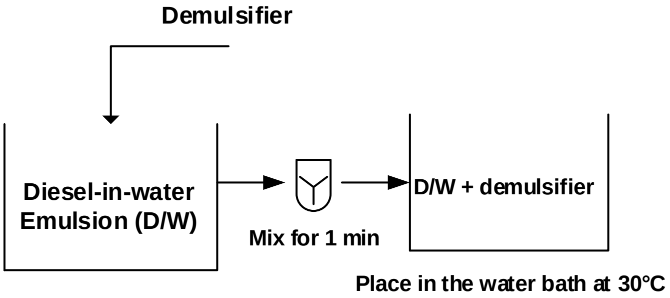


Figure 3:5: Experimental procedure for emulsions demulsification

$$\text{Demulsification efficiency} = \frac{\text{The volume of diesel separated (mL)}}{\text{The initial volume of diesel in the emulsions (mL)}} \times 100 \qquad (\mathbf{3.2})$$

(Roshan *et al.,* 2018a).

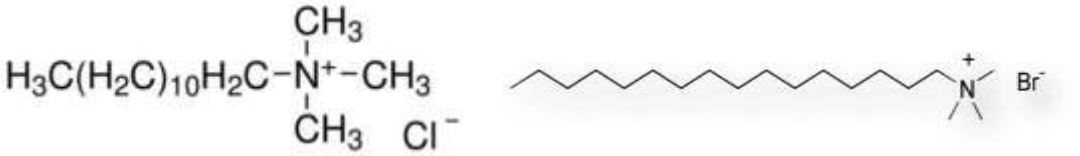


Figure 3.6: Molecular structure TTAC and CTAB

3.7. Effect of experimental variables on demulsification efficiency

The experiments were conducted by setting one variable constant and varying others. The selection of experimental variable levels was done based on previous investigations (Al-Sabagh *et al.,* 2009; Hamadi, 2010; Hajivand & Vaziri, 2015). The demulsifier concentration varied from 200 to 850 ppm, as described in the literature (Roshan *et al*., 2018a).

3.8. Statistical analysis

The experimental results obtained from the demulsification tests were used to optimize the demulsification process of the simulated emulsions using the design of experiments. The aim was to produce the best conditions to effectively demulsify the simulated oil-in-water emulsions. Design Expert (version11, State Ease) software was used to design the experimental runs, analyze the data and model the experimental response (demulsification efficiency). The experimental runs were designed using the Central Composite Design (CCD) method and response surface methodology (RSM) was used to fit the data to a second-order polynomial equation (**Equation 2.5**). The adequacy of the regression model was evaluated through the analysis of variance (ANOVA). ANOVA was used to test the level of significance of the experimental variables as well as the interaction terms on the model response (Roshan *et al.,* 2018b). The significance of factors was confirmed using the F-test and the *p*-value at a 95% confidence interval (Abdulredha *et al.,* 2019). The highest F-value and the p-value < 0.05 indicated that the variable concerned has the most significant effect on the model (Myers *et al.,* 2009).

3.8.1. Design of experiments (DoE)

Two levels, two numeric and one categorical factor were selected from the CCD and their effect on the response (demulsification efficiency) was studied. Each numerical factor varied over 5 levels, plus and minus axial or central point, plus and minus factorial points and the centre point, and the CCD experimental runs were duplicated for every combination of the categorical factor levels. The factors studied were the demulsifier concentration coded as X_1, settling time coded as X_2 and the emulsion formulation coded as X_3 with minimum (-) and maximum (+) levels. All the factors were examined at a high level, low level and centre points; the high levels, low levels and centre points were denoted as 1, -1, and 0 respectively shown in **Table 3.2 and Table 3.3.** A total number of 52 experimental runs were generated which consisted of 32 factorial points, and 5 centre points with the axial point set at $\alpha=1.414$ and 4 levels of categorical factors for the destabilization test of CTAB and TTAC. The actual design of experimental runs for the two tested demulsifiers are shown in **Table 3.4 and Table 3.5**. The experiments were performed three times for replicability and the average results were reported.

Table 3:2. Factors levels for the demulsification test for CTAB and TTAC

				Factors levels				
Factors	**Units**	**Type**	**Symbols**	**- α**	**-1**	**0**	**+1**	**+ α**
Time	h	Numeric	X_1	0.34	2	6	10	11.66
Concentration	ppm	Numeric	X_2	370	450	650	850	930
Emulsion formulation	%	Categoric	X_3	15:85	25:75		35:65	45:55

*emulsion formulation (diesel to water ratio)

Table 3:3. Factors levels for the demulsification test for CTAB and TTAC

				Factors levels				
Factors	**Units**	**Type**	**Symbols**	**- α**	**-1**	**0**	**+1**	**+ α**
Time	h	Numeric	X_1	0.34	2	6	10	11.66
Concentration	ppm	Numeric	X_2	370	450	650	850	930
Emulsion formulation	%	Categoric	X_3	15:85	25:75		35:65	45:55

*emulsion formulation (diesel to water ratio)

Table 3:4. Experimental runs of the demulsification efficiency for CTAB

			Input variables	
Std	Run	Time (h)	Demulsifier concentration (ppm)	Emulsion formulation (%)
1	1	2	450	15: 85
19	2	12	650	25: 75
29	3	2	850	35:65
45	4	12	650	45:55
6	5	12	650	15:85
20	6	6	367	25:75
16	7	2	850	25:75
33	8	6	367	35:65
12	9	6	650	15:85
3	10	2	850	15:85
24	11	6	650	25:75
26	12	6	650	25:75
47	13	6	930	45:55
7	14	6	367	15:85
21	15	6	930	25:75
15	16	10	450	25:75
9	17	6	650	15:75
32	18	12	650	35:65
2	19	10	450	15:85
30	20	10	850	35:65
41	21	10	450	45:55
35	22	6	650	35:65
22	23	6	650	25:75
10	24	6	650	15:85
37	25	6	650	35:65
34	26	6	930	35:65
23	27	6	650	25:75
13	28	6	650	15:85
11	29	6	650	15:85

43	30	10	850	45:55
4	31	10	850	15:85
51	32	6	650	45:55
31	33	1	650	35:65
39	34	6	650	35:65
28	35	10	450	35:65
25	36	6	650	25:85
36	37	6	650	35:65
5	38	1	650	15:85
44	39	1	650	45:55
50	40	6	650	45:55
38	41	6	650	35:65
14	42	2	450	25:75
18	43	1	650	25:75
8	44	6	930	15:85
48	45	6	650	45:55
40	46	2	450	45:55
17	47	10	850	25:75
49	48	6	650	45:55
27	49	2	450	35:65
42	50	2	850	45:55
46	51	6	367	45:55
52	52	6	650	45:55

*emulsion formulation (diesel to water ratio)

Table 3:5. Experimental runs of demulsification efficiency for TTAC

Input variables				
Std	**Run**	**Time (h)**	**Demulsifier concentration (ppm)**	**Emulsions formulation (%)**
15	1	10	450	25:75
50	2	6	650	45:55
38	3	6	650	35:65
41	4	10	450	45:55
34	5	6	930	35:65
8	6	6	930	15:85
7	7	6	370	15:85
43	8	10	850	45:55
22	9	6	650	25:75
13	10	6	650	15:85
39	11	6	650	35:65
20	12	6	370	25:75
33	13	6	370	35:65
36	14	6	650	35:65
23	15	6	650	25:75
35	16	6	650	35:65
3	17	2	850	15:85
47	18	6	930	45:55
49	19	6	650	45:55
17	20	10	850	25:75
11	21	6	650	15:85
18	22	1	650	25:75
21	23	6	930	25:75
51	24	6	650	45:55
6	25	12	650	15:85

16	26	2	850	25:75
45	27	12	650	45:55
30	28	10	850	35:65
19	29	12	650	25:75
40	30	2	450	45:55
25	31	6	650	25:75
9	32	6	650	15:85
1	33	2	450	15:85
4	34	10	850	15:85
48	35	6	650	45:55
46	36	6	370	45:55
27	37	2	450	35:65
24	38	6	650	25:75
44	39	1	650	45:55
14	40	2	450	25:75
28	41	10	450	35:65
32	42	12	650	35:65
37	43	6	650	35:65
26	44	6	650	25:25
5	45	1	650	15:85
2	46	10	450	15:85
10	47	6	650	15:85
52	48	6	650	45:55
42	49	2	850	45:55
29	50	2	850	35:65
12	51	6	650	15:85
31	52	1	650	35:65

*emulsion formulation (diesel to water ratio)

3.8.2. Evaluation of the regression model

It is always necessary to evaluate the reliability of the chosen model to ensure that it provides a good approximation of the model system. The adequacy of the developed regression model was tested using analysis of variance (ANOVA); the significance of the factors on the response was evaluated using the lack of fit test, the *p*-value, and coefficient of determination (R^2), the predicted R^2 and the adjusted R^2. The analysis consisted of the estimation of the effects of each parameter, their two-factor interactions on the response, and estimation of the regression coefficient and standard error for each coefficient. To validate the model, the *p*-value should be < 0.05 to obtain a 95% confidence interval and the lack of fit should be non-significant. The variability of the observed response was measured based on R^2. The value of the coefficient of determination should always lie between 0 and 1 and a value closer to 1 is considered good (Badr, 2011).

3.8.3. Optimization and validation of the regression model

The optimum conditions for efficient emulsification of oil-in-water emulsions were obtained using RSM as explained in **Section 3.6.2.** The model developed was validated by performing experiments under the optimum conditions suggested by the software and the results were compared with the suggested predicted values.

3.9. Evaluation of the ageing effect on the emulsion demulsification

The ageing study of the emulsions was carried out within sixty days at fifteen day intervals. The test consisted of measuring the emulsion stability index (ESI) and the droplet size of the emulsions at the end of day 15, 30, 45 and 60, and the demulsification test was carried out as explained in **Section 3.5**. The demulsification test was performed under optimum conditions obtained in **Section 3.6.3.** The results obtained from the ageing test were compared to those obtained from the fresh emulsion samples.

3.10. Chapter outcome

The experimental part of this study was explained in detail in this chapter. The factors that influenced the simulation of oil-in-water emulsion were screened and their effect on the average emulsion droplet size and on the ESI was investigated. The results are discussed in chapter 4. The maximum conditions for the demulsification of simulated oil-in-water emulsion were optimized using RSM and CCD and were used to predict the demulsification efficiency of oil-in-water emulsions, the effect of ageing on the stability of the emulsions was also assessed and the results will be discussed in chapter 5.

CHAPTER 4: SYNTHETIC OILFIELD EMULSIONS SIMULATION AND CHARACTERIZATION

4. Chapter summary

This chapter presents all the results obtained from the formulation of oil-in-water emulsions using the method described in chapter 3. Diesel (500-ppm type) was used as the oil phase for this study. This chapter aims to find the optimum condition to formulate stable oil-in-water emulsions. To achieve this aim, parameters such as emulsifier concentration, oil content, homogenization speed, and brine salinity were investigated by fixing one parameter constant while varying the others.

4.1. Diesel-in-Water emulsion simulation and stability investigation

Oil-in-water emulsions were simulated such as to achieve a maximum emulsion stability index (ESI), a point where no phase separation is observed. As a preliminary observation, 15:85 diesel-in-water (D/W) emulsion was prepared without an emulsifier, the mixing period was 5 minutes and the mixing speed was set at 14000 rpm. It was observed that about 90% (equivalent to 10% ESI) of diesel separated 2 minutes after the homogenization stopped **(**see picture R6 in **Appendix A)**. As the homogenization speed was further increased to 24000 rpm, it was noticed that it only took 10 minutes for all the diesel (meaning 0% ESI) to separate from the emulsions **(**see picture R7 in **Appendix A)**. This showed that even higher mixing alone could not enhance emulsion stability. Another experiment was run where 15:85 D/W emulsion was prepared at homogenization speed of 24000 rpm with 0.5% emulsifier concentration and 5 minutes mixing time. The emulsions stabilized for only 5 hours, and the percentage of diesel separated gradually increased until it was completely separated within 24 h **(**see pictures R3, R5 and R8 in **Appendix A)**. These observations showed that the emulsifier plays an important role in the formation and stabilization of diesel-in-water emulsions as it provides better distribution of the dispersed phase into the continuous phase.

4.1.1. Effect of emulsifier concentration on the emulsion stability index

Figure 4.1 represents the influence of the emulsifier concentration on the stability of diesel-in-water emulsions at various oil ratios. It was observed that all emulsions exhibited an increase in ESI as the emulsifier concentration increased from 1 to 2%, respectively. This finding was consistent with the work previously done by other researchers (Kumar & Mahto, 2017c; Patil *et al.,* 2015; Vilasau *et al.,* 2011). This result could be attributed to the fact that at high emulsifier concentration, more molecules of surfactant become present in the emulsion which is susceptible to adsorb at the interface of oil and water. As more emulsifier molecules accumulate at the interface, a steric barrier is formed between the dispersed oil phase and the continuous water phase which will hinder the phases (diesel and water) from approaching and coalescing, and thus promotes emulsion stability (Kumar & Mahto, 2017b).

The result also shows that a maximum ESI of 52% was achieved when the emulsifier concentration was 2% and this was observed for the emulsion containing 15:85 D/W only. Other emulsions, namely 25:75, 35:65 and 45:55 D/W could only achieve 50%, 46% and 45% ESI at this concentration (2% emulsifier) respectively. This could be because more emulsifier was needed in order to stabilize the emulsions with high diesel content.

However, it was surprisingly noticed that after increasing the emulsifier concentration to 2.5% there was no further increase in ESI of the emulsions. It can be concluded from this result that adding more emulsifier to the emulsion did not have any effect on the ESI. This result explains the polydispersity effect of the emulsifier micelles formed at the interface of diesel and water at high emulsifier concentration (Selim, 2014). Kristian & Greenway (2017) also explained that when the emulsifier molecules reached their critical micelle concentration in the emulsions, further addition of emulsifier will not cause any change in the interfacial tension (IFT) because the diffusion coefficient of micelle decreases as its concentration increases. Therefore, further addition of emulsifier will only lead to the waste of chemicals. This could be the case for this particular study, therefore it can be concluded that the critical micelle concentration of the emulsifier reached when its concentration was 2%.

To the best of the author's knowledge, no literature has reported on the amount of emulsifier required in the emulsion to reach its critical micelle concentration. Based on these findings it can be concluded that the emulsion stability index is not dependent on the diesel content in the emulsions but is a function of the emulsifier concentration. Considering this, 2% was considered the optimal concentration for the emulsion formation up to this stage.

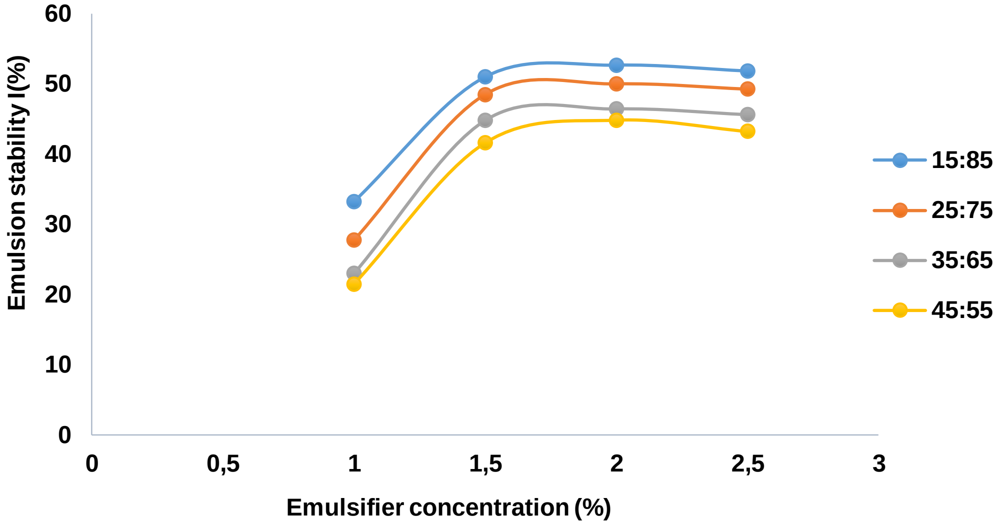


Figure 4:1: Effect of emulsifier concentration on the stability index of the emulsions

4.1.2. Effect of homogenization speed on the emulsion stability index

At determined emulsifier concentration of 2%, the influence of the homogenization speed on the stability of the emulsions was investigated and the observed result is presented in **Figure 4.2**. The homogenization is important in emulsion formulation because it provides the energy that is required to deform the interface between the two immiscible liquids and causes the mass transfer of the dispersed phase (diesel) and the emulsifying agent into the continuous phase (Dokic, 2013). In this study, the emulsions were simulated at different homogenization speeds ranging from 10000 to 24000 rpm, the brine salinity was kept constant at 1000 ppm and the homogenization time was 5 minutes. It can be seen from **Figure 4.2** that the emulsion stability index (ESI) of all the emulsions was enhanced considerably as the homogenization speed increased. All the emulsions remained stable (without phase separation) for more than 10 days when the homogenization speed was 24000 rpm, and only a small layer of oil appeared at the top of the vials at the end of the testing period (14 days) (see **Table 4.1**). The ESI of the 15:85, 25:75, 35:65 and 45:55 D/W emulsions increased from 53% to 99.33%, 50% to 92.5%, 48% to 91.2% and 45% to 90% respectively when the homogenization speed was raised from 10000 rpm to 24000 rpm. This is because at high homogenization speed more energy is supplied to the emulsion system to enhance the breaking up of oil droplets into smaller size (Kamarudin *et al.,* 2010), thus increasing the number of droplets in the emulsions, which consequently increase the emulsion viscosity and enhance the emulsion stability (Ghannam & Selim, 2009; Liyana *et al.,* 2015). This result is in agreement with the work done by Liyana (2015), who reported that no phase separation was observed for 70:30 crude oil-in-water emulsions when the homogenization speed increased from 10000 to 15000 rpm. Ghannam & Selim (2009) also studied the influence of homogenization speed on the stability of diesel in water emulsions; the emulsion was prepared in the presence of 1% emulsifier and 20% diesel content, and the homogenization speed ranged from 5000 to 15000rpm. They reported that the emulsion stability increased from 68 to 89% at this range.

Based on the observed result, 24000rpm was considered as optimum homogenization speed to simulate the emulsions.

Table 4:1. Oil separated on day 10 and the 14

Oil to water ratio (%)	**Oil separated (mL)** **Day 10th**	 **Day 14th**
15:85	0.0	0.2
25:75	0.0	2.0
35:65	0.0	3.0
45:55	0.0	4.5

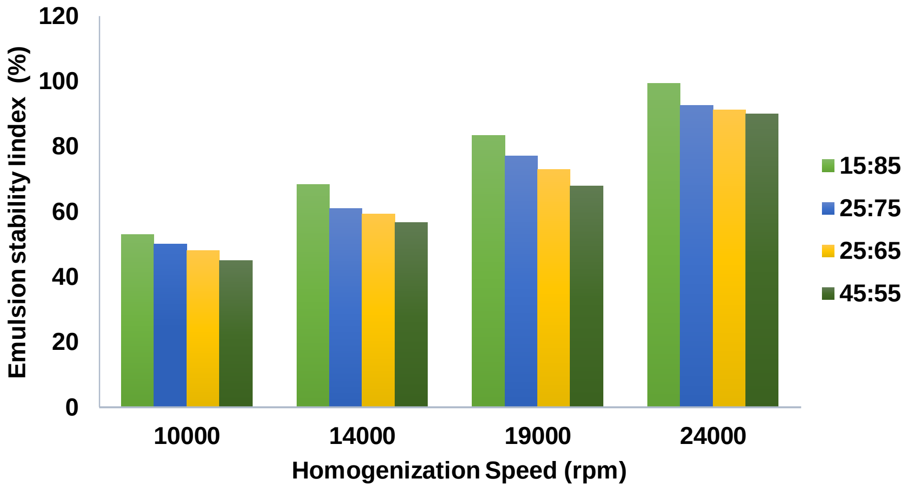


Figure 4:2: Effect of homogenization speed on the emulsion stability index

4.1.3. Effect of salinity on the emulsion stability index

The effect of brine salinity on the stability of diesel-in-water emulsions was investigated and the result is reported in **Figure 4.3**. The emulsions were simulated by varying the NaCl concentration from 1000 to 4000 mg/L in the presence of 2% emulsifier concentration, at a homogenization speed of 24000 rpm, and the homogenization time was 5 minutes.

The result shows that there was a significant decrease in the emulsion stability index (ESI) of all the emulsions when the NaCl concentration increased from 1000 to 4000mg/L. The emulsions containing lower salinity was more stable compared to those with higher salinity.

The ESI of 15:85, 25:75, 35:65 and 45:55 D/W emulsions decreased from 99.3% to 20%, from 92.5 to 28%, from 91.2% to 51%, and from 90% to 62.22% when the salinity increased from 1000 mg/L to 4000 mg/L respectively. This finding shows that high salt concentration hinders the activity of the emulsifying agent. Additionally, high salt content increases the ionic strength of the aqueous phase which produces an electrostatic interaction with the ionic compounds present in the oil phase, and consequently promotes fast coalescence of droplets which results in phase separation (Moradi *et al.*, 2011). This result was consistent with the study done by other authors (Maaref & Ayatollahi, 2018; Eftekhardadkhah & Hashemabadi, 2011; Moradi *et al.,* 2011). In their studies they investigated the effect of brine salinity on the stability of oil-in-water and water-in-oil emulsions and found that increasing the brine salinity leads to a decrease in the emulsion stability due to the increase of the surface tension between the oil and water which enhances the separation of the phases.

The order of emulsion stability was as follows: 15:85 < 25:75 < 35:65 < 45:55 diesel-in-water (D/W). Thus, it could be said that the coalescence mechanism is enhanced at high NaCl concentration and low diesel to water ratio. Considering the result of this investigation, 1000 mg/L NaCl was the maximum salinity to obtain high emulsion stability for this study.

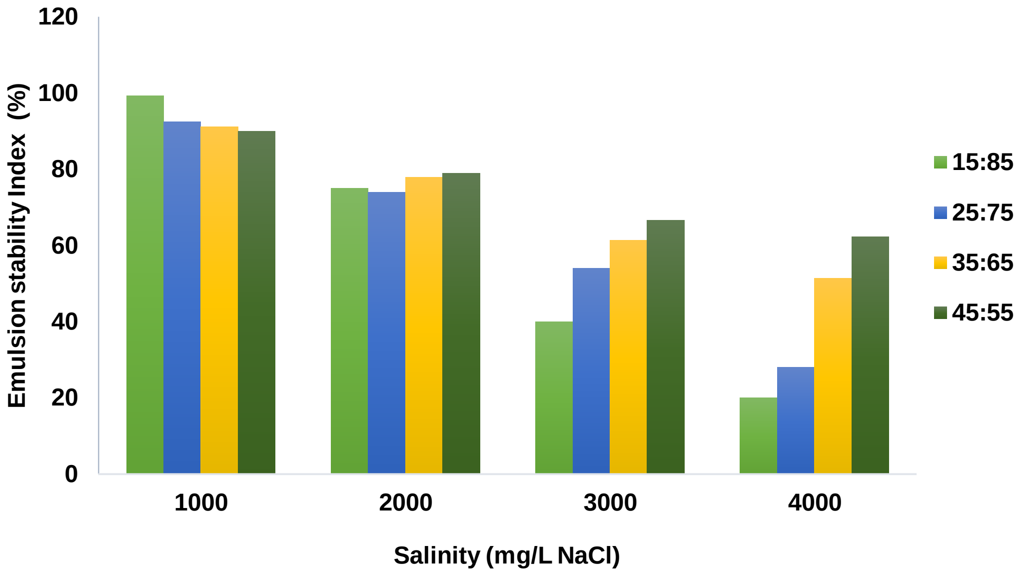


Figure 4:3: Effect of salinity on the emulsion stability index

4.2. Emulsions droplet size analysis

The average droplet size of emulsions is an important parameter that influences the stability of the emulsions. It is the most common method used to determine emulsion stability. The droplet size of emulsions depends on parameters such as the emulsifier concentration, homogenization speed, volume fraction of the dispersed phase and the salinity of the aqueous phase. The average droplet size of the emulsions was measured as a function of emulsifier concentration, homogenization speed, brine salinity, and diesel content, and the results are shown in **Figures 4.4 to 4.6**.

4.2.1. Effect of emulsifier concentration on the average emulsion droplet size

The emulsions were prepared at varied emulsifier concentrations (1 to 2.5%), at 10000 rpm, 1000 mg/L NaCl, and homogenization time of 5 minutes. The average droplet size of the emulsions was measured at each emulsifier concentration and the result is represented in **Figure 4.4**. The results show that the average droplet size of the emulsions decreased as the emulsifier concentration increased. As the emulsifier concentration increased from 1 to 2.5%, the average droplet size of 15:85 diesel water (D/W) decreased from 338.2 to 74.7 nm, that of 25:75 D/W decreased from 351.6 to 86.82 nm, 35:65 D/W went from 473.33 to

152.2 nm and 45:55 D/W decreased from 552.83 to 216.2 nm. This is because increasing the emulsifier concentration in the emulsion system caused the reduction of the interfacial tension (IFT) between the two phases (diesel and water) and increased the interfacial area around the droplets to facilitate the breaking of the oil droplets into a smaller size (Ashrafizadeh & Kamran, 2010).

This result is in agreement with previously reported works (El-Hamouz, 2007; Eftekhardadkhah & Hashemabadi, 2011; Ashrafizadeh & Kamran, 2010; Kumar & Mahto, 2017d). According to Hasani *et al. (*2015), when there are enough emulsifier molecules at the oil and water interface, the surface of oil droplets becomes sufficiently covered by the emulsifier, which then prevents the droplet from colliding.

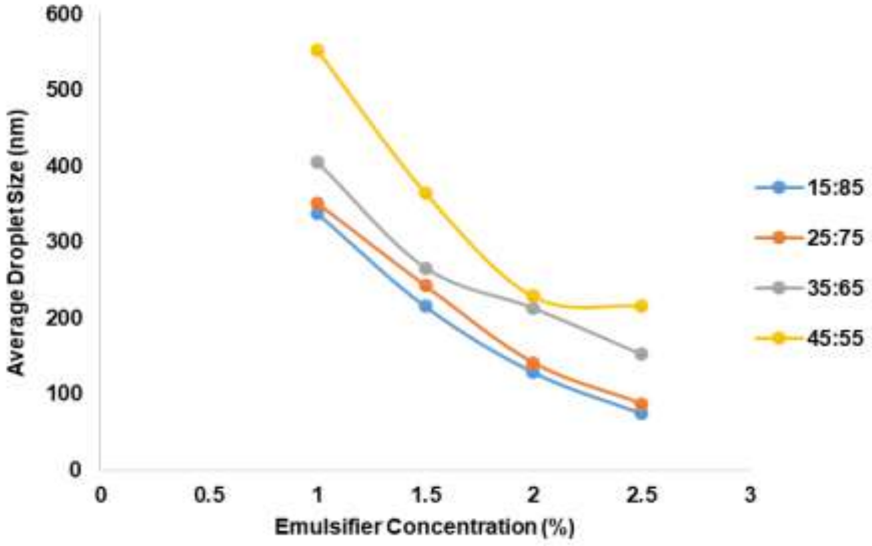


Figure 4:4: Effect of emulsifier concentration on the average droplet size

4.2.2. Effect of homogenization speed on the average droplet size

The influence of homogenization speed on the average droplet size of the emulsions was investigated at varied homogenization speed from 10000 to 24000 rpm. The emulsifier concentration, salinity and time were kept constant at 2%, 1000mg/L and 5 minutes respectively. The outcome of this investigation is reported in **Figure 4.5**.

It was found that there is a significant decrease in the average emulsion droplet size as the homogenization speed increased 10000 to 24000 rpm. The average droplet size of 15:85, 25:75, 35:65 and 45:55 D/W decreased from 216.9 to 8.586nm, 242 to 11.603nm, 275 to

19.99nm and 333.8 to 101.17nm respectively. This result shows that high homogenization speed resulted in the increase of the shear strength, thus causing distortion and breaking up of the diesel droplets into smaller ones. This result is in accordance with the work previously reported by Clark & Pilehvari (1993). It was also noticed that the emulsion droplet size varied as a function of diesel content, while the highest average droplet size was obtained from the emulsions containing high diesel fraction. This shows that the larger the dispersed phase (diesel) in the emulsion, the higher the tendency to form bigger droplet sizes.

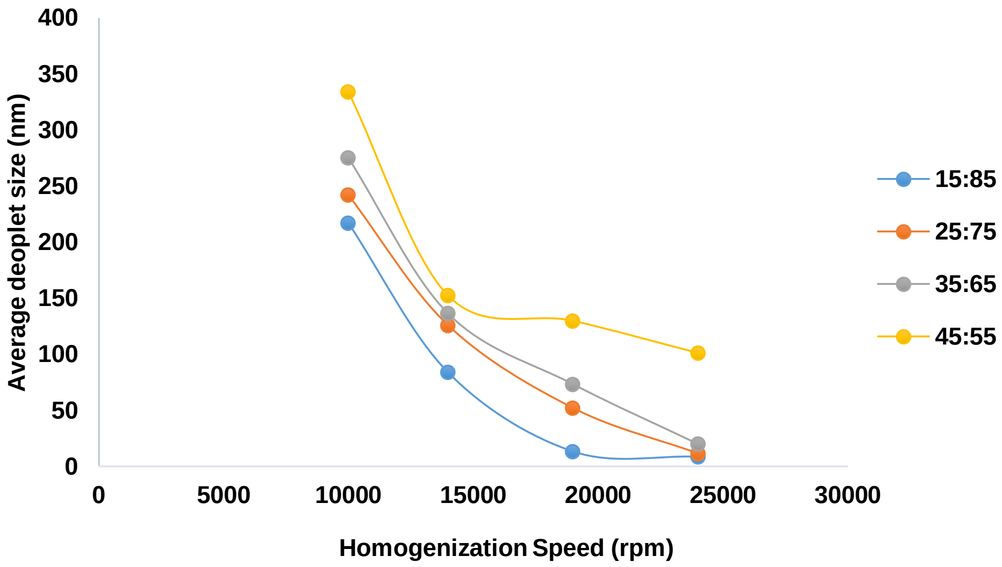


Figure 4:5: Effect of homogenization speed on the average emulsion droplet size

4.2.3. Effect of brine salinity on the average emulsion droplet size

The effect of salinity on the average droplet size of the emulsions was also studied. The emulsions were prepared in the presence of 2% emulsifier, 24000 rpm and 5 minutes homogenization speed, and the salinity was varied from 1000 to 4000 mg/L NaCl. **Figure 4.6** shows that as the concentration of NaCl increased the emulsion droplet size became larger. The average droplet size of the emulsions varied from 19.34 to 139.57nm, from 19.99 to 199.5nm, 101.1 to 246.37nm and 125.7 to 380.23nm for 15:85, 25:75, 35:65 and 45:75 D/W emulsions respectively. This indicates that at a high ionic strength of the brine phase, the dispersed phase of the emulsions tends to become larger due to the faster aggregation and coalescence of the droplets. This result was in reasonable agreement with the findings of Aman *et al.* (2017).

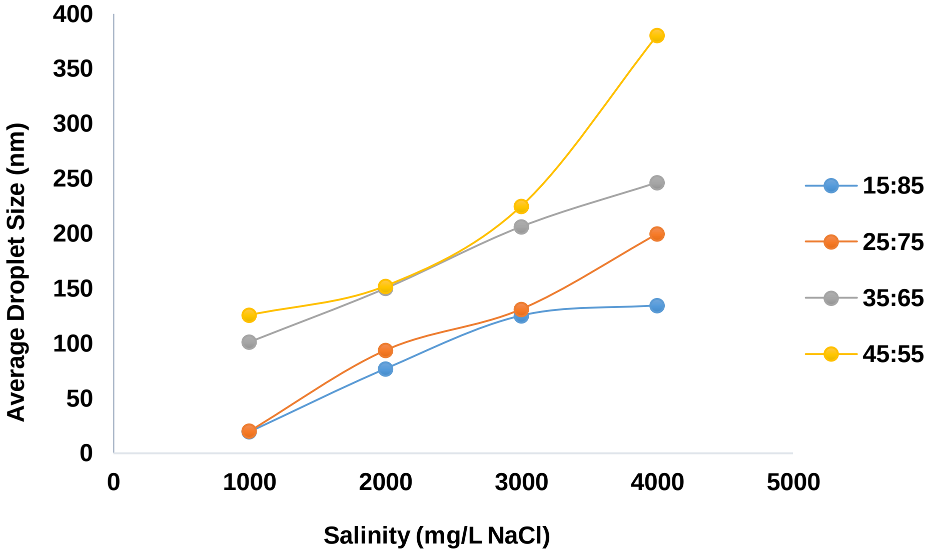


Figure 4:6: Effect of brine salinity on the emulsion droplet size

In this study, the optimum conditions for the preparation of diesel in water emulsions containing 15:85, 25:75, 35:65 and 45:55 diesel ratio was 2% emulsifier concentration at the homogenization speed of 24000 rpm with 1000 mg/L NaCl and the homogenization time of 5 minutes.

4.3. Emulsion stability test by multiple light scattering at optimum parameter conditions

The bottle test (**section 4.2 and 4.3**) showed no visible phase separation within the test period of 2 weeks. Hence, the emulsions were considered to be stable. In order to confirm this observation, the stability of the emulsions was studied by multiple light scattering (MLS) using the Turbiscan Classic Lab Expert (MA 2000, Formulation Company, France).

The backscattering (BS) and transmission (T) profiles as a function of tube length of 15:85, 25:75, 35:65 and 45:55 diesel water (D/W) emulsions are shown in **Figure 4.7** to **4.10**. The x-axis represents the tube length or sample height, the Y-axis represents the percentage change of backscattering relative to the initial state of the emulsion, and the color-coded column at the far right represents the time between each acquisition. The upper part of the graph represents the percentage transmission (%T) and the lower part represents the percentage backscattering (% BS).

According to Olejnik *et al.* (2015) the lower the value of the %transmission (%T) the more stable the emulsion. The test was conducted for a period of 12 h, and the interval between each acquisition was 30 minutes for all emulsion samples.

The backscattering (BS) profile as a function of tube length of 15:85 and 25:75 diesel-in-water (D/W) emulsions are represented in **Figure 4.7** and **Figure 4.8**. It can be seen from the graphs that these emulsions have similar BS profiles. This could be attributed to the fact that both emulsions presented the highest ESI of 99.3 and 92.5%, respectively (from the bottle test results **section 4.2**). Nevertheless, the % BS level decreased at the bottom of the tubes (from 0 to slightly above 10 mm) indicating that sedimentation had occurred within this region of the samples (slow migration of oil droplets from the bottom of the cylindrical tube to the top).

However, no visible change was observed on the %BS profiles as it moved along the sample height and all the profiles overlaid on one curve, indicating the absence of creaming or coalescence phenomena, which shows that there was no variation (particle growth) in particle size for both samples. Lu *et al.* (2017a) observed similar results. The percentage BS of emulsion containing 15:85 D/W was found to be 91.5% whereas that of 25:75 D/W was 90% respectively.

According to Maphosa *et al.* (2017), the highest percentage BS is an indication that the emulsions contained a high population of oil droplets with small particle that had dispersed a high amount of light. The highest percentage of BS was achieved with 15:85 D/W emulsions and was considered the most stable of all the emulsions. This could be explained by the fact that it also contained the smallest average droplet size (8.586 nm).

The transmission graph showed a smooth line along the length of the tubes and no variation of particle size was observed along the graph over the 12 h. The percentage transmission for both emulsions was 20%; according to Olejnik *et al.* (2015), the lower value of percentage transmission indicates that the emulsions are highly stable, hence both emulsions were considered stable over the testing time according to the following order of stability: 15:85 > 25:75 D/W emulsion.

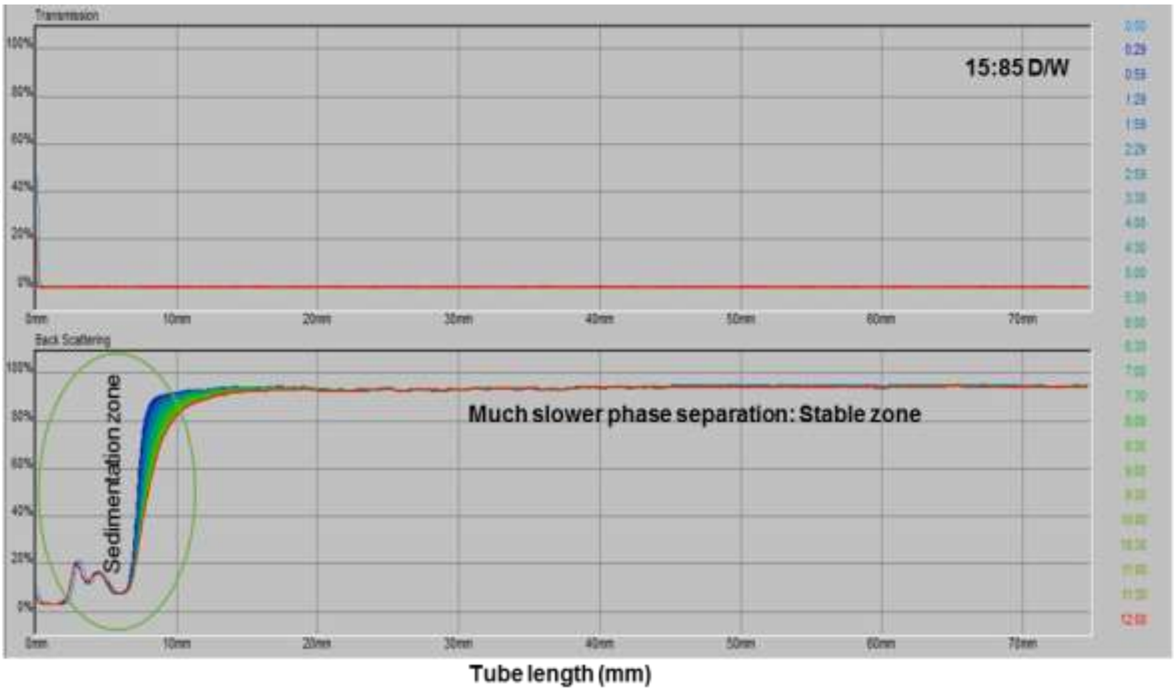


Figure 4:7: Backscattering and transmission profile for 15:85 D/W emulsion

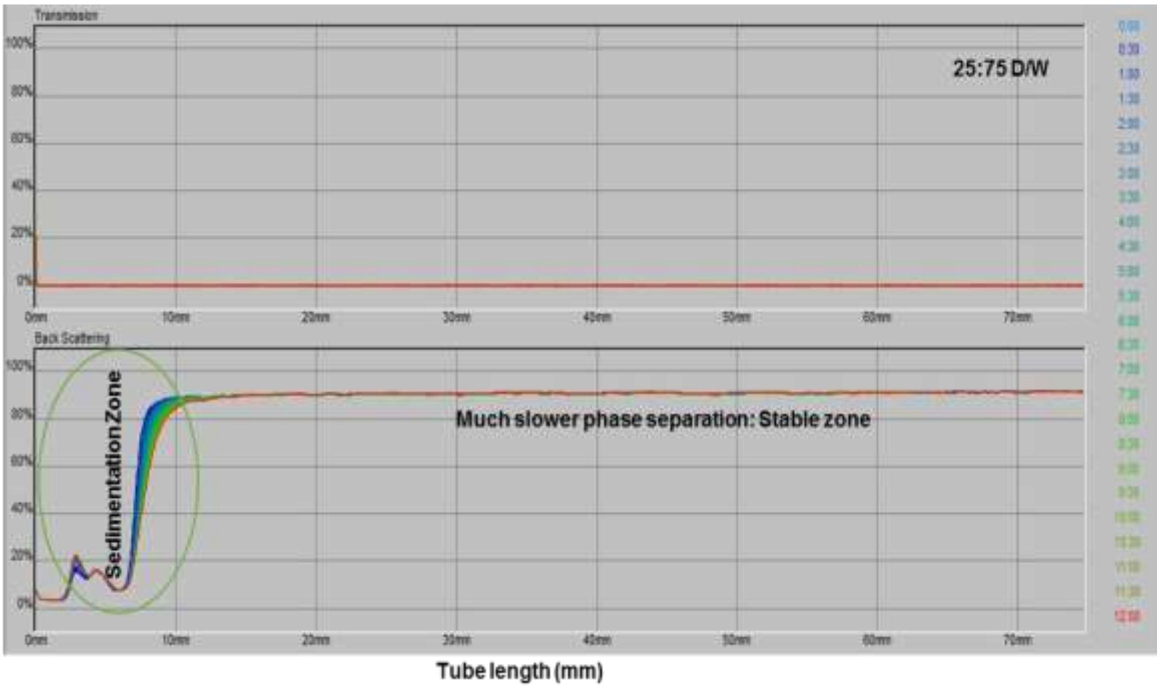


Figure 4:8: Backscattering and transmission profile for 25:75 D/W emulsion

Figures 4.9 and 4.10 represent the backscattering profiles for emulsions containing 35:65 and 45:55 D/W. It can be observed from **Figure 4.9** that the %BS decreased until about 42mm (length of tube) indicating the presence of flocculation and creaming due to the increase of the oil droplets within that particular length of the tube. However, there was no noticeable change above the 42 mm height of the testing tube. Meanwhile, the %BS of the 45:55 D/W emulsion decreased within almost the entire length of the tube, which also indicated faster flocculation and creaming leading to the growth of the oil droplet size. Due to the density difference between the oil phase and the water phase, as the droplets migrated, faster coalescence occurred which in term led to the creaming of the emulsion at the top of the tube. This result could be attributed to the increase in the oil phase volume fraction in these emulsions as compared to the other emulsions. This finding was consistent with the work done by Lu *et al.* (2017). A sharp increase was also observed in the transmission intensity for both emulsions which indicates the phenomenon of clarification due to Brownian motion of the diesel droplets. Apart from the sharp increase in the percentage transmission (%T) observed at the bottom of the tube, the emulsions remained stable during the testing period. The percentage backscattering (%BS) in terms of ESI for the 35:65 and 45:55 D/W emulsions was 89.7% and 88% respectively.

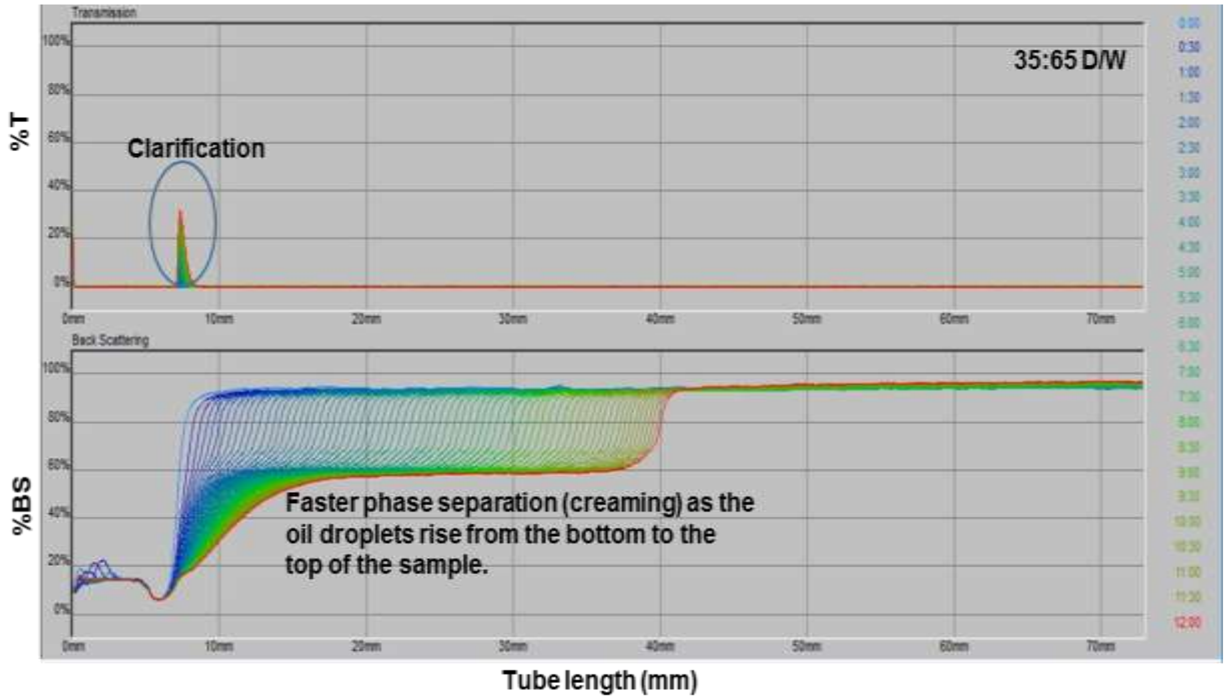


Figure 4:9: Backscattering and transmission profile for 35:65 D/W emulsion

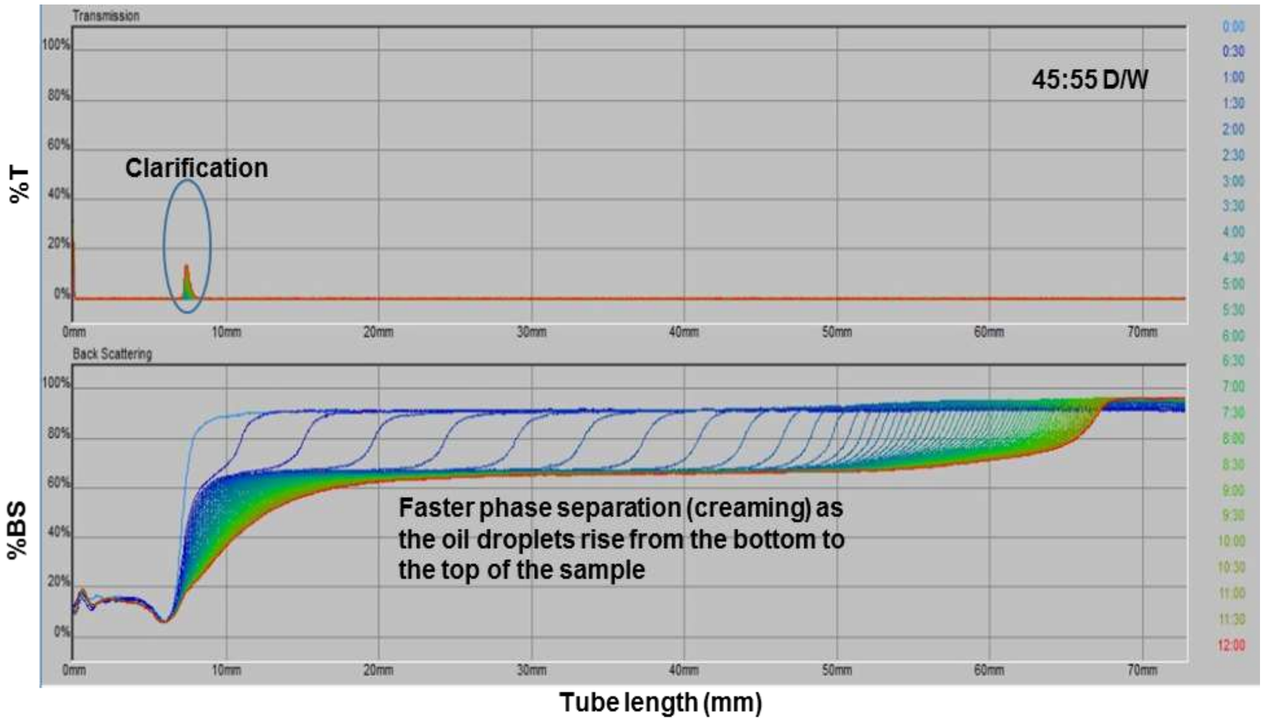


Figure 4:10: Backscattering and transmission profile for 45:55 D/W emulsion

Figure 4.11 represents the variation of the average droplet size and the emulsion stability index (ESI) as a function of oil content in the emulsions under optimum formulation conditions. It can be seen from **Figure 4.11** that the average droplet size and the ESI were greatly influenced by the amount of diesel present in the emulsions. The graph demonstrates that as the oil concentration increased in the emulsion, the average droplet size increased while ESI decreased. This result was expected and the findings were in accordance with work previously reported (Mollakhalili Meybodi *et al.,* 2014). This result can be attributed to the fact that at high volume of the dispersed oil phased, there is an increased chance of the droplets colliding with one another, thus promoting the formation of bigger oil droplets, which will promote coalescence and instability of the emulsions (Hadnad, *et al.,* 2013; Lin, 2009; Stobiecka & Maszewska, 2006).

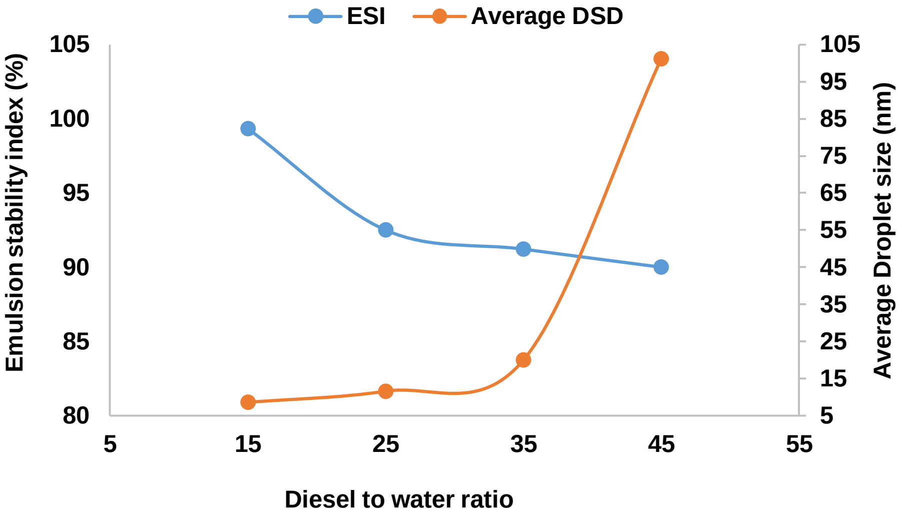


Figure 4:11: Effect of diesel to water ratio on emulsion stability and average emulsion droplet size

4.4. Structural images and appearances of the emulsions

Figure 4.12 represents the microscopic appearance of emulsions that were examined using a light microscope (Kenwood VisionA). The figure shows that there is a slight difference in the droplets of the emulsions depending on the oil ratio in the emulsions. **Figure 4.13** shows the physical appearance of the emulsions. It can be seen that there is no difference in the physical appearance of emulsions.

Figure 4:12: Microscopic image of diesel-in-water emulsions (a) 15:85, (b) 25:75, (c), 35:65, and (d) 45:55

Figure 4:13: Physical appearance of the emulsions

4.5. Chapter outcome

This chapter aimed at simulating stable synthetic petroleum emulsions containing different oil ratios. The oil used for this purpose was diesel fuel, a product derived from crude oil. To achieve this aim, various parameters, namely emulsifier concentration, homogenization speed, brine salinity, and oil content were evaluated and their effect on the stability of the emulsions was investigated one factor at a time. The emulsion stability index was measured using the bottle test method and the dynamic light scattering method using a Turbiscan M2000.

The results showed that the stability index of the emulsions was mainly influenced by the brine salinity, emulsifier concentration, and homogenization speed. This study found that emulsions formulated with high brine salinity were very unstable compared to those formulated at low brine salinity, even at high homogenization speed and high emulsifier concentration. It was found that the oil ratio did not have much influence on the emulsion stability index when the homogenization speed was high (19000rpm). **Table 4.1** shows the result of the ESI found by gravity separation and measured using the dynamic light scattering method. It can be observed in the table below.

Table 4:2. ESI measured by gravity separation and by dynamic light scattering methods

Oil to water ratio (%)	**ESI (%)**	
	Gravity separation	**Dynamic light scattering**
15:85	99.33	91.50
25:75	92.50	90.00
35:65	91.20	89.70
45:55	90.00	88.00

CHAPTER 5:OPTIMISATION OF THE DEMULSIFICATION EFFICIENCY OF OIL-IN-WATER EMULSIONS USING RESPONSE SURFACE METHODOLOGY

5. Chapter summary

The purpose of demulsification is to break and separate the emulsions into two phases, oil and water; this is usually achieved by chemical, physical and biological method. In this work, settling time oil to water ratio and demulsifiers concentration were set as physical factors and cationic surfactant Cetyltrimetylammonium bromide (CTAB) and Trimethyltetradecylammonium chloride (TTAC) were set as chemical factors. This chapter presents the results obtained for the demulsification of the simulated diesel-in-water emulsions. The influence of process variables such as settling time, demulsifier types, concentration, and oil content on the demulsification efficiency of diesel-in-water emulsions was investigated. The process conditions were optimized using response surface methodology RSM with central composite design (CCD). The analyzis of variance (ANOVA) was used to evaluate the significance of the process variables on the responses. A quadratic model was generated in order to predict the demulsification efficiency of Oil-in-Water emulsions. In this study, two types of demulsifiers namely Cetyltrimetylammonium bromide (CTAB) and Trimethyltetradecylammonium chloride (TTAC) were used to de-emulsify Oil-in-Water emulsions in order to separate into separate phases. The demulsifier concentration, settling time and oil content on the demulsification efficiency was investigated using CCD from the Design Expert Software. The optimum process conditions to obtain maximum demulsification efficiency were determined.

5.1. Effect of experimental factors on the demulsification efficiency

5.1.1. Test for the ability of trimethyl-tetradecyl ammonium chloride (TTAC) to be used as a demulsifier for oil-in-water emulsions

To the best of the researcher's knowledge, TTAC has never been used as a demulsifier for oil-in-water emulsions. However, it possesses similar chemical properties (cationic and water-soluble demulsifier) as the conventionally-used cetyl-trimethylammonium bromide (CTAB), hence the necessity to investigate the possibility of using the former as a demulsifier for oil-in-water emulsions.

Figure 5.1 shows the result of the percentage of oil separated using TTAC emulsifier. The graph shows a steep slope within the first two hours, indicating a faster oil separation within that time; after two hours the oil separation increased slowly. It was observed that a total amount of 18.8% of oil separated within the testing period (12 h). This finding showed that

TTAC is a potential demulsifier for oil-in-water emulsions. Therefore, it can be used effectively as a demulsifier for oil-in-water emulsions for this study.

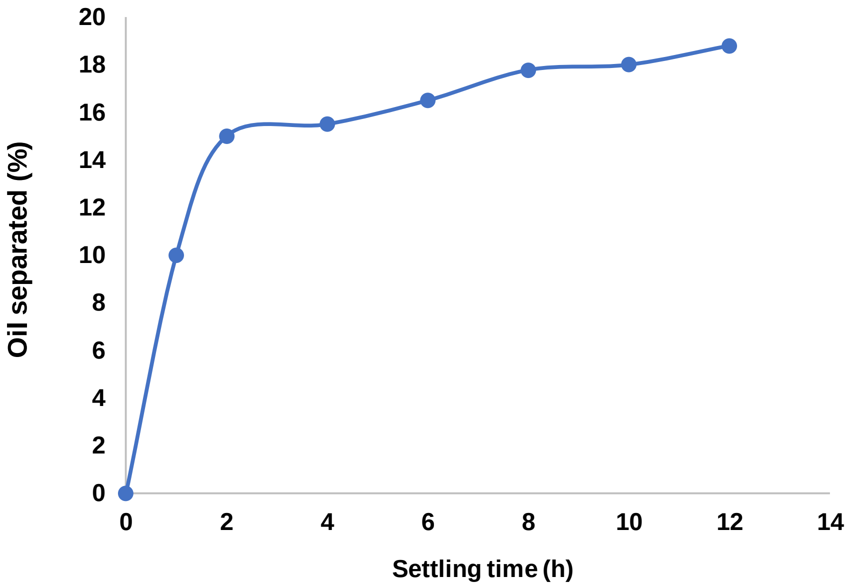


Figure 5:1: Oil separation using TTAC. Experimental conditions: 15%D/W Emulsion; time = 12h; temperature: 30ºC; TTAC concentration: 370ppm

In this study factors such as demulsifier concentration, settling time and oil to water ratio were investigated with regard to the demulsification efficiency of oil-in-water emulsions. These factors were selected based on previous experimental works (Al-Sabagh *et al.,* 2009; Hamadi, 2010; Hajivand & Vaziri, 2015) and also because they had more effect on the demulsification efficiency. The conventional CTAB and TTAC were used as chemical demulsifiers. These chemicals were selected based on the fact that they are cheap and they are environmentally friendly. Additionally, they are cationic demulsifiers which is the type of surfactants commonly used for crude oil demulsification.

5.1.2. Effect of demulsifier concentration on the demulsification efficiency

Figure 5.2 shows the result of the effect of demulsifier concentration on demulsification efficiency with regard to CTAB and TTAC respectively. The settling time was kept constant at 12 h and the concentration varied from 450 to 930 ppm. It was found that the demulsification efficiency increased proportionally with increasing demulsifier concentration for both demulsifier agents. Both the demulsifier agents have the ability to neutralize the emulsifying agent present in the emulsions, thus freeing more oil droplets at the surrounding interfacial film (Al-Otaibi *et al.,* 2003), and thus promoting demulsification efficiency. The presence of a demulsifier in the emulsions reduces the electrostatic repulsion between the oil droplets and facilitates the approach and coalescence of small oil droplets, thus helping the demulsification process (Deng *et al.,* 2005). When the demulsifier concentration in the emulsion increases, there is high adsorption of demulsifier molecules on the interface of oil and water; such an increase in the demulsifier concentration weakens the interfacial film until its rupture and therefore favours demulsification efficiency. This observation is consistent with the work of other researchers (Kokal *et al.,* 2006; Deng *et al.,* 2005; Ayoade & Ola, 2018; Rajak *et al.,* 2016).

Furthermore, it was observed that both demulsifiers showed the same trends on the graphs; this similarity could be attributed to the fact that the two demulsifiers have similarities in their chemical properties. Both CTAB and TTAC are cationic and water-soluble demulsifiers (Hirasaki *et al.,* 2011). Nevertheless, TTAC was more effective at a low concentration as compared to CTAB. The demulsification efficiency was found to be 31.78% when 370 ppm of TTAC was used whereas 23.67% was achieved with CTAB in the same experimental condition. However, at a concentration of about 770 ppm, CTAB was more effective, showing an efficiency of 75% as compared to TTAC which showed a lower efficiency of 70%. From this observation one can note that TTAC reached its critical micelle concentration more than CTAB, which shows that TTAC was effective up to 770 ppm, while above that CTAB was more effective. Overall, the highest demulsification efficiency of 87.11% was achieved with TTAC and 98% was achieved with CTAB, making it the most effective in the designed conditions (Settling time =12h, 15% D/W emulsion, Temperature =30^{o}C).

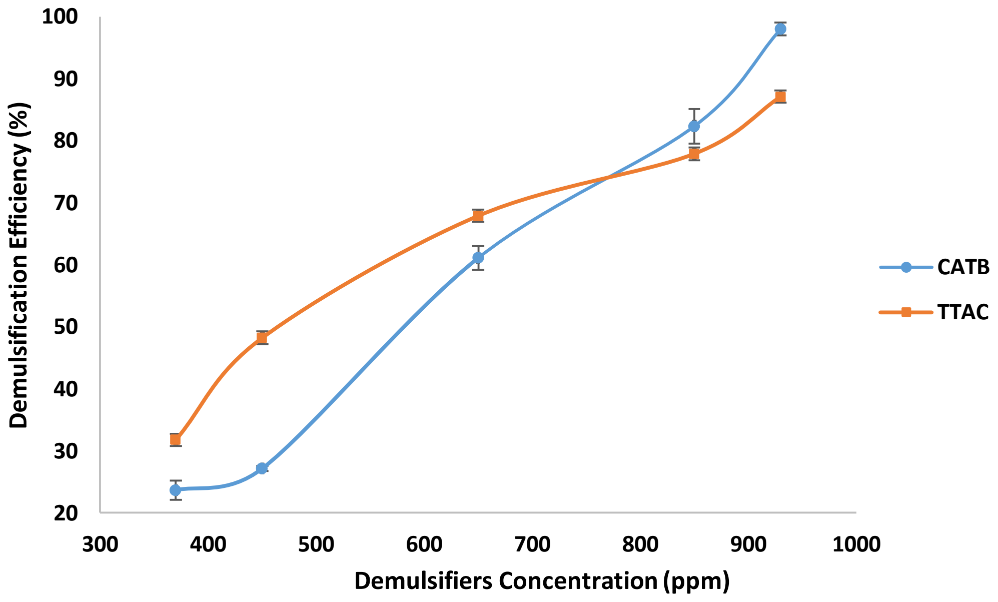


Figure 5:2: Effect of demulsifier concentration on demulsification efficiency. Experimental conditions: Settling time =12h, 15% D/W emulsion, Temperature =30^{o}C

5.1.3. Effect of settling time on demulsification efficiency

The influence of settling time on demulsification efficiency was experimentally investigated. The time varied from 1 to 12 h and the demulsifier concentration remained constant at 930 ppm.

Figure 5.3 represents the effect of settling time on the demulsification efficiency of CTAB and TTAC. The settling time was found to have a significant effect on the demulsification efficiency of both demulsifiers according to the ANOVA results (**Table 5.8** and **Table 5.9**). The results showed that an increase in the settling time led to an increase in the demulsification efficiency of both demulsifiers. This is because the availability of enough time increases the probability of the oil droplets colliding with one other, and thus promoting the phenomenons of flocculation and coalescence of the oil into bigger droplets. This enhances phase separation and increases demulsification efficiency (Abdulredha *et al.,* 2019). According to Abdulkadir (2010), increasing settling time aids the diffusion of the demulsifier through the interface of oil and water and promotes gravity settling, and consequently increases demulsification efficiency.

However, it was observed from the result that the efficiency of CTAB (blue graph of **Figure 5.3**) showed a sharp increase within the second and sixth hours as compared to that of TTAC. Then it increased smoothly after the sixth hour. The highest demulsification efficiency was found to be 98% with CTAB within the settling time of 12 h, whereas 87.1% demulsification efficiency could be achieved with TTAC within that time. Based on these experimental results one can conclude that CTAB was more effective in demulfying oil-in-water emulsions than TTAC.

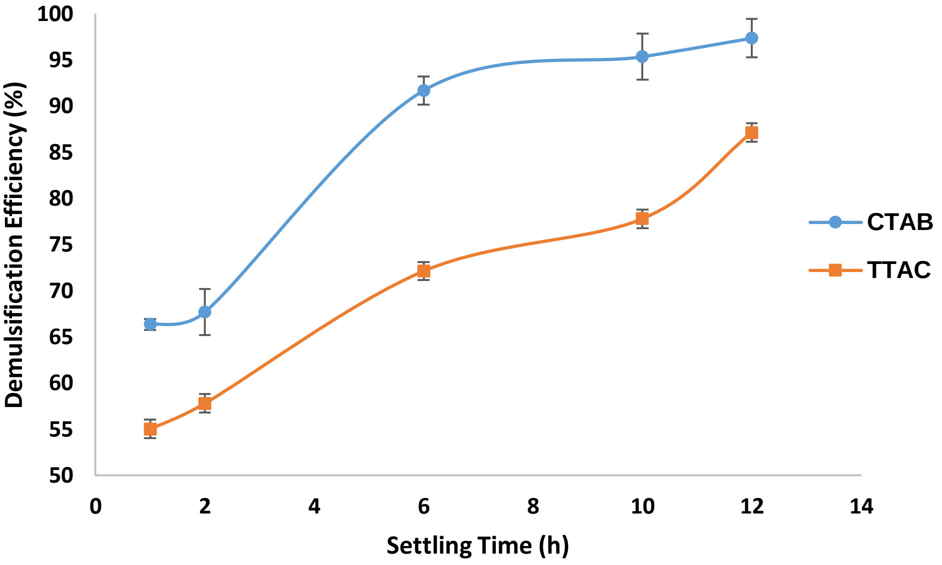


Figure 5:3: Effect of settling time on the demulsification efficiency. Experimental conditions: demulsifier concentration =930ppm, 15%D/W emulsion, Temperature = 30^{o}C

5.1.4. Effect of oil to water ratio on the demulsification efficiency

Figure 5.4 displays the effect of oil to water ratio on the demulsification efficiency of CTAB and TTAC respectively. The results of the statistical analysis (**Table 5.8** and **Table 5.9**) shows that the demulsification efficiency of both demulsifiers was influenced by the oil to water ratio of the emulsions. It was found that the demulsification efficiency decreased as the volume of oil in the emulsion increased. Studies have reported that a high oil ratio in the emulsions leads to high demulsification efficiency because of the high probability of coalescence of droplets (Luo *et al.,* 2019; Zaki, 1997); however, from the author's point of view, increasing the demulsifier concentration and settling time might improve the demulsification efficiency of emulsions containing a high oil to water ratio.

The maximum demulsification efficiency of 97.33% and 87.1% was achieved for CTAB and TTAC respectively using emulsions containing 15:85 D/W. Therefore emulsions with low oil content were easily separated compared to those with a high volume of oil, in this case study.

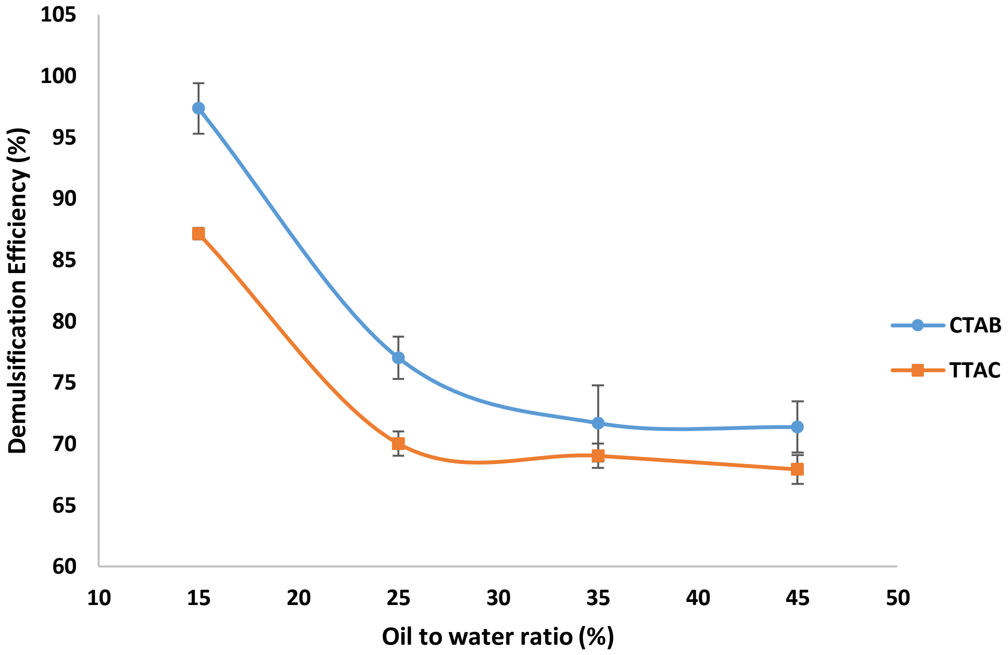


Figure 5:4: Effect of oil to water ratio on demulsification efficiency. Experimental conditions: Settling time =12h, demulsifier concentration = 930ppm, Temperature = 30^{o}C

From the above investigations the factor levels were screened and were used to optimize the demulsification efficiency of oil-in-water emulsions using response surface methodology.

5.2. Response surface methodology

The effect of demulsifier concentration, settling time and diesel to water ratio on the effectiveness of demulsifiers, namely CTAB) and TTAC was investigated and the best condition for maximum demulsification efficiency was optimized using response surface methodology (RSM) with central composite design (CCD). These factors were selected based on literature and previous investigations (Al-Sabagh *et al.,* 2009; Hamadi, 2010; Hajivand & Vaziri, 2015) and also because of their strong effect on demulsification efficiency. The factors levels are shown in **Table 5.1** and **Table 5.2** for both demulsifier types. The experimental runs, and the value of the actual and the predicted experimental response (demulsification efficiency) are presented in **Table 5.3** and **Table 5.4**.

Table 5:1. Factors levels for the demulsification test for CTAB

				Factors levels				
Factors	**Units**	**Type**	**Symbols**	**- α**	**-1**	**0**	**+1**	**+ α**
Time	h	Numeric	X_1	0.34	2	6	10	11.66
Concentration	ppm	Numeric	X_2	370	450	650	850	930
Emulsion formulation	%	Categoric	X_3	15:85	25:75		35:65	45:55

*emulsion formulation (diesel to water ratio)

Table 5:2. Factors levels for the demulsification test for TTAC

				Factors levels				
Factors	**Units**	**Type**	**Symbols**	**- α**	**-1**	**0**	**+1**	**+ α**
Time	h	Numeric	X_1	0.34	2	6	10	11.66
Concentration	ppm	Numeric	X_2	370	450	650	850	930
Emulsion formulation	%	Categoric	X_3	15:85	25:75		35:65	45:55

*emulsion formulation (diesel to water ratio)

Table 5:3. Actual and predicted demulsification efficiency with CTAB

		Input variables				
Std	**Run**	**Time (h)**	**concentration (ppm)**	**Emulsion formulation**	**Actual response (%)**	**Predicted response (%)**
		X_1	X_2	X_3	Y_1	Y_2
1	1	2	450	15: 85	13.33	18.33
19	2	12	650	25: 75	48.00	48.12
29	3	2	850	35:65	30.48	30.68
45	4	12	650	45:55	48.89	39.53
6	5	12	650	15:85	55.56	51.52
20	6	6	367	25:75	20.00	18.46
16	7	2	850	25:75	39.00	40.18
33	8	6	367	35:65	22.86	23.03

12	9	6	650	15:85	50.00	46.21
3	10	2	850	15:85	56.00	58.91
24	11	6	650	25:75	52.00	45.11
26	12	6	650	25:75	51.00	45.11
47	13	6	930	45:55	69.63	65.72
7	14	6	367	15:85	33.00	25.93
21	15	6	930	25:75	61.00	56.87
15	16	10	450	25:75	27.00	29.18
9	17	6	650	15:75	48.89	46.21
32	18	12	650	35:65	60.00	56.64
2	19	10	450	15:85	24.44	32.26
30	20	10	850	35:65	67.62	66.54
41	21	10	450	45:55	26.67	27.45
35	22	6	650	35:65	37.14	42.84
22	23	6	650	25:75	51.00	45.11
10	24	6	650	15:85	46.67	46.21
37	25	6	650	35:65	42.86	42.84
34	26	6	930	35:65	55.24	55.72
23	27	6	650	25:75	30.00	45.11
13	28	6	650	15:85	50.00	46.21
11	29	6	650	15:85	38.89	46.21
43	30	10	850	45:55	53.33	62.05
4	31	10	850	15:85	80.00	83.46
51	32	6	650	45:55	35.56	36.79
31	33	1	650	35:65	19.05	17.42
39	34	6	650	35:65	40.95	42.84
28	35	10	450	35:65	36.19	38.12
25	36	6	650	25:85	52.00	45.11
36	37	6	650	35:65	45.71	42.84
5	38	1	650	15:85	30.00	27.85
44	39	1	650	45:55	14.81	20.58
50	40	6	650	45:55	34.07	36.79
38	41	6	650	35:65	41.90	42.84
14	42	2	450	25:75	16.67	18.33
18	43	1	650	25:75	24.00	28.67
8	44	6	930	15:85	93.33	90.82
48	45	6	650	45:55	40.00	36.79
40	46	2	450	45:55	25.19	16.95
17	47	10	850	25:75	55.33	61.66
49	48	6	650	45:55	32.59	36.79
27	49	2	450	35:65	15.24	12.88
42	50	2	850	45:55	44.44	40.93
46	51	6	367	45:55	19.26	24.29
52	52	6	650	45:55	37.04	36.79

*emulsion formulation (diesel to water ratio)

Table 5:4. Design layout and experimental results for TTAC

Std			Input variables			
	Run number	Time (h)	Concentration (ppm)	Emulsion formulation	Actual response (%)	Predicted response (%)
		X_1	X_2	X_3	Y_1	Y_2
15	1	10	450	25:75	24.00	30.58
50	2	6	650	45:55	34.81	38.09

38	3	6	650	35:65	51.43	46.64
41	4	10	450	45:55	13.33	18.46
34	5	6	930	35:65	85.71	74.79
8	6	6	930	15:85	86.67	86.97
7	7	6	370	15:85	35.56	30.92
43	8	10	850	45:55	51.11	69.03
22	9	6	650	25:75	57.50	54.87
13	10	6	650	15:85	33.00	56.95
39	11	6	650	35:65	47.62	46.64
20	12	6	370	25:75	13.04	18.40
33	13	6	370	35:65	22.22	22.49
36	14	6	650	35:65	40.00	46.64
23	15	6	650	25:75	52.50	54.87
35	16	6	650	35:65	51.43	46.64
3	17	2	850	15:85	47.00	50.72
47	18	6	930	45:55	84.44	66.42
49	19	6	650	45:55	34.81	38.09
17	20	10	850	25:75	88.00	98.51
11	21	6	650	15:85	60.00	56.95
18	22	1	650	25:75	30.00	31.65
21	23	6	930	25:75	95.65	95.35
51	24	6	650	45:55	40.00	38.09
6	25	12	650	15:85	87.00	71.57
16	26	2	850	25:75	60.00	59.41
45	27	12	650	45:55	53.33	41.73
30	28	10	850	35:65	67.62	77.66
19	29	12	650	25:75	78.00	64.54
40	30	2	450	45:55	22.22	13.35
25	31	6	650	25:75	64.00	54.87
9	32	6	650	15:85	70.00	56.95
1	33	2	450	15:85	20.00	23.65
4	34	10	850	15:85	87.00	96.43
48	35	6	650	45:55	37.04	38.09
46	36	6	370	45:55	17.78	13.78
27	37	2	450	35:65	28.57	21.81
24	38	6	650	25:75	52.50	54.87
44	39	1	650	45:55	6.67	19.90
14	40	2	450	25:75	22.00	17.42
28	41	10	450	35:65	25.71	27.33
32	42	12	650	35:65	53.33	50.58
37	43	6	650	35:65	45.71	46.64
26	44	6	650	25:25	53.00	54.87
5	45	1	650	15:85	33.33	29.59
2	46	10	450	15:85	27.00	43.42
10	47	6	650	15:85	67.00	56.95
52	48	6	650	45:55	35.56	38.09
42	49	2	850	45:55	40.00	37.98
29	50	2	850	35:65	45.71	46.19
12	51	6	650	15:85	64.44	56.95
31	52	1	650	35:65	17.14	28.19

*emulsion formulation (diesel to water ratio)

5.2.1. Model selection

Design-Expert provided a collection of polynomial transformations namely linear, two factor interactions (2FI), quadratic and cubic, which can be used to fit the model. It then automatically suggests by underlining the transform which best fits the model. The model summary statistics of CTAB and TTAC are summarized in **Table 5.5** and **Table 5.6**.

Table 5:5. Model statistic summary for CTAB

Source	*Sequential p-value*	*Lack of Fit p-value*	*Std*	*Adjusted R^2*	*Predicted R^2*	*press*	*Comment*
Linear	< 0.0001	0.0223	8.27	0.7624	0.7203	4102.30	
2FI	0.0268	0.0626	7.42	0.8088	0.7246	4038.71	
Quadratic	***0.0071***	***0.1703***	***6.66***	***0.8457***	***0.7626***	***3481.99***	***Suggested***
Cubic	0.0593	0.4906	5.73	0.8857	0.6949	4474.56	Aliased

Table 5:6. Model statistic summary for TTAC

Source	*Model p-value*	*Lack of Fit p-value*	*Std*	*Adjusted R^2*	*Predicted R^2*	*PRESS*	
Linear	< 0.0001	0.0506	10.25	0.7674	0.7251	6413.06	
2FI	0.1124	0.0811	10.00	0.7929	0.6835	8550.88	
Quadratic	***0.0693***	***0.1222***	***9.23***	***0.8111***	***0.6807***	***8248.41***	***Suggested***
Cubic	0.0152	0.6502	7.49	0.8800	0.7079	15810.22	Aliased

The most suitable model exhibits the lowest standard deviation, the highest predicted R-square values and lowest PRESS values. The quadratic transform was suggested by the software to be the best transform for the case of this study for both CTAB and TTAC respectively (see Table **5.5** and **Table 5.6**). Although the cubic transform showed the highest predicted R-square and the lowest standard deviation for both CTAB and TTAC, it was found that it was aliased and could not be used to fit the models.

5.2.2. Model regression equations

To predict the effectiveness of CTAB and TTAC on the demulsification efficiency of oil-in-water emulsions at a 95% confidence level, the effect of the independent variables estimated for linear, cross-product (interaction) and quadratic expression were analyzed using polynomial regression expressed in terms of mathematical equations (see **Equations 5.1** to **5.10**). The best fit of the quadratic model can be used to make predictions about the desired output (demulsification efficiency) at any given level of each process variable (Oladipo & Betiku, 2019). The experimental data were analyzed using **Equation 2.5**. The final coded and actual factors for the demulsification efficiency of diesel-in-water emulsions using CTAB and TTAC are shown in **Equations 5.1 to 5.10** below. By default, the high levels of factors are coded as + 1 and the low levels are coded as - 1. The coded equation is useful for identifying the relative impact of the factors by comparing the factor coefficients. The minus and plus signs that appear on the model equations imply that the factors have a positive or a negative effect on demulsification efficiency (Abdulredha *et al.,* 2019).

$$\text{Demulsification efficiency (CTAB)} = 42{,}75 + 10.22\text{A} + 15{,}68\text{B} + 6.49\text{C}[1] - 0.6498\text{C}[2] - 1.69\text{C}[3] + 2.66\text{AB} - 06973\text{AC}[1] - 2.04\text{AC}[2] + 5.11\text{AC}[3] + 7.26\text{BC}[1] - 2.10\text{BA}[2] - 4.12\text{BC} - 4.05A^2 + 1.18B^2$$

(5.1)

Final equation in terms of Actual Factors for CTAB

For oil content = 15%D/W emulsion

$$\text{Demulsification efficiency (CTAB)} = -23.298 + 3.261\ \text{Settling Time} + 0.0564\ \text{CTAB Concentration} + 0.00332\ \text{Settling Time} \times \text{CTAB Concentration} - 0.2531\ \text{Settling Time}^2 + 0.00003\ \text{CTAB Concentration}^2$$

(5.2)

For oil content = 25%D/W emulsion

$$\text{Demulsification efficiency (CTAB)} = 2.00747 + 2.92495\ \text{Settling Time} + 0.0095\ \text{CTAB Concentration} + 0.00332\ \text{Settling Time} \times \text{CTAB Concentration} - 0.2531\ \text{Settling Time}^2 + 0.00003\ \text{CTAB Concentration}^2$$

(5.3)

For oil content = 35%D/W emulsion

$$\text{Demulsification efficiency (CTAB)} = -3.18689 + 4.713\ \text{Settling Time} - 0.000578\ \text{CTAB Concentration} + 0.00332\ \text{Settling Time} \times \text{CTAB Concentration} - 0.2531\ \text{Settling Time}^2 + 0.00003\ \text{CTAB Concentration}^2$$

(5.4)

For oil content = 45%D/W emulsion

$$\text{Demulsification efficiency (CTAB)} = -4.444 + 2.8415\ \text{Settling Time} + 0.00332\ \text{CTAB Concentration} + 0.00332\ \text{Settling Time} \times \text{CTAB Concentration} - 0.2531\ \text{Settling Time}^2 + 0.00003\ \text{CTAB Concentration}^2$$

(5.5)

Final equation in terms of code factors for TTAC

$$\text{Demulsification efficiency (TTAC)} = 49.12 + 11.93\text{A} + 21.24\text{B} + 7.81\text{C}[1] + 5.73\text{C}[2] - 2.5\text{C}[3] + 6.49\text{AB} + 4.44\text{AC}[1] + 1.13\text{AC}[2] - 2.68\text{AC}[3] - 1.23\text{BC}[1] + 6.24\text{BA}[2] - 2.57\text{BC}[3] - 4.41A^2 + 1.02B^2$$

(5.6)

Final equation in terms of actual factors for TTAC

For oil content = 15%D/W emulsion

$$\text{Demulsification efficiency (TTAC)} = -0.1936 + 2.1317\ \text{Settling Time} + 0.018265\ \text{TTAC Concentration} + 0.0081\ \text{Settling Time} \times \text{TTAC Concentration} - 0.27575\ \text{Settling Time}^2 + 0.000026\ \text{TTAC Concentration}^2 \tag{5.7}$$

For oil content = 25%D/W emulsion

$$\text{Demulsification efficiency (TTAC)} = -21.5629 + 1.3057\ \text{Settling Time} + 0.0556\ \text{TTAC Concentration} + 0.0081\ \text{Settling Time} \times \text{TTAC Concentration} - 0.27575\ \text{Settling Time}^2 + 0.000026\ \text{TTAC Concentration}^2 \tag{5.8}$$

For oil content = 35%D/W emulsion

$$\text{Demulsification efficiency (TTAC)} = 4.5389 + 0.3513\ \text{Settling Time} + 0.0116\ \text{TTAC Concentration} + 0.0081\ \text{Settling Time} \times \text{TTAC Concentration} - 0.27575\ \text{Settling Time}^2 + 0.000026\ \text{TTAC Concentration}^2 \tag{5.9}$$

For oil content = 45%D/W emulsion

$$\text{Demulsification efficiency (TTAC)} = -4.0889 + 0.30\ \text{Settling Time} + 0.01216\ \text{Concentration} + 0.008106\ \text{Settling Time} * \text{Concentration} - 0.27575\ \text{Settling Time}^2 + 0.2.6 * 10^{-5}\ \text{Concentration}^2 \tag{5.10}$$

5.2.3. Statistical analysis

5.2.3.1. Analysis of variance (ANOVA) for the quadratic model

Table 5.7 shows the ANOVA results for the quadratic model for the demulsification efficiency of CTAB. The model F-value of 16.03 shows that the model is statistically significant and there is only a 0.01% chance that a model F-value this large could occur due to noise. The model *p*-value < 0.0001 implies that the model terms are significant and values greater than 0.001 indicate that the terms are not significant (Abdulredha *et al.,* 2019).

In this study, the parameters that showed a significant impact on the demulsification efficiency of CTAB are settling time (A), CTAB concentration (B), diesel to water ratio (C). The interaction between CTAB concentration and the oil content (BC), the quadratic term of the settling time (A^2), the interaction of the quadratic term of settling time and CTAB concentration (AB^2), the interaction of the quadratic term of the settling time and the oil content (B^2C) were also significant. The CTAB concentration exhibited the highest influence on predicting the demulsification efficiency because of its high F-value of 229.05 whereas the diesel to water ratio showed the least effect on the response with the lowest F-value of 7.88.

The Lack of Fit F-value of 1.10 implies that the Lack of Fit is not significant relative to the pure error. Moreover, the Lack of Fit value of this magnitude could occur at 41.78% chances due to noise. This proved that the developed model is in good agreement with the experimental data and could be used to predict the demulsification efficiency of CTAB.

Table 5:7. ANOVA results for the quadratic model for the demulsification efficiency of CTAB

Source	*Sum of Squares*	*Df*	*Mean Square*	*F-value*	*p-value Pob>F*	*Comment*
Model	13772.61	25	550.90	16.03	< 0.0001	***Significant***
A-Time	2858.66	1	2858.66	83.21	< 0.0001	
B-Concentration	7869.37	1	7869.37	229.05	< 0.0001	
C-Oil content	812.23	3	270.74	7.88	0.0007	
AB	112.82	1	112.82	3.28	0.0815	
AC	279.74	3	93.25	2.71	0.0654	
BC	601.81	3	200.60	5.84	0.0026	
A^2	507.21	1	507.21	14.76	0.0007	
AB^2	146.77	1	146.77	4.27	0.0488	
B^2C	472.20	3	157.40	4.58	0.0105	
Residual	893.27	26	34.36			
Lack of Fit	363.75	10	36.38	1.10	0.4178	***Not significant***
Pure Error	529.51	16	33.09			
Cor Total	14665.88	51				

Table 5.8 depicts the results obtained for the developed second-order model for the demulsification efficiency of TTAC. From the ANOVA results, the F- and p-value of 16.64 and <0.0001 estimated for the model demonstrates that the developed quadratic model is significant. The significant terms in the regression model to predict the demulsification efficiency are the settling time (A), the TTAC concentration (B), the interaction between the settling time and the TTAC concentration (AB) and quadratic term of TTAC concentration (B^2) respectively. These terms also exhibited the *p*-values < 0.05. As in the case of CTAB, the concentration of TTAC presented the most impact on the model with the highest F-value of 144.30 while the oil content presented the least influence with F-value of 6.79. The Lack of Fit value of 1,78 suggests that the Lack of Fit is not significant relative to the pure error and there is 12.22% chance that the Lack of Fit this large could occur due to noise hence, the developed model is in good agreement with the experimental data and could be used to predict the results.

Table 5:8. ANOVA results for the reduced quadratic model for the demulsification efficiency of TTAC

Source	***Sum of Squares***	***Df***	***Mean Square***	***F-value***	***p-value Pob>F***	***Comment***
Model	23082.61	14	1648.76	16.64	< 0.0001	***Significant***
A-Time	3930.01	1	3930.01	39.66	< 0.0001	
B-Concentration	14298.41	1	14298.41	144.30	< 0.0001	
C-Oil content	2926.25	3	975.42	9.84	< 0.0001	
AB	672.91	1	672.91	6.79	0.0131	
AC	285.15	3	95.05	0.9592	0.4222	
BC	419.45	3	139.82	10.41	0.2549	
A^2	507.91	1	507.91	5.13	0.0295	
B^2	28.26	1	28.26	0.2852	0.5965	
Residual	3666.26	37	99.09			
Lack of Fit	2565.90	21	122.19		0.1222	***Not significant***
Pure Error	1100.35	16	68.77			
Cor Total	26748.86	51				

5.2.3.2. Statistical fit summary

The reliability of the model in predicting the experimental responses is determined based on the fit summary presented in **Table 5.9**. Generally, with the coefficient of determination R^2, the value of R^2 always lies between 0 and 1 ($0<R^2<1$); the closer the R^2 coefficient is to 1 the better the predicted model (Roshan *et al.,* 2018a). From the observed fit summary, CTAB and TTAC presented the R^2 values of 0.9440 and 0.8629 respectively. These values implied that 94.40% and 86.29% of the variance of the sample is attributed to the factors and only 5.6% and 13.71% occurred due to chance for the R^2 values this high indicated good fit for both CTAB and TTAC (Aanchal *et al.,* 2016). This also indicates that the models are reliable at 94.5% and 86.29%. Additionally, the predicted R^2 values were consistent with adjusted R^2 values and only showed a difference of 0.19 and 0.13 for CTAB and TTAC respectively; a difference of less than 0.2 is desired (Trinh & Kang, 2010). The adequate precision measured the signal to noise ratio; a ratio greater than 4 is desired, and both models showed a ratio greater than 4. From the above observations, one can conclude that both models demonstrate good fit and can be used to predict the response. The coefficient of variation (CV) for each model was found to be 13.91%, and 21.03 respectively. These values are reasonably low; a value this low indicates the high precision and reliability of the experiments. In addition, a low CV shows that the variation of the mean value is low and satisfactorily develops an adequate response model (Seyed *et al*., 2011).

Table 5:9. Fit summary

	CTAB	TTAC
R^2	0.9440	0.8629
Adjusted R^2	0.8857	0.8111
Predicted R^2	0.6949	0.6807
Adequate Precision	18.7569	15.9289
Standard deviation	5.73	9.95
Mean	41.23	47.34
C.V. %	13.91	21.03

5.2.3.3. Model validation and adequacy testing using a diagnostic plot

It is important to ensure that the selected design approximates the predicted results and those of the actual experiments. Diagnostic plots are used to evaluate if the developed model can be used to predict the experimental response (Roshan *et al.,* 2018a). The points scattered around the straight lines represent the output responses (demulsification efficiency).

Figure 5.5 (a) and **(b)** show the plots of the predicted versus the observed demulsification efficiency for both demulsifiers CTAB and TTAC respectively. It can be seen from the figure that the data points are randomly scattered along the diagonal lines of both graphs. According to Martin *et al.* (2017), for a model to be used to predict the experimental result, the points of predicted versus actual plot should be randomly scattered along the diagonal line and should lie close to one other. This observation confirms that the developed model could be used to predict the experimental results.

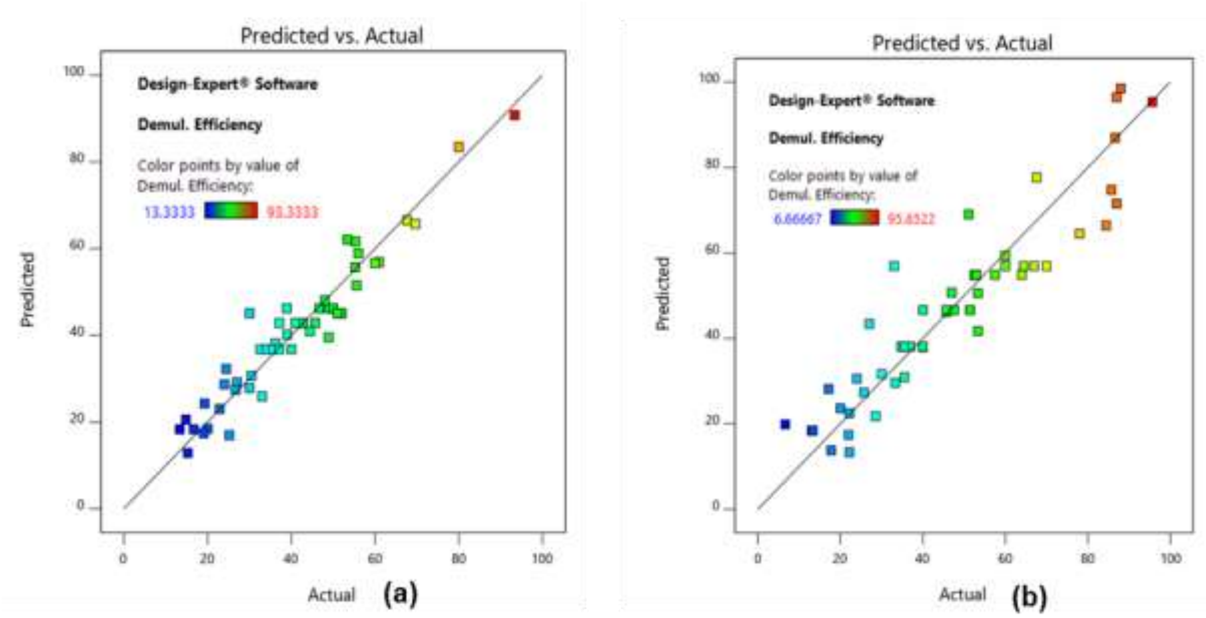
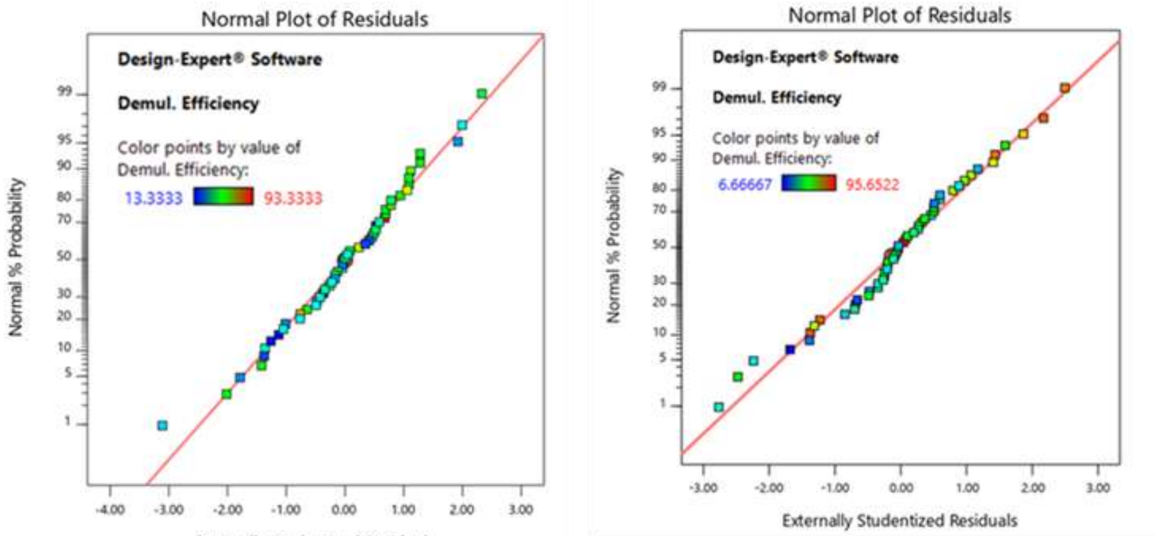


Figure 5:5: Predicted versus actual demulsification efficiency: (a) with CTAB and (b) with TTAC

Figure 5.6 (a) and (b) illustrate the plots of normal probability against the externally studentized residuals of the demulsification efficiency of both CTAB and TTAC respectively. These plots are used to check the normality of the assumptions made. In another word, they check if the difference between the observed and the predicted values are normally distributed. A good model should be normally distributed (Abdulredha *et al.,* 2019). **Figure 5.6** clearly shows that the residuals are normally distributed along the straight line showing a linear relationship between normal probability and the externally studentized residual. Besides, no outlier is observed in the regression line for both graphs, indicating the goodness if fit of the models.



(a) **(b)**

Figure 5:6: Normal plot of residual versus external studentized residuals (a) with CTAB and (b) with TTAC

The residuals versus experimental runs were used to analyze the goodness-of-fit. The plots of the residuals versus experiment run number and predicted for both demulsifiers are shown in **Figures 5.7 (a)** and **(b)** and **Figures 5.8 (a)** and **(b)** respectively. The assumption made from this test is that a good model is obtained when the data points are randomly scattered within the confidence limit and no trends or patterns should be observed. It can be seen from the plots that the design points of the residuals are randomly scattered (constant range of residuals across the graphs) between the confidence limit of [-3.62513, 3.62513]. No data point went beyond the interval [-3.62513, 3.62513] showing that there were no outliers of the residuals for both models. Additionally, no specific pattern or unusual structure of the residuals was observed in the graphs, suggesting a constant variability of the original observation for all values of the responses (Fouladitajar & Ashtiani, 2014). These plots confirm the adequacy and reliability of the developed response models for the prediction of the demulsification process of oil-in-water emulsions using CTAB and TTAC as chemical demulsifiers.

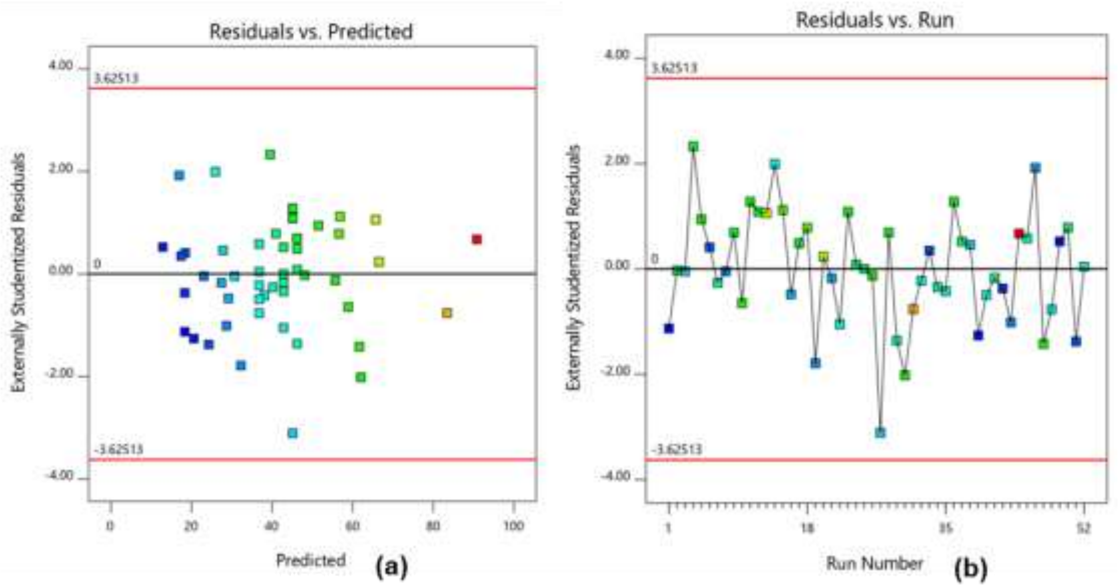


Figure 5:7. External studentized residual (a). External situdentize vs run number (b) with CTAB

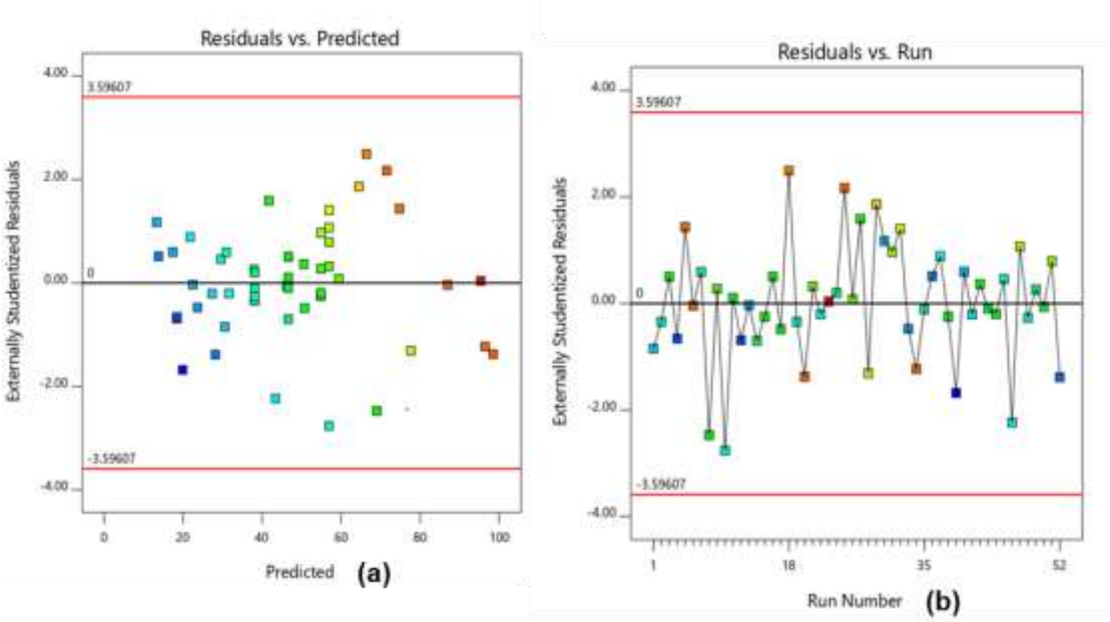


Figure 5:8: External studentized residual (a). External situdentize vs run number (b) with TTAC

5.2.4. Factors interaction

The 3D surface plots of the response functions were used to study the interaction effects of the experimental variables on the responses. According to the ANOVA results from **Table 5.8** and **5.9**, the interaction of demulsifier concentration and the oil to water ratio (BC) and the interaction of settling time and demulsifier concentration had significant effects on the demulsification efficiency of CTAB and TTAC demulsifiers respectively.

Figure 5.9 illustrates the graphs of the effect of the interactions between CTAB concentration and the oil to water ratio (BC) on the demulsification efficiency of CTAB. It can be seen from the graph that the interaction of low oil ratio and high CTAB concentration led to an increase in demulsification efficiency. The interaction of the emulsion containing 15:85 oil to water ratio (D/W) and 839.76 ppm demulsifier concentration exhibited a maximum efficiency of 75.16%, as seen in **Figure 5.9**.

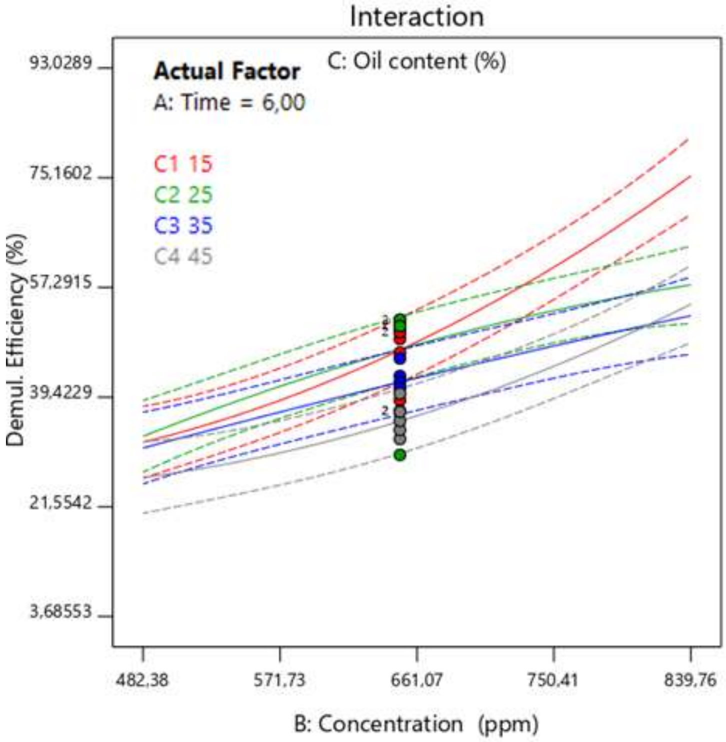


Figure 5:9. Effect of CTAB concentration and settling time interaction on the demulsification efficiency.

Figure 5.10 represents the contour and the 3D plots of the interaction effects of settling time and demulsifier concentration (AB) on demulsification efficiency using TTAC. The figure shows a directly proportional relationship between the demulsification time and demulsifier concentration on the response. Increase in either settling time or TTAC concentration results in an increase in demulsification efficiency. Moreover, it can be seen that an increase in the TTAC concentration at the constant time led to an increase in the demulsification efficiency, whereas an increase in the settling time at constant TTAC concentration did not show a significant effect on the demulsification efficiency. The maximum TTAC demulsification efficiency of 93.3% was achieved when there was a simultaneous increase in the settling time and the demulsifier concentration.

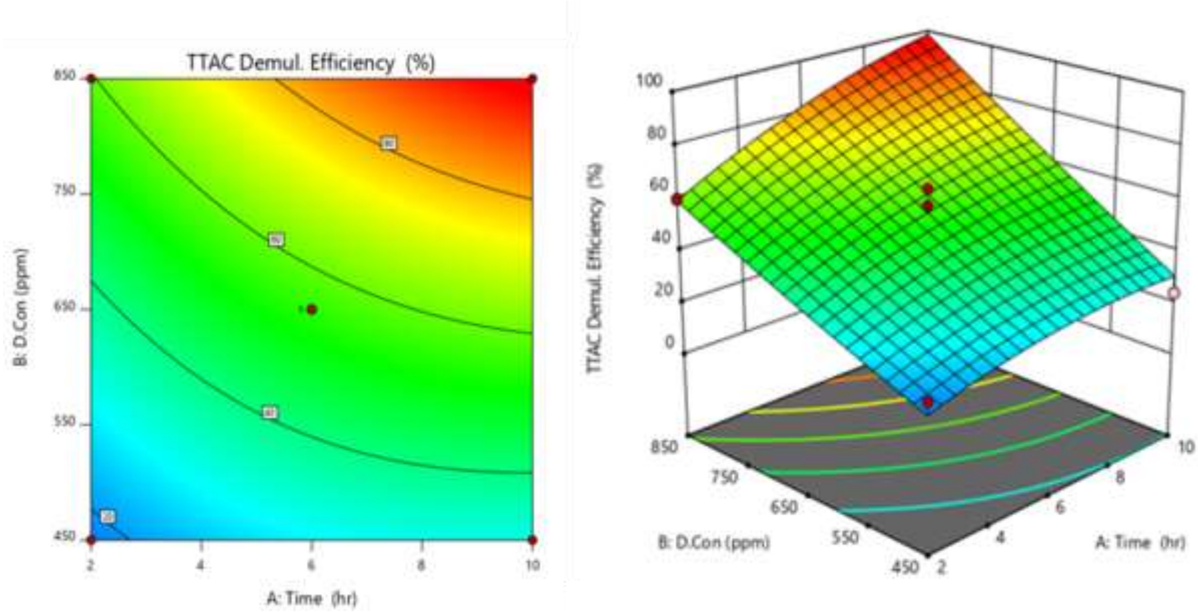


Figure 5:10. Effect of TTAC concentration and settling time interaction on the demulsification efficiency.

5.3. Optimization of process parameters

One of the objectives of this study was to determine the optimum process conditions to obtain maximum demulsification efficiency. The optimization process was done by selecting the optimization node of Design-Expert 11 software. The criteria were set to ''maximum'' for demulsification efficiency, ''in range'' for the demulsifier concentration, oil content and the settling time. 77 solutions were suggested for the demulsification efficiency of TTAC and 45 for that of CTAB in the case of this study. According to the criteria selected and the desirability suggested, the optimum process parameters were selected.

Table 5.11 shows the optimum experimental conditions for maximum demulsification efficiency for both demulsifiers predicted by the software. These predicted results were verified experimentally for both demulsifiers, as reported in the confirmation report in **Table 5.11**. The predicted demulsification efficiency of 79.374% and 95.92% were predicted for CTAB and TTAC, and the observed demulsification efficiency of 82.67% and 80% was achieved. The observed demulsification efficiency of 82.67% of CTAB confirms the suitability of the model, whereas that of TTAC of 80% revealed that some errors might have occurred during the experiments.

Table 5:10. Predicted optimum factor values

Demulsifiers	Time (h)	Concentration (ppm)	Oil content (%)	Efficiency (%)	Desirability
CTAB	10	850	15	79.374	0.826
TTAC	10	850	25	95.92	1

Table 5:11. Confirmation report of the results

Response	Predicted mean	Predicted median	Observed	Std dev	n	SE pred	95 PI low	Data mean	95 PI high
CTAB Efficiency	79.374	79.374	82.67	5.73	1	7.49	63.94	81.02	94.8
TTAC Efficiency	95.92	95.925	80	9.95	1	11.52	72.57	85.96	119.27

This study showed that the demulsifier concentration, settling time and oil to water ratio as well as their interaction play a significant role in the demulsification efficiency of oil-in-water emulsions. The demulsification efficiency increased with increased settling time and demulsifier concentration irrespective of the time of the demulsifier used in this study.

5.4. Investigation of ageing effect on the emulsions

5.4.1. Effect of ageing on emulsions droplet size

Table 5.12 shows the average droplet size of the emulsions measured on the 1st 15th, 30th, 45th and 60th day after simulation. It was observed that the average droplet size of the emulsions slightly increased from the first to the sixtieth day. The average droplet size increased from 8.57 to 27.38 nm and 11.6 to 37.37 nm from the 1st day to the 60th day of ageing for CTAB and TTAC respectively. This observation could be the reason why the emulsion stability index (ESI) did not change significantly as the emulsions aged (see Table 5.13). Similar observations were reported by Maia Filho, *et al.* (2012). In the case of this study, ageing of the emulsions did not affect the average droplet size, therefore, it did not affect the stability of the emulsions.

Table 5:12. Emulsions average droplet size of aged emulsions

Ageing time (days)	**Average droplet size (nm)**	
	15% D/W emulsion	**25% D/W emulsion**
0	8.57	11.6
15	12.54	13.36
30	15.50	16.38
45	15.50	19.34
60	27.38	37.37

Table 5:13. Emulsion stability index (ESI) of aged emulsions

	ESI (%)	
Ageing time (days)	**15%D/W**	**25% D/W**
0	98. 67	92
15	98.00	92
30	98.00	91
45	98.00	91
60	98.00	91

5.4.2. Ageing effect on the demulsification process

Tables 5.10 and **Table 5.11** illustrates the results of the ageing effect on the demulsification efficiency of CATB and TTAC respectively. The results showed that there was a progressive decrease in demulsification efficiency as the emulsions aged. The demulsification efficiency of CTAB decreased from 82.67% from the first day to 50% on the 60th day. The same result was observed with TTAC where the efficiency decreased significantly from 80% to 36% after 60 days of ageing. This observation shows that emulsions might have undergone some changes in their internal properties, more specifically in the interfacial tension since there was no significant change in average droplet size and stability of the aged emulsions. According to Maia Filho *et al. (*2012b), when the emulsions are subjected to ageing there is high adsorption of the emulsifier at the interface of the oil and water facilitating the formation of more elastic interfacial films. This could be the case in the present study.

Table 5:14. Effect of emulsion ageing on the demulsification performance of (CTAB)

Demulsification efficiency (%) with CTAB	
Ageing time (days)	**15% D/W emulsion**
0	82.67
15	70.00
30	65.00
45	65.00
60	50.00

**Cetyltrimetylammonium bromide (CTAB)*

Table 5:15. Effect of emulsion ageing on the demulsification performance of (TTAC)

Demulsification efficiency (%) with TTAC	
Ageing time (days)	**25% D/W emulsion**
0	80.0
15	69.1
30	48.0
45	46.5
60	36.0

*Trimethyltetradecylammonium chloride (TTAC)

5.5. Chapter outcome

This chapter discussed applying response surface methodology to optimize the demulsification efficiency of oilfield emulsions. The emulsions were synthesized and diesel was used as the oil phase. The influence of settling time or separation time, demulsifier concentration and oil content on the performance of CTAB and TTAC demulsifiers were investigated and the response was reported as demulsification efficiency. A second-order polynomial model in Design-Expert software using response surface methodology and central composite design was developed and was used to optimize the process parameters. The result showed that an increase in the demulsifier concentration, as well as the settling time and their interactions, promoted the demulsification efficiency for both CTAB and TTAC demulsifiers. However, an increase in the oil content in the emulsions decreased demulsification efficiency. The optimum demulsification efficiency was achieved at the demulsifier concentration of 850 ppm and at the settling time of 10 h. A maximum demulsification efficiency of 82.67 was achieved for emulsions containing 15:85 oil to water ratio using CTAB whereas 80% demulsification efficiency was obtained for emulsions containing 25:75 oil to water ratio using TTAC.

CHAPTER 6: CONCLUSION AND RECOMMENDATIONS

CONCLUSION

This study contributed to solving the ongoing challenge faced during the extraction of crude oil using enhanced oil recovery techniques. Enhanced oil recovery refers to extraction methods in which chemicals, steam, or microbes are injected into the oil reservoirs to improve oil extraction efficiency. These methods, however, result in the formation of stable emulsions which are difficult to treat (Deng *et al.,* 2005). Many studies have been done in an attempt to address this challenge. Kokal & Aramco (2005) reviewed the methods used for demulsification of petroleum emulsions and concluded that chemical demulsification was the most efficient method for crude oil demulsification. Nasser & Khamis (2014) studied the effect of demulsifier concentration, demulsification time, temperature and water content on the demulsification efficiency of water-in-crude oil emulsion and observed that the highest demulsification efficiency was at low demulsifier concentration (400 ppm) at a temperature of 60^oC, at 15 minutes settling time with emulsions containing 70:30 crude to water ratio. Hafiz *et al.* (2005) synthesized novel demulsifiers for treating oil-in-water emulsions and found that demulsification efficiency was influenced by the structure, molecular weight, and degree of solubility of the demulsifiers. However, despite advanced research in the field, the application of response surface methodology (RSM) and central composite design (CCD) to optimize the conditions for efficient crude oil-in-water emulsions demulsification has not been reported.

In this study, oil-in-water emulsions containing 15:85, 25:75, 35:65 and 45:55 oil to water ratios were simulated. Diesel was used as the oil phase. The emulsion stability index (ESI) was investigated based on the emulsifier concentration, homogenization speed, brine salinity and oil to water ratio. The effect of the above-mentioned parameters on the average emulsion droplet size was also investigated. The goal of this investigation was to obtain the optimum conditions to simulate stable oil-in-water emulsions. Then response surface methodology and central composite design was applied to optimize the demulsifier concentration, settling time and oil to water ratio for maximum demulsification efficiency of the simulated emulsions. The simulated emulsions were kept for 60 days and the effect of ageing on the emulsion stability index, emulsion droplet size and demulsification efficiency was investigated.

It was found that the emulsion stability index (ESI) and average emulsion droplet size were influenced by the emulsifier concentration, homogenization speed, and brine salinity. An increase in the homogenization speed and the emulsifier concentration led to an increase in the emulsion stability index and a decrease in the average droplet size. An increase in the brine salinity and the oil to water ratio led to a decrease in the ESI and the increase in the average droplet size. The maximum ESI was achieved at a homogenization speed of 24000 rpm, at emulsifier concentration of 2%, with brine salinity containing 1000 mg/L of NaCl.

Oil-in-water emulsions were simulated using the above optimized parameters. Response surface methodology (RSM) and the central composite design (CCD) using Design-Expert version 11 software were used to design and optimize the demulsification efficiency of cetyl trimethylammonium bromide (CTAB) and trimethyl-tetradecyl ammonium chloride (TTAC) as demulsifiers. The factors optimized were the demulsifier concentration of CTAB and TTAC, settling time and the oil to water ratio. The experiments were designed with 2 factors and 1 categoric factor for each demulsifier type.

The model obtained was validated using analysis of variance (ANOVA) through the F-test and the *p*-value and the coefficient of determination R^2. The model was significant and the *p*-value < 0.0001 was obtained for all the factors for both demulsifiers. The F-value of 16.03 and 16.63 was obtained for CTAB and TTAC demulsifiers respectively. It was found that the interaction of the settling time and the demulsifier concentration (AB) and the demulsifier concentration and the oil to water ratio (BC) had a significant impact on the response for both demulsifier types. The coefficient of determination (R^2) was found to be 0.944 and 0.863 for CTAB and TTAC demulsifiers respectively. These high values validated the accuracy of the model. The optimum demulsification efficiency was achieved at the demulsifier concentration of 850 ppm and at the settling time of 10 h. A maximum demulsification efficiency of 82.67 and 80% was achieved for emulsions containing 15:85 and 25:75 using CTAB and TTAC respectively. From the observed results one could note that CTAB is efficient for emulsions containing low oil to water ratios whereas TTAC is more efficient for emulsions containing high oil to water ratios.

The influence of ageing on the emulsion droplet size, emulsion stability index and emulsion demulsification efficiency was investigated. It was found in this study that the average emulsion droplet size and the emulsion stability index was not influenced by ageing of the emulsions. Nevertheless, the demulsification efficiency decreased as the emulsions aged for both demulsifiers. The demulsification efficiency decreased from 82.67 to 50% and from 80 to 38% from the first day to the sixtieth day after the emulsions were simulated.

RECOMMENDATIONS

This study proposed some operating parameters to simulate oilfield emulsions containing 15:85, 25:75, 35:65 and 45:55 oil to water ratio (with diesel as the oil phase). It has also revealed certain optimum process conditions for the demulsification of the simulated emulsions based on the type of oil utilized. Based on the outcome of this study, further studies could still be done, including the following:

- Crude oil could be used as the oil phase instead of diesel in investigating the influence of the viscosity of the emulsions on the stability and demulsification of the emulsions since they contain different oil ratios,
- Further studies could be done on the synergy effect of both demulsifiers on the demulsification efficiency of the emulsions.

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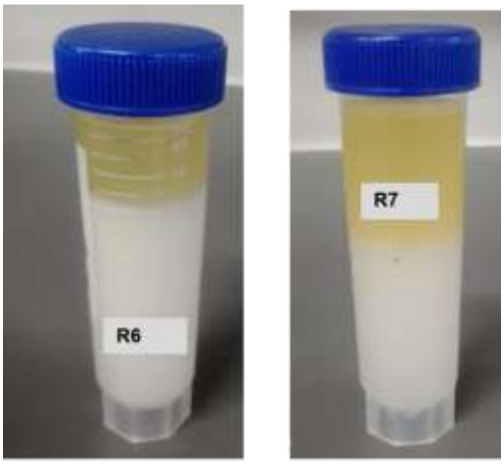
Appendix A:

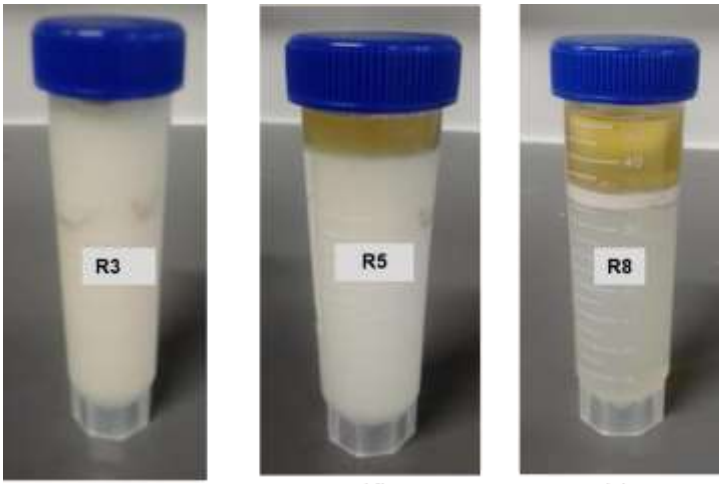
Preliminary observation on emulsion simulation



(a) (b)

D/W emulsion

- •Time after simulation: (a) 2min, (b) 10min
- •Homogenization speed: (a) 14000 rmp, (b) 24000 rpm
- •No emulsifier



(c) (d) (e)

D/W emulsion

- •Time after simulation: (c) 5h, (d) 12h, (e) 24h
- •Homogenization speed: 24000 rmp
- •Emulsifier concentration: 0.5%

Diesel-in-water emulsions (D/W)	Average droplet size (nm)	Emulsion stability index (%)
15:85	8.586	91.5
25:75	11.6	90
35:65	19.99	89.7
45:55	101.17	88

Average droplets size

Appendix B

The tables below show the demulsification efficiency measured at various times and demulsifiers concentrations

Demulsification efficiency (%) 15:85 D/W with CTAB					
Time (h)	**370 ppm**	**450 ppm**	**650 ppm**	**850 ppm**	**930 ppm**
1	12.17	15.79	30.00	54.67	66.33
2	16.50	20.67	35.33	56.00	67.67
6	18.33	22.33	46.67	68.33	93.00
10	20.33	24.44	54.00	80.00	95.33
12	26.67	27.00	55.53	94.50	96.00

Demulsification efficiency (%) 25:75 D/W emulsion with CTAB					
Time (h)	**370ppm**	**450ppm**	**650ppm**	**850ppm**	**930ppm**
1	13.00	14.93	22.00	31.67	48.33
2	15.67	18.67	21.67	37.50	48.67
6	17.67	21.60	34.67	55.33	66.67
10	19.33	26.67	42.67	55.33	75.00
12	22.00	26.67	48.00	67.33	77.00

Demulsification efficiency (%), 35:65 D/W emulsion with CTAB					
Time (h)	**370ppm**	**450ppm**	**650ppm**	**850ppm**	**930ppm**
1	15.00	19.67	19.05	21.33	38.33
2	17.33	19.33	19.05	21.33	39.33
6	21.61	34.33	42.86	53.33	57.50
10	22.67	36.19	55.83	63.81	68.00
12	24.00	36.33	60.00	66.67	72.67

Demulsification efficiency (%) 45:55 D/W emulsion with CTAB					
Time (h)	**370ppm**	**450ppm**	**650ppm**	**850ppm**	**930ppm**
1	6.33	14.67	18.00	31.00	44.67
2	8.33	16.30	25.19	34.07	57.69
6	16.67	26.33	41.48	51.00	66.67
10	19.67	26.67	42.33	53.33	68.67
12	22.67	27.33	50.67	58.67	71.33

D/W emulsions	15:85	25:75	35:65	45:55
Time (h)	**930ppm**	**930ppm**	**930ppm**	**930ppm**
1	68	46.5	37.07	45.00
2	81	48.3	38.90	57.69
6	93	65.0	55.24	69.64
10	93	72.5	61.80	75.00
12	94.5	75.7	63.00	76.00

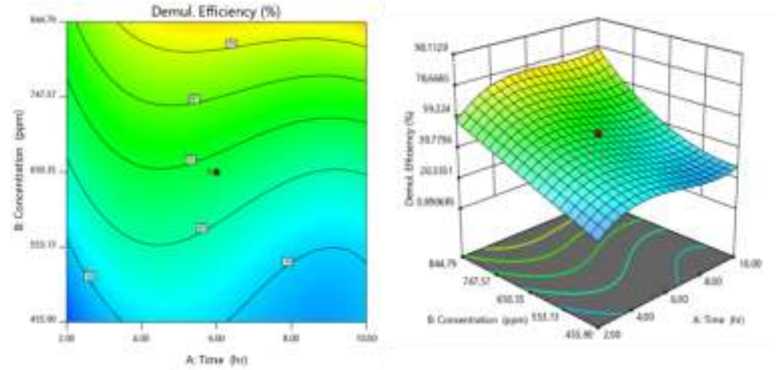
Demulsification efficiency (%), 15:85 D/W emulsion with TTAC					
Time (h)	**370ppm**	**450ppm**	**650ppm**	**850ppm**	**930ppm**
1	11.33	12.33	33.33	50.40	55.00
2	15.50	20.00	43.67	53.33	57.78
6	30.00	40.00	48.89	57.78	64.44
10	33.33	41.11	54.44	68.89	77.78
12	37.78	48.89	65.56	76.67	78.89

Demulsification efficiency (%) 25:75 D/W emulsion with TTAC					
Time (h)	**370ppm**	**450ppm**	**650ppm**	**850ppm**	**930ppm**
1	6.33	9.67	27.33	46.33	50.33
2	10.17	13.33	30.67	48.00	53.00
6	20.00	23.33	53.33	57.33	58.67
10	28.67	33.33	55.33	62.67	65.33
12	33.33	46.67	60.00	66.67	71.33

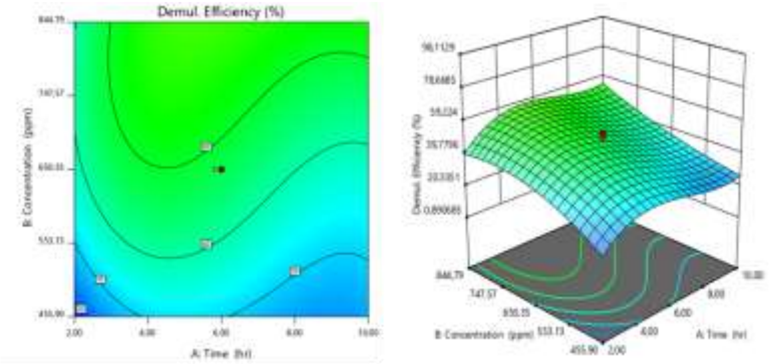
Demulsification efficiency (%) 35:65 D/W emulsion with TTAC					
Time (h)	**370ppm**	**450ppm**	**650ppm**	**850ppm**	**930ppm**
1	8.57	12.67	20.95	31.67	46.67
2	12.33	20.95	21.67	36.19	52.67
6	20.95	27.62	34.29	49.52	53.33
10	23.81	30.48	49.52	52.38	55.24
12	24.76	34.29	53.33	62.86	66.67

Demulsification efficiency (%) 45:55 D/W emulsion with TTAC					
time (hrs)	**370ppm**	**450ppm**	**650ppm**	**850ppm**	**930ppm**
1	3.70	5.93	9.63	25.93	36.30
2	11.33	22.22	24.33	38.52	39.83
6	17.78	25.19	34.81	42.22	51.85
10	19.26	29.63	45.93	49.63	52.59
12	27.41	35.56	51.85	58.52	65.93

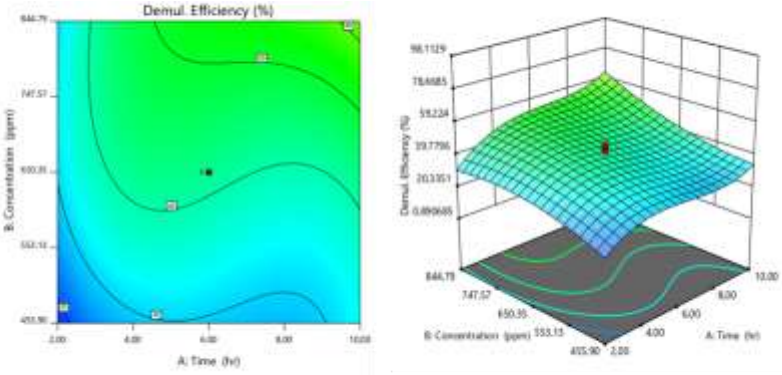
Appendix C:



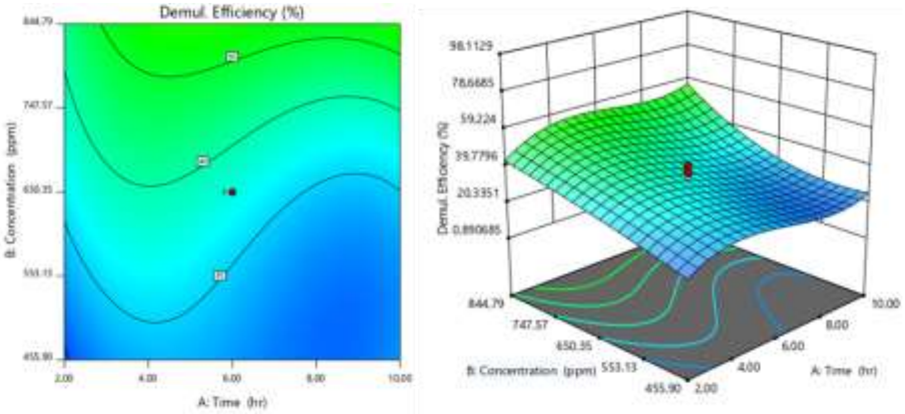
15:85 D/W emulsion with CTAB



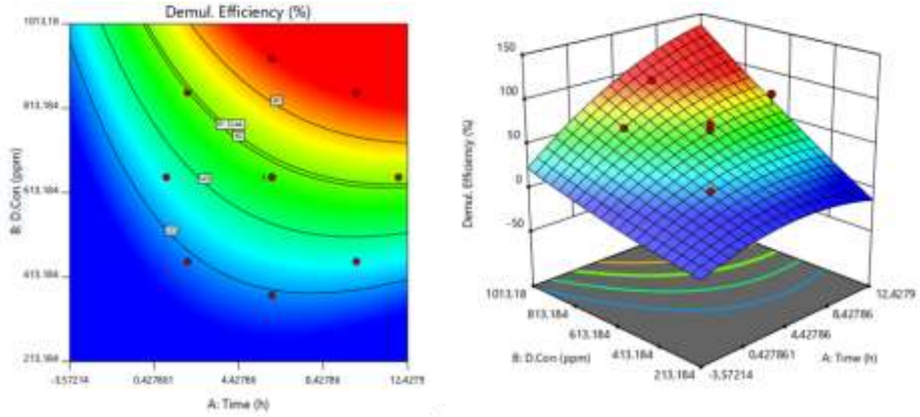
25:75 D/W emulsion with CTAB



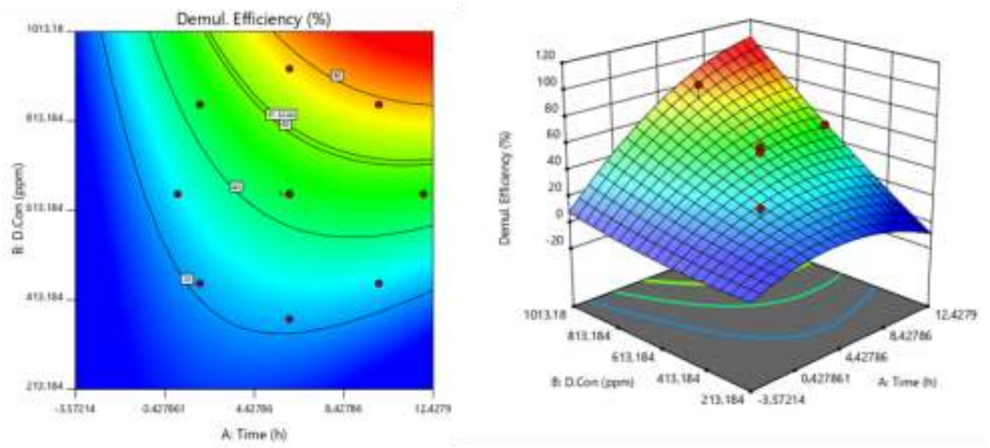
35:65 D/W emulsion with CTAB



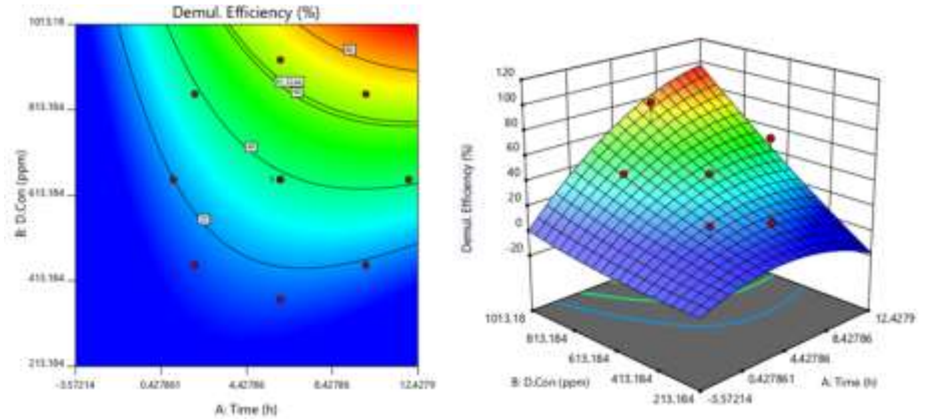
45:55 D/W emulsion with CTAB



25:75 D/W emulsion TTAC



35:65 D/W emulsion with TTAC



45:55 D/W emulsion with TTAC