

**SELECTION AND OPTIMIZATION OF DEMULSIFIER BASED ON
PHYSIO-CHEMICAL CHARACTERISTICS OF EMULSION**

BY

ALI RIDHA ALTOWILIB

A Thesis Presented to the
DEANSHIP OF GRADUATE STUDIES

KING FAHD UNIVERSITY OF PETROLEUM & MINERALS

DHAHRAN, SAUDI ARABIA

In Partial Fulfillment of the
Requirements for the Degree of

MASTER OF SCIENCE

In

PETROLEUM ENGINEERING

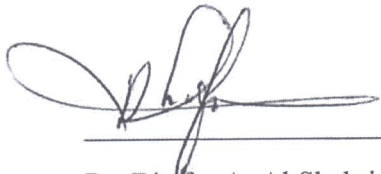
APRIL 2021

KING FAHD UNIVERSITY OF PETROLEUM & MINERALS

DHAHRAN- 31261, SAUDI ARABIA

DEANSHIP OF GRADUATE STUDIES

This thesis, written by **ALI RIDHA ALTOWILIB** under the direction of his thesis advisor and approved by his thesis committee, has been presented and accepted by the Dean of Graduate Studies, in partial fulfillment of the requirements for the degree of **MASTER OF SCIENCE IN PETROLEUM ENGINEERING**.

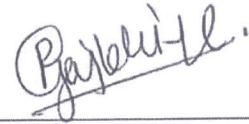


Dr. Dhafer A. Al Shehri
Department Chairman

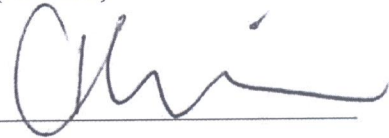


Prof. Suliman Saleh Al-Homidan
Dean of Graduate Studies

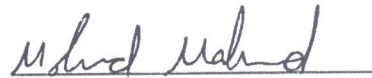
Date



Dr. Rahul N. Gajbhiye
(Advisor)



Dr. Theis Ivan Solling
(Member)



Dr. Mohamed Mahmoud
(Member)



© Ali Ridha Altowilib

2021

[To my loved ones and to myself]

ACKNOWLEDGMENTS

[In the Name of Allah, the Most Beneficent, the Most Merciful. All the praises and thanks be to Allah for giving me the health, the strength, the patience, the determination, and the persistence to start this journey and end it with a smile filling my heart. All the praises and thanks be to Allah for giving me love and support from my family and my wife throughout my life and throughout this challenging voyage. I am grateful for the mentorship and guidance provided by Dr. Rahul N. Gajbhiye, Dr. Theis Ivan Solling, and Dr. Mohamed Mahmoud throughout my thesis work. I am thankful to King Fahd University of Petroleum & Minerals and College of Petroleum Engineering and Geosciences for providing a positive learning environment.]

TABLE OF CONTENTS

ACKNOWLEDGMENTS	V
TABLE OF CONTENTS	VI
LIST OF TABLES	VIII
LIST OF FIGURES	IX
LIST OF EQUATIONS	X
LIST OF ABBREVIATIONS	XI
ABSTRACT	XII
ملخص الرسالة	XIV
CHAPTER 1 INTRODUCTION	1
CHAPTER 2 LITERATURE REVIEW	3
2.1 Emulsion Definition	3
2.2 Crude Oil Emulsion Types	3
2.3 Formation of Crude Oil Emulsions	7
2.4 Emulsion Properties	8
2.5 Emulsion Stability & Associated Factors	11
2.6 Emulsion Stability Measurement	15
2.7 Demulsification Overview	15
2.8 Demulsification Mechanisms	16
2.9 Demulsification & Stoke's Law	18
2.10 Chemical Demulsification	19
CHAPTER 3 PROBLEM STATEMENT AND RESEARCH OBJECTIVE	25
3.1 Problem Statement	25
3.2 Objectives	26
CHAPTER 4 METHODOLOGY	27
4.1 Materials	27
4.1.1 Oil Samples	27
4.1.2 Water Samples	27
4.1.3 Chemical Demulsifiers	27
4.2 Experimental Work	28
4.2.1 SARA Analysis	28

4.2.2	Viscosity and Density Measurements	29
4.2.3	Sulfur Content	29
4.2.4	Geochemical Water Analysis	30
4.2.5	Emulsification and Demulsification	30
CHAPTER 5 RESULTS AND DISCUSSION		31
5.1	Oil Analysis	31
5.2	Water Analysis	34
5.3	Emulsion Analysis	34
5.4	Demulsifier Analysis	38
5.5	Root Cause of Demulsifier Ineffectiveness	39
CHAPTER 6 CONCLUSIONS AND RECCOMENDATIONS		41
References		43
APPENDICES		57
Vitae		62

LIST OF TABLES

Table 1: HLB ranges and their applications	21
Table 2: HLB numbers to emulsify different oil	21
Table 3: Examples of water-soluble groups	24
Table 4: Oil soluble demulsifier and water soluble demulsifiers	24
Table 5: Examples of different groups of demulsifiers	25
Table 6: Composition of Type 1 Demulsifier	28
Table 7: Composition of Type 2 Demulsifier	28
Table 8 Results of Oil Samples.....	31
Table 9: Deviation of Density Measurement in Sample 7	33
Table 10: Water Geochemical Analysis	34
Table 11: ESI for Formation Water	35
Table 12: ESI for Seawater	35
Table 13: Demulsifier Types	39
Table 14: Demulsifier Analysis	39

LIST OF FIGURES

Figure 1: Water-in-oil emulsion	4
Figure 2: Photomicrograph of water-in-oil emulsion	4
Figure 3: Oil-in-water emulsion	5
Figure 4: Photomicrograph of invert emulsion	5
Figure 5: Multiple emulsion	6
Figure 6: Photomicrograph of oil-in-water-in-oil emulsion	6
Figure 7: Surfactant structure	8
Figure 8: Droplets size distribution of crude oil emulsions	10
Figure 9: Water cut & shear effects on emulsion viscosity	10
Figure 10: Solubilization of asphaltenes by resin	12
Figure 11: Hypothetical structures of resins	12
Figure 12: SARA Analysis Using MAZE Technology	13
Figure 13: Flow assurance problems due to wax deposition	13
Figure 14: Wettability of solids	14
Figure 15: Demulsification mechanisms	18
Figure 16: Example and structure of surfactant molecules	23
Figure 17: Densitometer & Viscometer	29
Figure 18: Elemental Analyzer	29
Figure 19: Experimental Emulsification and Demulsification Plan	30
Figure 20: Emulsification & Demulsification	30
Figure 21: Sulfur Content vs Density	31
Figure 22: Sulfur Content vs Viscosity	32
Figure 23: Sulfur Content vs Asphaltene and Resin	32
Figure 24: Asphaltene and Resin vs Density	33
Figure 25: Asphaltene and Resin vs Viscosity	33
Figure 26: Formation Water Emulsion Separation Index vs Asphaltene	36
Figure 27: Formation Water Emulsion Separation Index vs Resin	36
Figure 28: Formation Water Emulsion Separation Index vs Viscosity	36
Figure 29: Formation Water Emulsion Separation Index vs Density	37
Figure 30: Seawater Emulsion Separation Index vs Asphaltene	37
Figure 31: Seawater Emulsion Separation Index vs Resin	37
Figure 32: Seawater Emulsion Separation Index vs Density	38
Figure 33: Seawater Emulsion Separation Index vs Viscosity	38
Figure 34: Emulsion Separation Index: Formation Water	40
Figure 35: Emulsion Separation Index: Seawater	40

LIST OF EQUATIONS

Equation 1: Stoke's Law	19
Equation 2: HLB Equation.....	20

LIST OF ABBREVIATIONS

BS&W	:	Basic Sediments and Water
SARA	:	Saturates Aromatics Resins and Asphaltene
TDS	:	Total Dissolved Solids
IUPAC	:	The International Union of Pure and Applied Chemistry
W/O	:	Water-in-Oil
O/W	:	Oil-in-Water
IFT	:	Interfacial Tension
ASTM	:	American Society for Testing and Materials
TAN	:	Total Acid Number
PPT	:	Parts Per Thousand
ESI	:	Emulsion Separation Index
HLB	:	Hydrophilic-Lipophilic Balance
HPLC	:	High-Performance Liquid Chromatography
RPM	:	Rotation per Minute

ABSTRACT

Full Name : [ALI RIDHA ALTOWILIB]

Thesis Title : [SELECTION AND OPTIMIZATION OF DEMULSIFIER BASED
ON PHYSIO-CHEMICAL CHARACTERISTICS OF EMULSION]

Major Field : [Petroleum Engineering]

Date of Degree : [April 2021]

The presence of crude oil/water emulsions is a burden in the petroleum industry. It leads to several operational and economic issues related to crude production, transportation, and refining processes. The stability of the emulsified oil is affected by water content, presence of organic/inorganic materials, formation brine salinity, temperature, and droplet size. In reservoir fluid studies, it is a common practice to apply chemical demulsifiers on emulsion samples to break the emulsion and reduce the water content to an acceptable level (less than 1 wt. %) to ensure generate representative fluid composition results. However, this process depends heavily on the crude and the water compositions along with the type of demulsifier used. Incompatible choice of demulsifier could strengthen the stability of the emulsion or alter the composition of reservoir fluid. This introduces the need to understand certain physiochemical properties to identify the root causes of demulsifier ineffectiveness.

In this study, two demulsifiers containing different functional groups (Type 1 and Type 2) were evaluated for their emulsion breakage ability. Nine oil samples from different fields were mixed with formation water in the first round and seawater in the second one. The water-oil ratio of 80:20 was achieved using a blender for 1.5 minutes at 300 RPM. Saturates, Aromatics, Resins, and Asphaltene (SARA), viscosity, density, and sulfur content were determined for all oil samples. Furthermore, water chemical analysis was

conducted on all water samples to determine Total Dissolved Solids (TDS). After applying both demulsifiers at the same concentration (1% of total volume), volumes of water separated were measured at 5, 10, 15, and 20 minutes and used in calculating the emulsion separation index (ESI).

Results of this work showed that Type 1 demulsifier showed a better performance than Type 2 in formation water and seawater and while using different oils due to the resistance of non-ionic surfactant to salinity, polarity, and water hardness. This study shows a methodology of determining the optimum chemical demulsifier type to break emulsions effectively through developing a proper understanding of the chemistry of the oil, brine, resulting emulsions and demulsifiers used.

ملخص الرسالة

الاسم الكامل: علي رضا سعيد آل طويلب

عنوان الرسالة:

التخصص: هندسة البترول

تاريخ الدرجة العلمية: أبريل 2021

يعد وجود مستحلبات النفط عبئاً في صناعة البترول. يؤدي إلى العديد من المشاكل التشغيلية والاقتصادية المتعلقة بإنتاج الخام وعمليات النقل والتكرير. يتأثر تماسك الزيت المستحلب بمحتوى الماء ووجود المواد العضوية / غير العضوية وملوحة الماء ودرجة الحرارة وحجم قطرة المستحلب. في دراسات سوائل المكنن ، من الممارسات الشائعة تطبيق مزيلات المستحلب الكيميائية على عينات المستحلب لتفكيك المستحلب وتقليل محتوى الماء إلى مستوى مقبول (أقل من 1% من إجمالي الوزن) لضمان الحصول على نتائج دقيقة لمكونات السوائل. ومع ذلك ، فإن هذه العملية تعتمد بشكل كبير على مكونات النفط الخام والمياه جنباً إلى جنب مع نوع مزيل الاستحلاب المستخدم. يمكن أن يؤدي الاختيار غير المتوافق لمزيل الاستحلاب إلى تقوية استقرار المستحلب أو تغيير مكونات نפט المكامن. فمن المهم فهم بعض الخصائص الفيزيوكيميائية لتحديد الأسباب الجذرية لعدم فعالية مزيل الاستحلاب.

في هذه الدراسة ، تم تقييم اثنين من مزيلات المستحلب تحتوي على مجموعة وظيفية مختلفة (النوع 1 والنوع 2) لمعرفة قدرتها على كسر المستحلب. تم خلط تسع عينات زيت من حقول مختلفة بمياه التكوين في الجولة الأولى ومياه البحر في الجولة الثانية. تم تحقيق نسبة زيت الماء 80:20 باستخدام خلاط لمدة 1.5 دقيقة عند 300 دورة في الدقيقة. تم قياس تركيز المشبعات والعطريات والراتجات والاسفلتين واللزوجة والكثافة ومحتوى الكبريت لجميع عينات الزيت. علاوة على ذلك ، تم إجراء تحليل كيميائي للمياه على جميع عينات المياه لتحديد إجمالي المواد الصلبة الذائبة (TDS)، بعد تطبيق كلا مزيلات الاستحلاب بنفس التركيز (1% من الحجم الكلي) ، تم قياس أحجام المياه المفصولة عند 5 ، 10 ، 15 ، و 20 دقيقة واستخدمت في حساب مؤشر فصل المستحلب (ESI). أظهرت نتائج هذا العمل أن مزيل الاستحلاب من النوع الأول أظهر أداءً أفضل من النوع الثاني في مياه التكوين ومياه البحر وأثناء استخدام الزيوت المختلفة بسبب مقاومة الفاعل بالسطح غير الأيوني للملوحة والقطبية وعسر الماء.

يوضح هذا البحث منهجية لتحديد النوع الأمثل لمزيج المستحلب الكيميائي لكسر المستحلبات بشكل فعال من خلال تطوير الفهم الصحيح لكيمياء الزيت والمحلول الملحي والمستحلبات الناتجة ومزيجات الاستحلاب المستخدمة.

CHAPTER 1

INTRODUCTION

The emulsion can be defined as a dispersion or a suspension of several droplets of one liquid inside another immiscible liquid¹. The presence of crude oil emulsion is undesirable in the petroleum industry⁵⁸. Such an inevitable phenomenon leads to several operational issues related to crudes' treatment, specifications, transportation, market value, and refining processes. Emulsified oil samples require specific treatment to meet the acceptable level of basic sediments and water (BS&W) for fluid characterization studies purposes². Additionally, crude oil emulsions require a higher pumping capacity compared to emulsion-free crude oil due to an increase in liquid viscosity³. Catalysts inside a downstream refinery are also affected by the presence of emulsion⁴. The cost per barrel of oil with emulsion is higher than that without it due to additional treatment.

To overcome this challenge, several demulsification techniques have been used in the industry. Yet, some of these techniques could aggravate the situation if are not well understood or incorrectly applied. A clear example of this is the focus of this work; the usage of chemical demulsifiers. Service providers usually apply chemical demulsification techniques on oil samples to reduce the water content to an acceptable level (less than 1 wt. %) to ensure generating representative fluid composition results. Using an incompatible demulsifier might not help in achieving this goal. This introduces the need to understand the physiochemical properties to understand the root causes of demulsifier ineffectiveness, which will help in the proper chemical selection. This section provides a review of crude

oil emulsions and demulsification techniques while focusing solely on the application of chemical demulsification.

CHAPTER 2

LITERATURE REVIEW

In this chapter, a general review of emulsions and demulsification techniques is included in terms of emulsion types, formation of emulsion, emulsifying agents, and emulsion properties. Factors affecting the stability of emulsion were addressed also include droplet size, droplet size distribution, viscosity, surface film, asphaltene, wax, resins, inorganic materials, and fine solids. Furthermore, thermal, mechanical, electrical, and chemical demulsification techniques are highlighted. Demulsification mechanisms (flocculation, coalescence, sedimentation) along with enhancement factors were discussed in detail. As mentioned before, the focus of this work is on the application of chemical demulsification and hence topics related to chemical demulsifier selection criteria, chemical demulsifier dosage, functional groups, proper mixing, and retention time are included.

2.1 Emulsion Definition

The International Union of Pure and Applied Chemistry (IUPAC) defines emulsion as “a fluid colloidal system in which liquid droplets and/or liquid crystals are dispersed in a liquid”⁸. In other words, it is a heterogeneous system made of continuous and discontinuous phases.

2.2 Crude Oil Emulsion Types

Crude emulsions can be classified into three groups according to what is being suspended and what is acting as a continuous phase.

- **Water-in-oil (W/O) emulsions:** The most common type encountered in the oil industry. In this type, water droplets (discontinuous phase) are suspended in a continuous oil phase^{9, 57} as shown in **Figures 1-2**.

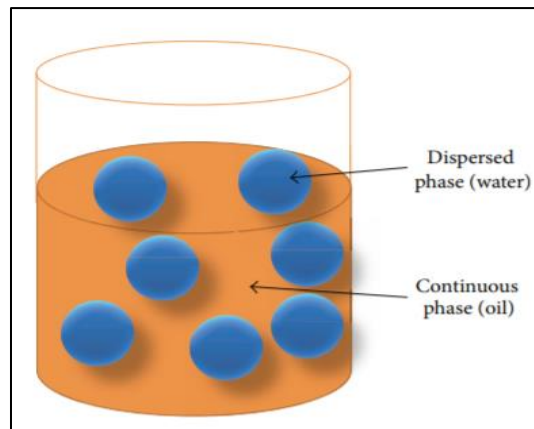


Figure 1: Water-in-oil emulsion [9]

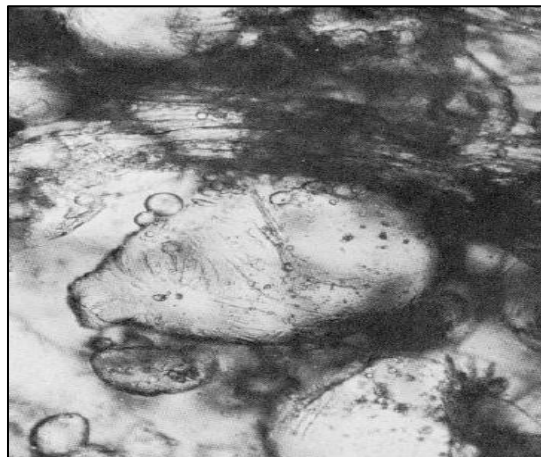


Figure 2: Photomicrograph of water-in-oil emulsion [41]

- **Oil-in-water (O/W) emulsions:** Also known as invert or reverse emulsions. Oil is the suspended phase and water is the continuous phase in this type; the opposite of water-in-

oil emulsion^{9,57} as shown in **Figures 3-4**.

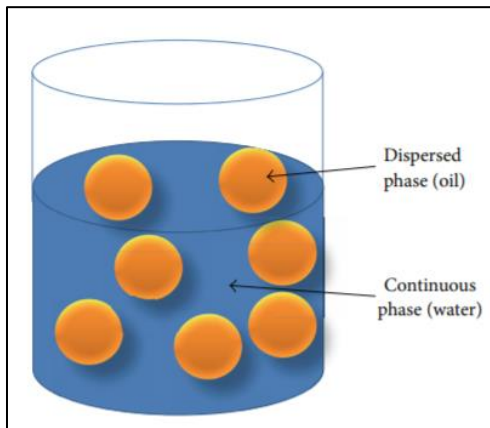


Figure 3: Oil-in-water emulsion [9]

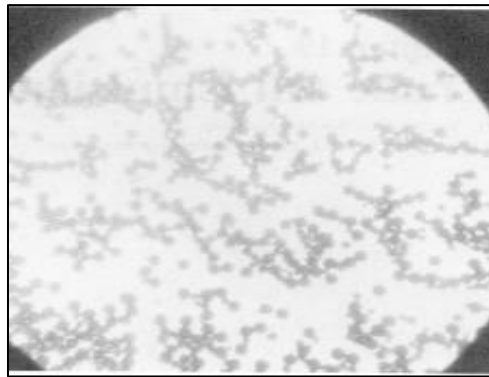


Figure 4: Photomicrograph of invert emulsion [41]

- **Multiple emulsions:** this type is made of several tiny droplets inside larger ones that are carried in a continuous phase. **Figure 5** shows water-in-oil-in-water (left) and oil-in-water-oil (right) emulsions whereas **Figure 6** shows a photomicrograph of oil-in-water-in-oil emulsion¹².

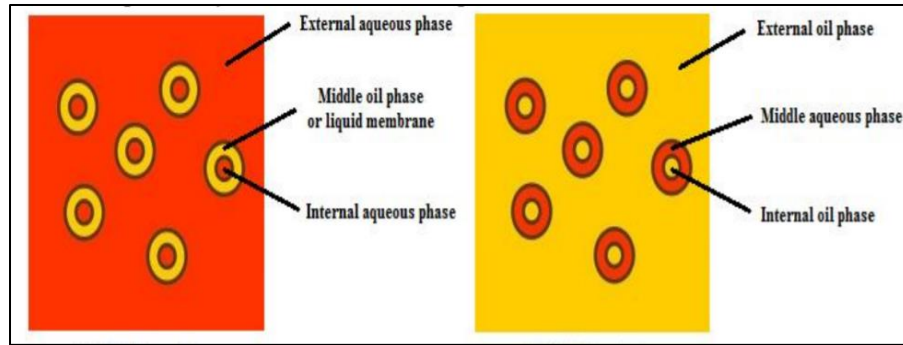


Figure 5: Multiple emulsion [10]

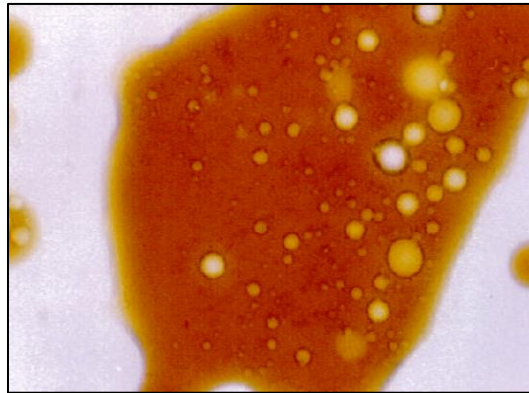


Figure 6: Photomicrograph of oil-in-water-in-oil emulsion [12]

It is worth mentioning that the ratio of the two phases along with other factors help in determining the type of emulsion formed. In general, the dominant portion is the continuous phase. Another way to classify the emulsions is through the size of the droplets as follows:

- **Macroemulsions:** The dispersed droplets size is in the range of 0.1-5 μm .¹¹ Macroemulsions are commonly encountered in the oil industry and considered thermodynamically unstable. In other words, the continuous and dispersed phase separates over time to reduce the emulsion's interfacial energy¹².
- **Nanoemulsions:** The dispersed droplets size is in the range of 20-100- nm and they are stable kinetically and unstable thermodynamically^{11,89}.
- **Microemulsion:** The dispersed droplets size is in the range of 5-50 nm¹¹. Unlike

macroemulsion, microemulsions is considered thermodynamically stable and has low interfacial energy¹².

2.3 Formation of Crude Oil Emulsions

In order to form the emulsion, the followings conditions should be fulfilled²²:

- **Two immiscible liquids in contact with each other:** Water is usually in contact with oil in different downhole and surface locations (reservoir, near wellbore, wellhead, flow lines, and plants).
- **Adequate mixing between the two liquids:** In the case of oil and water, the required mixing to form emulsion is originated from phase behavior changes, high shear rate, and fluid flow in different locations (wellheads, flow lines, valves, etc.). The relationship between the amount of shear or mixing and the droplet radius is inversely proportional. Meaning, tight emulsion with tiny droplets is a result of high shear^{12,6}.
- **A presence of emulsifiers or emulsifying agents:** Emulsifiers work on stabilizing the emulsion formed. Heavy organic fractions, stimulation/drilling fluids, and corrosion/scale inhibitors might contain surface-active agents and fine solids that serve as emulsifying agents. The strength of the emulsion formed is directly related to the composition and the concentration of emulsifiers present.

Both surface active agents and fine solids contribute majorly to the formation of an emulsion. Surface-active agents or surfactants are partially soluble in oil and water due to having two parts with unique behaviors. The first part is nonpolar and has an affinity or

attraction to oil only and hence it is called the hydrophobic tail. The other part is called the hydrophilic head and it has an affinity to water because of its polarity ¹³ (**Figure 7**). These two parts are usually found in the interface between water and oil and they form what is called interfacial film. The presence of surfactants in emulsion results in lowering interfacial tension (IFT) and enhancing emulsification and dispersion of droplets^{14,7}. On the other hand, finely divided solids, that are smaller than the droplets, concentrate near the oil/water interface. These tiny particles act as mechanical stabilizers/protectors for emulsion. The effectiveness of these mechanical stabilizers is affected by their size, wettability, and interparticle interaction. Sand, clay particles, and scales are common examples of fine solids that stabilize emulsion mechanically¹⁵.

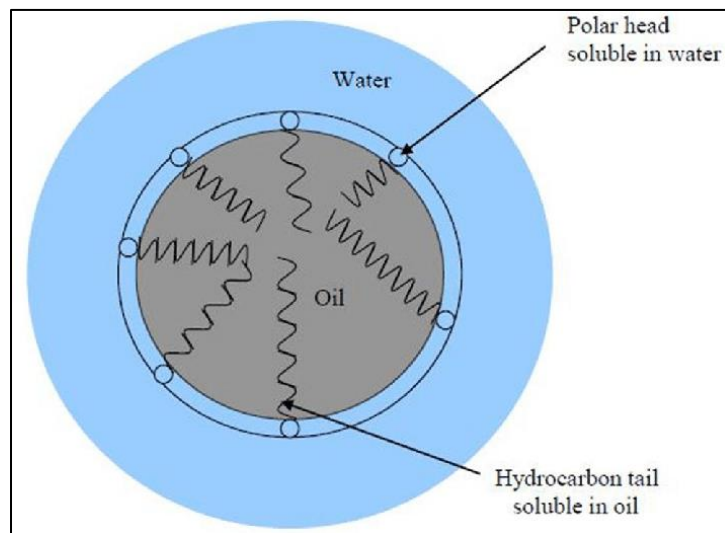


Figure 7: Surfactant structure [45]

2.4 Emulsion Properties

- **Color:** the color of emulsion is affected by the water content, brine compositions, and oil

composition. The emulsion phase can be distinguished due to light scattering across the interface².

- **Basic Sediment & Water (BS&W):** BS&W can be defined as the solids and water settling at the bottom of a sample. Examples of techniques to determine the BS&W level are heating/cooling cycles, centrifuge, gravity segregation, microwave-based meters, and gamma-ray attenuation¹⁶. One of the most common methods used in determining the water or moisture content of emulsion is Karl-Fischer titration¹⁷. ASTM 4007 standard method is also used to determine BS&W through the application of centrifuge¹⁸.
- **Droplet Size:** The droplet size in the emulsion is directly related to the amount of shear/mixing that helped in forming it originally. In general, tiny droplets are tight and takes a longer time to get broken². The droplet size distribution is affected by interfacial tension, level of mixing, type of emulsifier, and presence of solids. Macroscopy, light scattering, neutron scattering, X-ray scattering, and image analysis techniques are all used to determine the range of droplet sizes that exist in emulsions¹⁶. In addition, beta and other distribution functions could be used in modeling emulsion droplet size distribution (**Figure 8**)^{19, 20}.

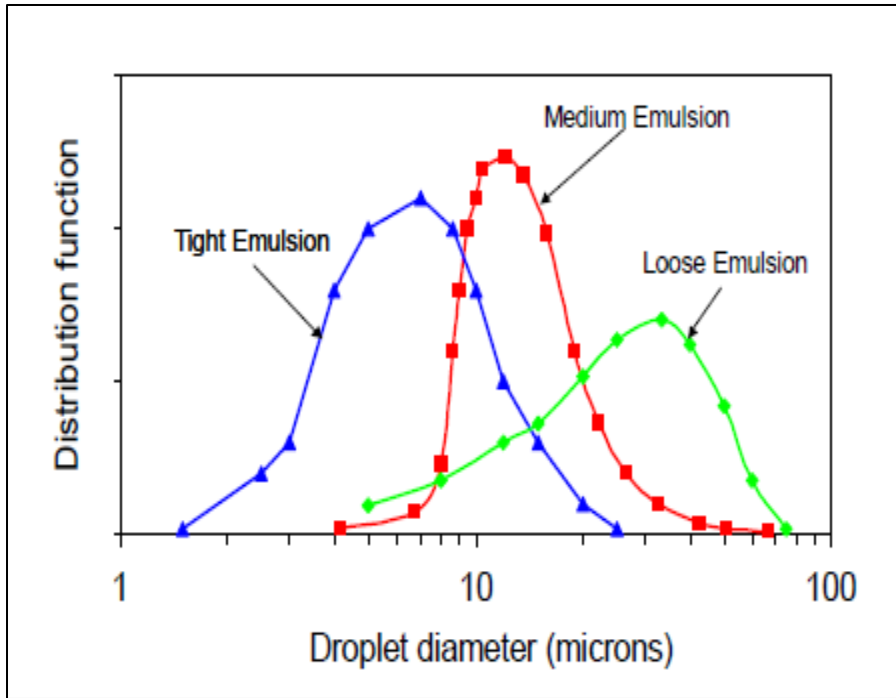


Figure 8: Droplets size distribution of crude oil emulsions [12]

- Viscosity:** Emulsion viscosity is directly influenced by the amount of shear or force applied to it. Emulsions tend to behave as non-Newtonian fluid due to droplet gathering and crowding in a certain region. At a low water cut level, emulsion could behave as a Newtonian fluid (**Figure 9**)¹².

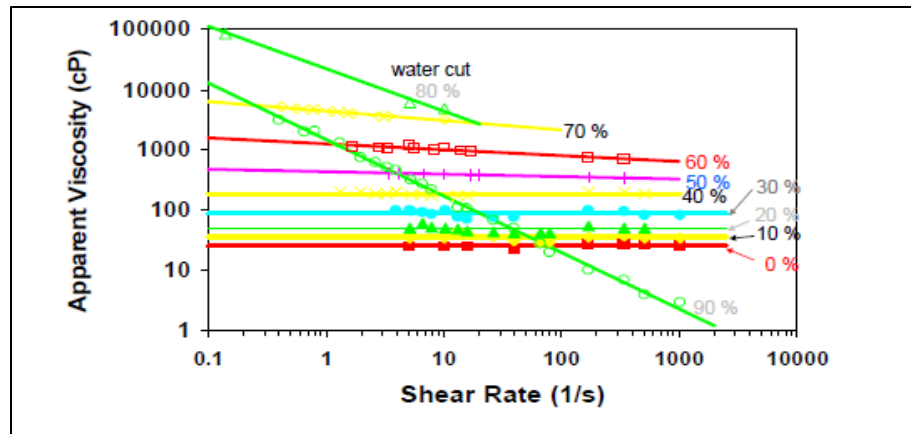


Figure 9: Water cut & shear effects on emulsion viscosity [12]

- Interfacial Viscosity:** Interfacial viscosity is defined as the resistance of the interfacial film to shear in the plane occurring between the two immiscible fluids²¹. Meaning,

interfacial viscosity is a two-dimensional bulk resistance that operates in the interfacial region²². High values of interfacial viscosity and low interfacial tension indicate the stability of emulsion and rigidity of interfacial film; films are capable of entrapping water droplets. Furthermore, a viscous film retards the rate of emulsion breakage and hence its behavior and composition must be studied prior to any demulsification attempt¹².

2.5 Emulsion Stability & Associated Factors

In general, the presence of small droplets surrounded by the viscous emulsified film in a suitable medium provides kinetic stability for emulsions. This kinetic stability overcomes mechanisms that help in the breakage of emulsions. The adsorption of surfactant-like behavior hydrocarbons molecules and the presence of fine solids all contribute to the formation and stability of interfacial films. These films can be classified as rigid or mobile. Rigid films have higher interfacial viscosity compared to mobile ones. The presence of high molecular weight components such as asphaltene, wax, and resins could strengthen the interfacial film of emulsions¹².

- **Asphaltenes:** Asphaltenes are made of polyaromatic and naphthenic ring compounds, which have heteroatoms molecules attached to them. These molecules include nitrogen, sulfur, oxygen, nickel, and vanadium^{23, 24}. The carbon number of asphaltenes could go up to C₁₅₀ whereas the range for molecular weight ranges from 500 to more than 2000 g/mol^{25, 26}. Asphaltenes are known to be soluble in ethyl acetate but not in n-alkanes²⁷. In crude oil, asphaltenes are stabilized by resins (peptizing agent) and form micelles²⁸. Micelles particles have surface-active agent properties resulted from the presence of the heteroatoms^{81, 82}. Consequently, micelles make asphaltenes an effective emulsifying agent and a good film stabilizer due to their dual affinity to oil and water. The high concentration of micelles increases the interfacial viscosity, the strength of the interfacial film, and prevents the rapture of droplets. In addition, the presence of asphaltenes alters the wettability of nearby fine solids forcing them to act as emulsifiers²⁹ (**Figure 10**).

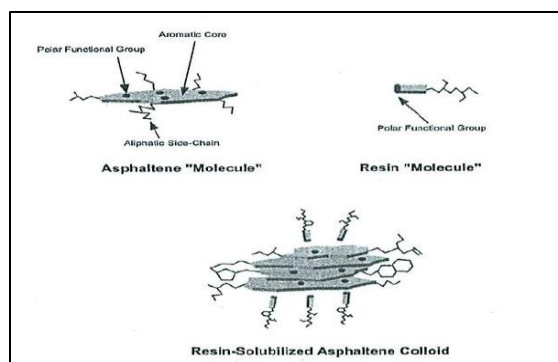


Figure 10: Solubilization of asphaltenes by resin [30]

- Resins:** Unlike asphaltenes, resins are part of the maltenes (saturates, aromatics, resins) that are soluble in n-alkanes but not in ethyl acetate. Resins are directly linked to the formation of micelles and hence to the stability of emulsions¹². Resins have the ability to dissolve asphaltene molecules and taking their place at the water/oil interface⁶⁸. Like asphaltenes, resins are compounds with heteroatoms (**Figure 11**).

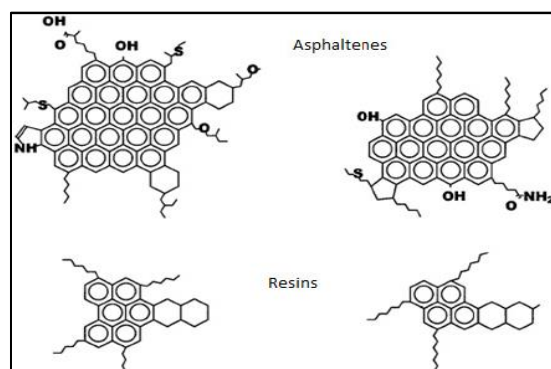


Figure 11: Hypothetical structures of resins [46]

SARA analysis is used to fractionize dead oil samples into four solubility classes with distinct polarity and solubility in different solvents⁶³. In this work, the microfluidic technique (MAZE) is used to generate SARA fractions based on their respective weight in the sample⁶⁴ (**Figure 12**).

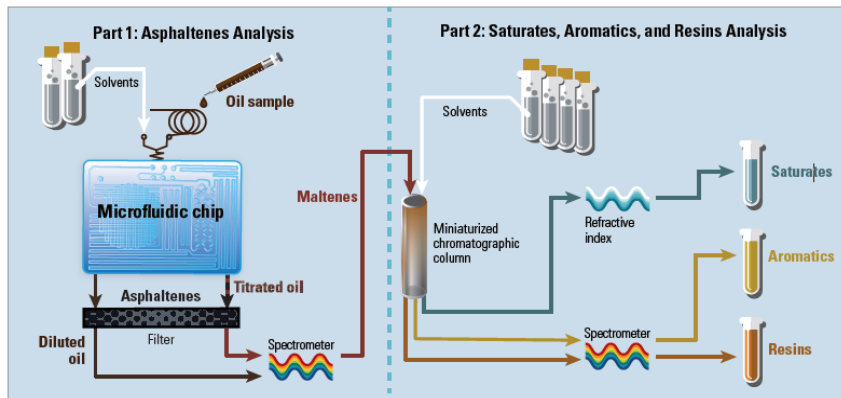


Figure 12: SARA Analysis Using MAZE Technology [64]

- Wax:** Waxes are heavy alkanes that tend to crystalize when the temperature is below the cloud point. They tend to block flow lines and storage tanks (**Figure 13**)⁴⁷. Waxes are oil-soluble and can be classified into paraffin (normal alkane) and microcrystalline (iso-alkanes). Waxes are oil-wet and thus can stabilize water-in-oil emulsions. In addition, waxes do not form emulsions alone due to their solubility in oil unless asphaltene is introduced. Crudes with low cloud point have a lower tendency to form stable waxy emulsions compared to those with high cloud point values^{30, 39}.

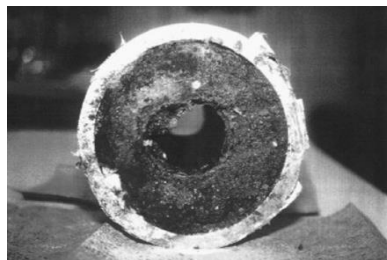


Figure 13: Flow assurance problems due to wax deposition [47]

- Wettability of Solids:** Finely divided solids concentrated at the oil/water interface act as mechanical stabilizers for the emulsion¹⁵. However, the wettability of these particles controls their effectiveness in stabilizing emulsion film. Wettability or the tendency of a solid to be wetted by either water or oil is determined through the measurement of contact angle. Acute contact angle (less than 90°) indicates oil-wet whereas obtuse angle (more than 90°) indicates water-wet. Intermediate wettability means that the contact angle is 90 and solids are wetted by both liquids equally, which stabilizes the interfacial film (**Figure 14**). Asphaltenes and waxes are oil-wet and tend to strengthen water-in-oil emulsions

whereas sand and inorganic scales are water-wet solids that stabilize oil-in-water emulsion
31, 32 .

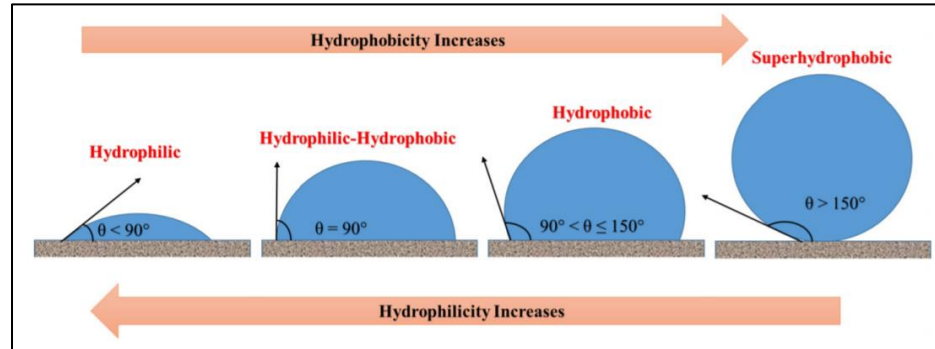


Figure 14: Wettability of solids [48]

- Temperature:** A change in temperature reduces oil viscosity and could dissolve wax back into crude oil. In addition, increasing the thermal energy results in rapid droplet collisions, which accelerates film-drainage and droplets settling rate. The downside of rising the temperature blindly includes volume shrinkage and loss of light valuable ends from the crude¹².
- pH and Total Acid Number:** The stability and rigidity of interfacial film are affected by the acidity/basicity of brine and oil. Films made of asphaltenes are strong in acidic medium and weak in basic solutions while films made of resins are the opposite²⁹. In addition, an alteration of solids wettability resulted from heavy coating of polar compounds could strengthen or weaken the stability of emulsion depending on the type of coating and pH of the water. Also, the composition of formation water and oil phase is linked to the pH of the water⁹⁰. Brines with high calcium to magnesium ratio tends to stabilize emulsions^{33, 34}. pH can be measured through conductivity meter, pH meter, or indicators in solutions. Total Acid Number (TAN) refers to the measurement of the level of acidity found in the crude oil sample. TAN is based on titration where the needed amount of potassium hydroxide in milligrams to neutralize the acids in one gram of crude oil is determined^{62,5}.
- Total Dissolved Solids (TDS) & Salinity:** TDS, expressed in parts per million (ppm), refers to the estimation of the total mass of solids that are dissolved within the solution. On

the other hand, salinity refers to the estimation of the total concentration of salts that are dissolved within the solution and expressed in parts per thousand (ppt). TSD and salinity are not direct measurements since they are derived from conductivity measurements⁶⁵. Results from TDS and salinity will help in determining the concentration of divalent ions (calcium and magnesium) that could affect the tightness of emulsion or lead to water hardness^{33, 34}.

2.6 Emulsion Stability Measurement

Emulsion stability is inferred through the ease of water separation, the time for separation to occur, and the dosage of chemical demulsifier required. Bottle test⁵⁴ and Emulsion Separation Index (ESI) (**Appendix A**) are used to determine the strength of an emulsion. The bottle test is also used as a quick preliminary test for commercial demulsifiers through recording how much water is separated in a specific duration at a fixed concentration of different demulsifiers³⁵. Other industry procedures used to determine the stability of emulsions include ASTM G205–16 and ASTM F3045-15E1^{36, 37}.

2.7 Demulsification Overview

Demulsification refers to the process of breaking emulsions into separated liquid phases, i.e., oil and water. There are thermal, mechanical, electrical, and chemical demulsification methods. The thermal method involves the use of a heater to destabilize emulsions. Mechanical methods include the use of free-water knockout drums, settling tanks, coalescer, and desalters. High voltage electrostatic grids are used as electrical means to break emulsions whereas the addition of demulsifiers is considered as the chemical method¹². Also, different nano materials were are fabricated recently to separate oil from water such as recyclable magnetic graphene oxide⁵⁵. In general, emulsion separation is a

result of destroying interfacial film and coalescing trapped droplets. Demulsification of water-in-oil emulsion is considered effective if it results in a fast separation rate, low water content, and low cost¹². Temperature, shear, retention time, solids removal, and control of emulsifying agents are examples of techniques used to accelerate emulsion breakage if applied incorrectly⁷⁵. High agitation/shear is not desirable as it increases the stability of emulsion and results into the formation of smaller and more stable droplets^{12, 41,53}. Therefore, shear should be controlled through valves and chokes but also should provide sufficient agitation to ensure proper mixing of chemical demulsifiers added into treated oil¹². On the other hand, high retention, residence, or treating time is desirable as it reduces water content and improves separation efficiency¹². It is also recommended to remove fine solids from emulsion as they tend to stabilize interfacial film, especially in the case of intermediate wettability solids³⁸. Another important aspect is the control and compatibility of emulsifying agents such as acidizing additives, corrosion inhibitors, surfactants, polymers, and even chemical demulsifiers. Blending different crudes should be avoided as possible as it helps in the formation of emulsion as in the case of the asphaltic and paraffinic crude mix (due to asphaltenes precipitation)⁴⁰. Lastly, retrofitting and installation of equipment such as heaters and coalescers help in destabilizing emulsions¹².

2.8 Demulsification Mechanisms

There are three main processes that are involved in demulsification and determine the rate of separation which are aggregation, coalescence, and sedimentation (**Figure 15**).

- **Aggregation or flocculation** refers to the clumping and clustering of suspended water droplets without coalescing (unless the interfacial film is weak)^{42, 12}. Higher water content results in a higher rate of aggregation due to having higher internal pressure in the water

droplets compared to the external pressure outside exerted by the oil phase⁴³. This pressure difference increases the interface film thinning and expedites coalescence^{73, 74}. In contrast, at a low water level, the pressure outside the droplets is much higher than the inside one, which enhances the mechanical stability of the interfacial film and even prevents accessing it by demulsifier components^{73,74,76}. In addition, the chance of droplets collision is small at low water content.⁷¹ On the other hand, higher temperature (thermal energy) results in a higher probability of collision between droplets and lower oil viscosity, which decreases the settling time and increases the rate of flocculation.

- **Coalescence:** This step comes after aggregation and during which the droplets coalesce and unite to form larger droplets⁴². This means the number of small stable droplets decreases during this step. Another phenomenon that includes the formation of large droplets at the expense of tiny ones is referred to as Ostwald ripening. Like aggregation, there are factors that expedite the coalescence process. Higher rate of flocculation results in a higher chance of droplet collisions and coalescence. In other words, all previously mentioned factors that contribute to a higher aggregation rate contribute to coalescence as well^{16, 43}. Also, the weaker the interfacial film the higher the chance of coalescence to occur.
- **Sedimentation & Creaming:** Creaming refers to the rise of oil droplets above the continuous water phase resulting in a formation of a layer. In contrast, sedimentation is the settling and layering of water droplets below the continuous oil phase. The main driver behind these two steps is the gravitational effect due to density differences between oil and water; the higher the difference, the higher the sedimentation rate⁴². Phase inversion could also occur during the demulsification process between oil and water.

While the main goal is to eliminate the presence of emulsion fully, an accumulation of stabilized unresolved nearby the water-oil interface might still exist. This accumulation is called emulsion pad or rag layer and it hinders demulsification mechanisms. It is a result of utilizing an ineffective demulsifier, incorrect dosage, or due to the presence of solids¹².

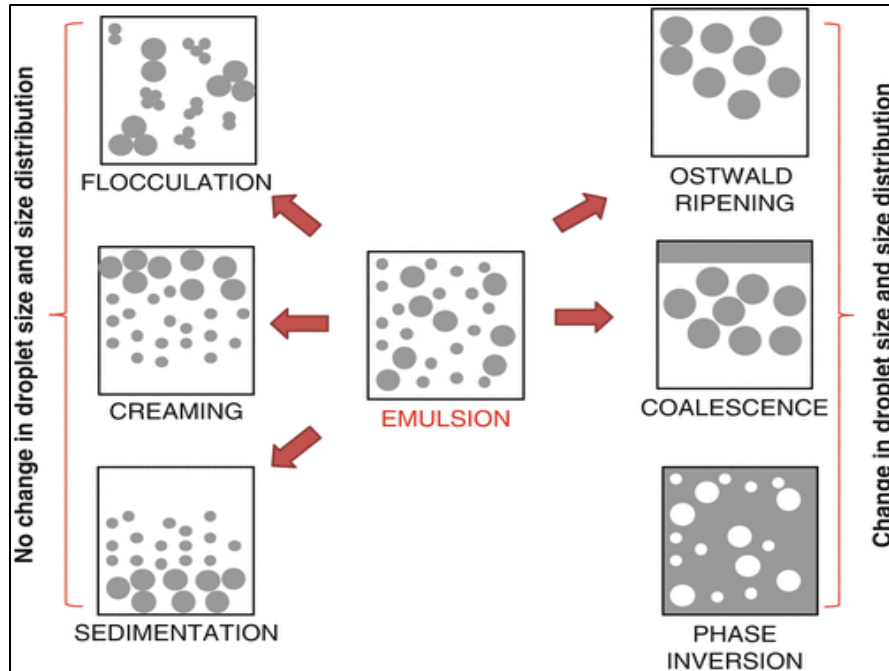


Figure 15: Demulsification mechanisms [49]

2.9 Demulsification & Stoke's Law

Stoke's law is an equation used to calculate the terminal velocity of a hard-sphere falling through a liquid⁴⁴.

$v = \frac{2gr^2(\rho_w - \rho_o)}{9\mu}$	Where;
	v: droplets settling velocity
	g: gravitational acceleration
	r: droplets radius
	$(\rho_w - \rho_o)$ is the density difference between water and oil
	μ : oil viscosity

Equation 1: Stoke's Law

Based on **Equation 1**, the settling velocity of water droplets (water-in-oil emulsion) can be increased by increasing the droplets size, increasing the density difference, and lowering the viscosity of the medium. Something to keep in mind that Stoke's law is for hard-sphere which is not the precise description for phase droplets. By looking at the above equation, droplet size impacts the settling velocity the most since it is a squared term in the equation. Increasing droplet size can be done through coalescence but it is not always achievable due to the nature of emulsifiers and interfacial film. The reduction of interfacial viscosity can be achieved by heating but there is the risk of degrading the quality of the produced crude by vaporizing light ends.

2.10 Chemical Demulsification

- **Chemical Demulsifier:** The main goal behind using this common method is to stabilize or weaken the effect of emulsifiers. This happens through replacing rigid and kinetically stable films with a conducive film that eases coalescence of water droplet^{66, 67}. The main components of demulsifiers or dehydration chemicals are surfactants that move towards interfacial film attempting to weaken/rapture interfacial films and enhance the coalescence process⁴¹. Chemical demulsifiers can suppress interfacial tension/film and emulsion stabilization (due to emulsifiers, solid articles, and polar components). Therefore, the selected chemical for this process should⁵⁹:
 - Have a sludge conditioner to alter the wettability of the solid particles.
 - Have polar ends to neutralize the polar components that are stabilizing the emulsion.
 - Have water-dropping capability after emulsion breakage.
 - Allow the movement of salt with water after emulsion breakage (desalter).

- Enhance aggregation of water droplets (flocculent).

However, the effectiveness of emulsion breakage using chemical demulsifiers depends on proper chemical selection, adequate mixing, right dosage, enough retention time, and most importantly developing a proper understanding of the chemistry of oil, emulsion, brine, solids, and demulsifier used.

- **Chemical Selection:** It is important to understand the compounds that are included in any chemical demulsifiers since they are related to the adsorption rate on the interfacial film⁷⁸. This adsorption is crucial because it results in reversing interfacial tension gradient and enhancing film thinning and drainage^{79, 80}. Chemical demulsifiers are made of surface-active agents, solvents, and flocculants agents. Examples of flocculants agents include benzene and toluene. In addition, heavy aromatic naphtha is used as carriers for active constituents¹².
 - **Solvents:** The presence of solvents in chemical demulsifiers is crucial since solvents can alter the solubility of the emulsifying agent or re-dissolve it back into solution, i.e., asphaltene. This consequently weakens the stability of emulsions¹². Different surfactants including propylene oxide, amines, and copolymers of ethylene oxide are carried in aromatics, heavy aromatic naphtha, or solvents like short-chain alcohols⁶⁹.
 - **Surface-active ingredients:** Surface-active components are characterized by a value called hydrophilic-lipophilic balance (HLB). This semi-empirical scale ranging from 0 to 20 was developed by Griffin⁵⁰ and it relates the percentage of hydrophilic to lipophilic/hydrophobic groups in the surfactant molecules. This number can be used as a tool to select the optimum composition of emulsifying agents. Low HLB number indicates lipophilic nature whereas a high HLB number indicates hydrophilic affinity. For invert emulsion, water-soluble demulsifiers destabilize its film whereas oil-soluble demulsifiers suits water-in-oil emulsion^{86,91}.

- The average of HLB number of a mixture can be calculated using **Equation 2**. X_1 and X_2 are the weight fraction of surfactant 1 and surfactant 2 respectively. **Table 1** shows HLB ranges and their respective applications¹¹. Oils with different compositions require different HLB values to emulsify them as shown in **Table 2**¹¹.

$$HLB = X_1 HLB_1 + X_2 HLB_2$$

Equation 2: HLB Equation [11]

HLB range	Application
3–6	W/O emulsifier
7–9	Wetting agent
8–18	O/W emulsifier
13–15	Detergent
15–18	Solubilizer

Table 1: HLB ranges and their applications [11]

Oil	W/O emulsion	O/W emulsion
Paraffin oil	4	10
Beeswax	5	9
Linolin, anhydrous	8	12
Cyclohexane	—	15
Toluene	—	15

Table 2: HLB numbers to emulsify different oil [11]

- Flocculants: Flocculation is one of the demulsification mechanisms that was discussed earlier and flocculants refer to additives that enhance the flocculation or the aggregation of water droplets.
- **Mixing:** The chemical demulsifier must be mixed properly to ensure it gets in contact with the interfacial film. After that, the agitation should be stopped to allow gravity separation. Excessive mixing should be avoided as it results in re-emulsification¹².
- **Dosage:** It is vital to know the right concentration of chemical demulsifier to be added.

Meaning, overdosing could result in strengthening the interfacial film due to the presence of surface-active agents in chemical demulsifiers while underdosing will not solve the problem fully⁷⁷. There is no standard dosage because there are different chemicals and different crudes. Therefore, the dosage should be evaluated on a case-by-case basis.¹²

- **Demulsifier Efficiency:** Similar to dosage, there is no single effective demulsifier. Moreover, factors that impact the stability of emulsions will also affect the efficiency of the used demulsifier. For example, increasing the temperature usually results in disturbing the stability of the interfacial film, and hence lower dosage is needed to break the film. An effective demulsifier is capable of reducing the interfacial film and diffusing it into the film effectively^{71, 87}. Demulsifiers that have molecules with close apportioning between water and oil are considered the most effective demulsifiers⁷⁰.
- **Demulsifier Chemistry:** Demulsifiers can be classified based on the chemical structures of the hydrophilic group into are anionic, cationic, nonionic, and amphoteric^{71, 72, 88} as shown in **Figure 16**. On the other hand, hydrocarbons chains with 6-22 carbon atoms make the hydrophobic part.^{83,84}
- **Anionic Demulsifier:** This type is easy to produce and is mainly used in detergents⁷². The surfactant in this type of demulsifier is negatively charged and contains a long-chain hydrophobe carrying the negative charge as well. Anionic demulsifiers are a stable foaming agent while being sensitive to pH changes and the presence of minerals in water⁷¹.
- **Cationic Demulsifier:** Unlike anionic demulsifier, this type carries a positive charge on its surface-active part. This type is also sensitive to pH changes and presence of minerals in water⁷¹.
- **Nonionic Demulsifier:** The surface-active part of this type does not contain a charged group and thus it does not ionize the aqueous solution. Therefore, it has a balance between hydrophobicity and hydrophilicity. Nonionic demulsifiers resist pH changes and water

hardness⁷¹.

- **Amphoteric Demulsifier:** Also known as zwitterionic demulsifier since surfactant part has negative and positive charges^{86, 51}.

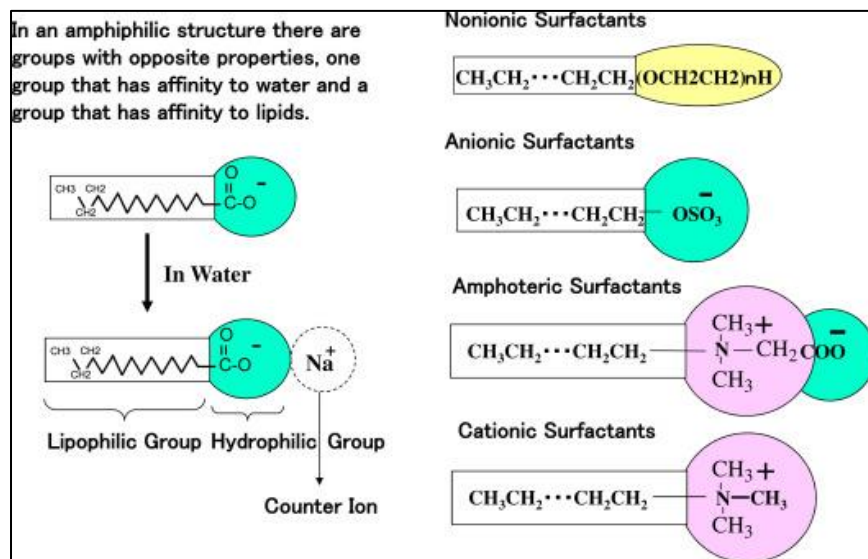


Figure 16: Example and structure of surfactant molecules [85]

Table 3 shows an example of water-soluble groups that are used in demulsifiers with their properties⁷¹. **Table 4** shows a comparison between oil-soluble and water-soluble demulsifiers.

Hydroxyl	C-OH	Poor hydrophilic properties
Ether	C-O-C	Poor hydrophilic properties
Amine oxide	N → O	Excellent hydrophilic properties
Phosphine oxide	P → O	Excellent hydrophilic properties
Sulphoxide	S → O	Excellent hydrophilic properties
Triple unsaturation	C≡C	Very poor hydrophilic properties
Ester group	COO-	Very poor hydrophilic properties
Amide group	CONH-	Very poor hydrophilic properties

Table 3: Examples of water-soluble groups [71]

Types No.	Oil soluble demulsifiers	Water soluble demulsifiers
1.	Moderately 2000-50,000 molecular weight (mw). High mw are the preference.	10,000-15,000 molecular weight. Lower mw are the preference.
2.	Polydispersed interfacially active polymers.	Tetrapolymer or pentapolymer
3.	Mostly non-ionic block polymer with hydrophilic and hydrophobic segments.	The polymer present hydrophilic (-COOH) and hydrophobic (alkyl) groups.
4.	Dangerous and expensive chemicals like ethylene and propylene oxide.	Easy handling chemicals like methyl metachrylate, butyl acrylate, acrylic acid and methacrylic acid.

Table 4: Oil-soluble demulsifier and water-soluble demulsifiers [92]

- Common chemical demulsifiers are shown in **Appendix B**⁵¹ and **Appendix C**⁵². Several companies supply demulsifiers around the world, as shown in **Appendix D**⁵⁹.
- Groups of Chemical Demulsifier:** Table 5 shows a list of different groups of demulsifiers^{60,56}:

Phenol formaldehyde resin alkoxylates	Alkoxylated alkyl polyglycosides
Alkoxylated EO/PO block polymers	Alkoxylated polyethylene amines
Alkoxylated alkyl phenols	Alkoxylated polyethylene glycols
Alkoxylated amines	Alkoxylated diglycidyl ethers

Alkoxylated dicarbamates	Resin sulfonates and maleates
Alkoxylated diisocyanates	Phosphate esters of resins and glycols

Table 5: Examples of different groups of demulsifiers [60]

In addition, **Appendix E** shows general formulas for chemical demulsifiers with their preferred solubility.⁶⁰

CHAPTER 3

PROBLEM STATEMENT AND RESEARCH

OBJECTIVE

3.1 Problem Statement

The presence of crude oil/water emulsions is a burden in the petroleum industry. It leads to several operational and economic issues related to crude production, transportation, and refining processes. The stability of the emulsified oil is affected by water content, presence of organic/inorganic materials, formation brine salinity, temperature, and droplet size. In reservoir fluid studies, it is a common practice to apply chemical demulsifiers on emulsion samples to break the emulsion and reduce the water content to an acceptable level (less than 1 wt. %) to ensure generate representative fluid composition results. However, this process depends heavily on the crude and the water compositions along with the type of

demulsifier used. Incompatible choice of demulsifier could strengthen the stability of the emulsion or alter the composition of reservoir fluid. This work intends to understand certain physiochemical properties to identify the root causes of demulsifier ineffectiveness.

3.2 Objectives

The main objectives of this work are:

- To determine the optimum chemical demulsifier type to break emulsions effectively through achieving a deeper understanding of the underlying physical chemistry of oil, emulsion, brine, and demulsifier used (different functional groups).
- To evaluate the performance of different commercially available demulsifiers in terms of water separation
- To study the relationship between asphaltene, sulfur, density, viscosity, resin, type of demulsifier, and emulsion separation index.

CHAPTER 4

METHODOLOGY

4.1 Materials

4.1.1 Oil Samples

Twelve dead oil samples were used in this work. These samples were collected from different fields. The water content of these samples was measured using the Karl-Fischer titration¹⁷ technique to confirm that they did not have any trapped water.

4.1.2 Water Samples

A formation water sample and a seawater sample were used in this work to prepare various emulsion samples.

4.1.3 Chemical Demulsifiers

Two demulsifiers with different compositions were used in this work. The composition of each is shown in **Table 6** and **Table 7**:

Type 1		
Component	Weight%	Remarks
Methanol	30-60	Carrier solvent
Oxyalkylated Alkyl Alcohol (1)	5-10	non-ionic surfactant
Oxyalkylated Alcohol (1)	1-5	non-ionic surfactant
Oxyalkylated Alcohol (2)	5-10	non-ionic surfactant
Heavy aromatic naphtha	1-5	Solvent
Quaternary ammonium compounds	1-5	Cationic surfactants
Naphthalene (impurity)	0.1-1	Precursor

Table 6: Composition of Type 1 Demulsifier

Type 2		
Component	Weight%	Remarks
Organic sulfonic acid amine salt	50-60	Anionic surfactants
Oxyalkylated alcohols	40-60	non-ionic surfactant
Methanol	5-10	Carrier solvent
Morpholine	1-5	Solvent

Table 7: Composition of Type 2 Demulsifier

4.2 Experimental Work

The experiments in this work include analyzing oil, emulsion, and water phases separately along with understanding the chemistry and the functional groups making up the used demulsifiers.

- **Oil phase analysis** includes determining Saturates Aromatics Resins Asphaltenes (SARA), viscosity, density, and sulfur content.
- **Water phase analysis** comprises of determining pH and Total Dissolved Solids(TDS)
- **Emulsion phase analysis** includes calculating emulsion separation index
- **Demulsifier analysis** includes understanding the chemistry of the used demulsifiers.

4.2.1 SARA Analysis

All dead oil samples were fractionized using MAZE technology SARA common fractions.

4.2.2 Viscosity and Density Measurements

The viscosity and density of all dead oil samples were measured simultaneously using Anton Paar SVM kinematic viscometer⁹³ as shown in **Figure 17**.



Figure 17: Densitometer & Viscometer [93]

4.2.3 Sulfur Content

The sulfur content was determined using vario MACRO cube organic elemental analyzer that has two detectors thermal conductivity detector (for hydrocarbon and nitrogen) and infrared detector (for sulfur)⁹⁴ as shown in **Figure 18**.



Figure 18: Elemental Analyzer [94]

4.2.4 Geochemical Water Analysis

A routine geochemical analysis was conducted on all water samples to determine the concentration of anions and cations, TDS along with the pH.

4.2.5 Emulsification and Demulsification

All emulsion samples were propagated using different water and oil samples as in **Figure 19**. The oil/water ratio is 20/80, which mimics high water cut wells or invert emulsion. Oil and water were blended at 300 rotation per minute (RPM) FOR 1.5 minutes. Following that the two different demulsifiers were added separately at the same concentration, which is 1% of the total volume (1 ml). Lastly, the volumes of separated water at 5, 10, 15, and 20 minutes at 25 C were all recorded to determine ESI values as shown in **Figure 20**.

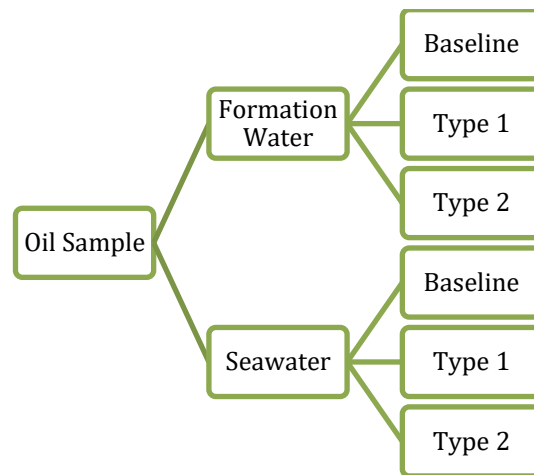


Figure 19: Experimental Emulsification and Demulsification Plan



Figure 20: Emulsification & Demulsification

CHAPTER 5

RESULTS AND DISCUSSION

This section demonstrates, analyzes, and discusses the outcomes of the several emulsification and demulsification scenarios conducted in this work. Oil, water, emulsion, and demulsifier analysis will be presented and discussed separately.

5.1 Oil Analysis

Samples 3, 6, and 8 did not have enough volume to complete the entire experiment. **Table 8** shows a summary of SARA, density, viscosity, and sulfur content, which indicates variations.

Sample Number	Maltenes			Asphaltene (%)	Density	Viscosity	N [%]	C [%]	H [%]	S [%]
	Saturates (%)	Aromatics (%)	Resin (%)							
S1	29.11	34.65	18.71	17.53	0.910	13.00	0.64	82.77	10.12	3.45
S2	68.65	22.17	8.31	0.87	0.806	1.17	0.36	85.77	12.69	0.49
S4	25.08	41.81	16.98	16.13	0.893	29.71	0.51	81.51	9.87	3.14
S5	36.46	39.04	16.36	8.14	0.887	4.14	0.44	80.71	10.71	2.38
S7	52.89	34.75	10.76	1.60	0.871	1.20	0.34	82.09	11.34	1.51
S9	33.63	45.70	14.94	5.73	0.864	6.00	0.33	81.90	10.73	2.27
S10	41.29	40.16	13.58	4.97	0.860	5.39	0.35	82.47	11.13	1.86
S11	50.50	35.19	11.40	2.90	0.835	1.30	0.29	82.65	11.56	1.26
S12	51.11	34.89	11.32	2.67	0.833	1.49	0.39	80.50	11.12	1.32
Max	68.65	45.70	18.71	17.53	0.910	29.71	0.64	85.77	12.69	3.45
Min	25.08	22.17	8.31	0.87	0.806	1.17	0.29	80.50	9.87	0.49

Table 8 Results of Oil Samples

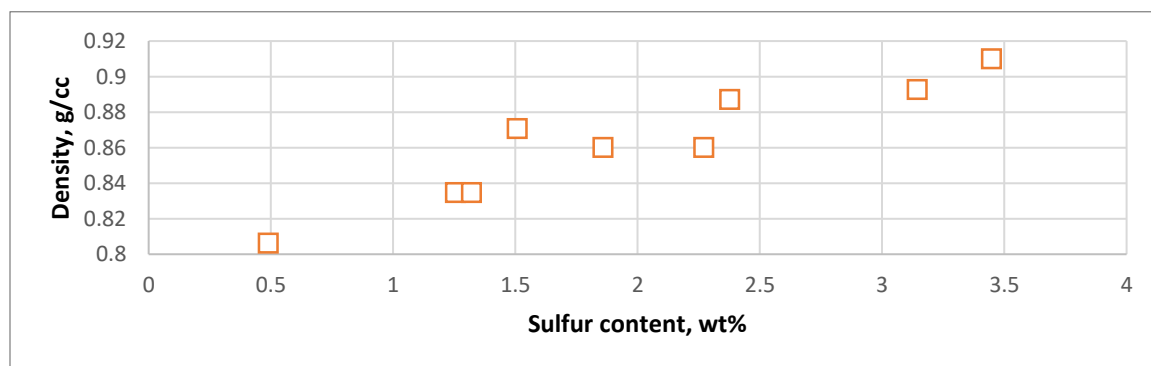


Figure 21: Sulfur Content vs Density

Figure 21 shows that crude oil density increases with an increase in sulfur content, which can be found in both resin and asphaltene at different concentrations. Similarly, crude oil viscosity increases with an increase in sulfur content, which can be found in both resin and asphaltene at different concentrations as shown in **Figure 22**. Also, the data point that is marked in green has the lowest saturates content among all samples which could explain the extreme viscosity value.

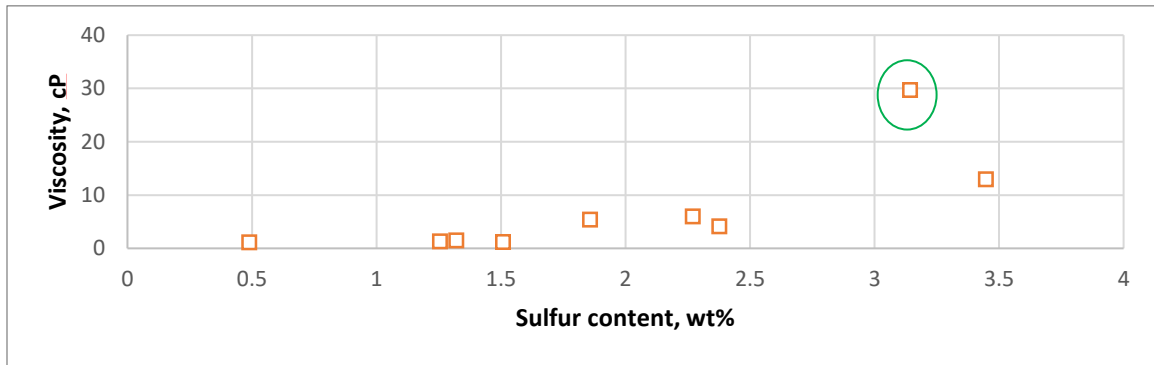


Figure 22: Sulfur Content vs Viscosity

Sulfur can be found in both resin and asphaltene at different concentrations. **Figure 23** indicates that asphaltene and resin contents increase with an increase in sulfur content.

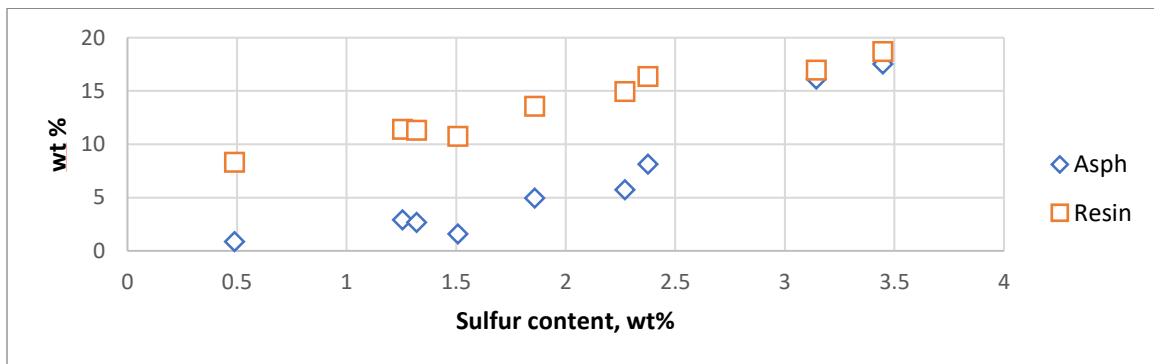


Figure 23: Sulfur Content vs Asphaltene and Resin

Density increases with an increase in asphaltene or resin content due to their high molecular weight and density as can be seen in **Figure 24**. By comparing samples 11 and 12 to sample 7, the data point that is marked (S7) could have an error in density measurement

Sample Number	Saturates (%)	Aromatics (%)	Resin (%)	Asphaltene (%)	Maltenes (%)	Density	Viscosity	N [%]	C [%]	H [%]	S [%]
S7	52.89	34.75	10.76	1.60	98.40	0.871	1.20	0.34	82.09	11.34	1.51
S11	50.50	35.19	11.40	2.90	97.10	0.835	1.30	0.29	82.65	11.56	1.26
S12	51.11	34.89	11.32	2.67	97.33	0.833	1.49	0.39	80.50	11.12	1.32

Table 9: Deviation of Density Measurement in Sample 7

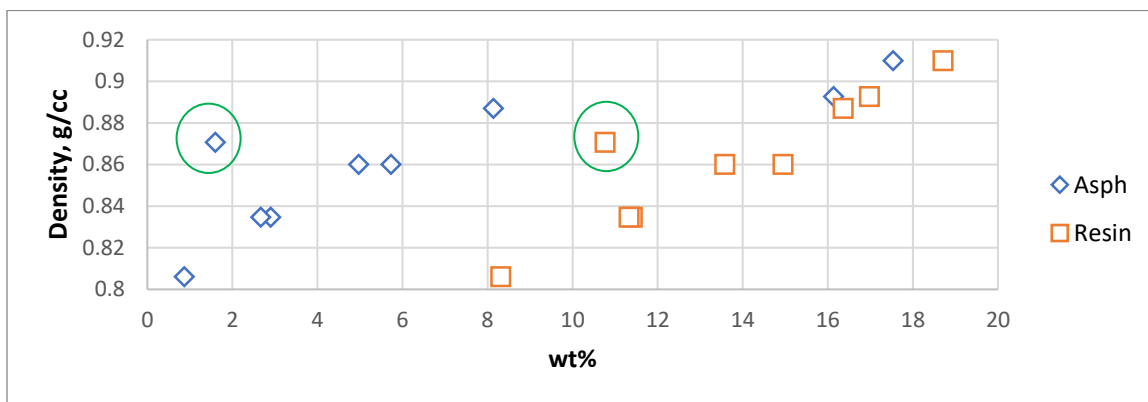


Figure 24: Asphaltene and Resin vs Density

Figure 25 shows that viscosity increases with an increase in asphaltene or resin content due to their high molecular weight and density. The data point that is marked has the lowest saturates content among all samples which could explain the extreme viscosity value.

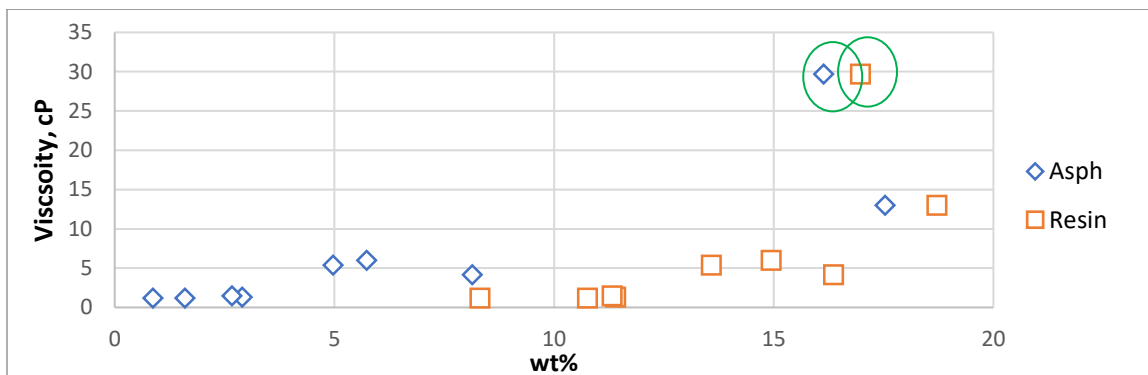


Figure 25: Asphaltene and Resin vs Viscosity

5.2 Water Analysis

Table 10 shows the results of the geochemical analysis conducted on water. The concentration of anions and cations in formation water is higher than that of the seawater. Also, sulfate ions and pH are higher in seawater than in formation water. Overall, formation water has a higher salinity, polarity, water hardness than seawater.

Sample		Seawater	Formation water
Bicarbonate	(mg/L)	204	618
Carbonate	(mg/L)	0	0
Hydroxide	(mg/L)	0	0
Chloride	(mg/L)	30463	121135
Conductivity @ 25 c	S/m	>10000	>10000
pH @25 c		7.4	6.3
Sulfate	(mg/L)	4481	454
Calcium	(mg/L)	573	18920
Potassium	(mg/L)	573	2132
Sodium	(mg/L)	17752	42845
Strontium	(mg/L)	10	683
Total Dissolved Solids	(mg/L)	55455	192160

Table 10: Water Geochemical Analysis

5.3 Emulsion Analysis

Table 11 and **Table 12** show the summary of ESI calculations along with the volume of separated water at 20 minutes intervals.

	Base Line				Type 1				Type 2				Emulsion Separation Index, %		
	Volume of water separated with time, cc				Volume of water separated with time, cc				Volume of water separated with time, cc						
	5 mins	10 mins	15 mins	20 mins	5 mins	10 mins	15 mins	20 mins	5 mins	10 mins	15 mins	20 mins	Base line	Type 1	Type 2
S1+Formation water	70	72	73	73	71	71	71	72	0	0	0	0	72	71	0
S2+Formation water	20	20	20	21	71	72	74	76	63	63	64	65	20	73	64
S4+Formation water	69	70	70	72	75	77	80	80	0	0	0	0	70	78	0
S5+Formation water	40	42	45	45	0	0	0	0	16	17	17	19	43	0	17
S7+Formation water	70	70	71	73	70	71	73	74	76	78	79	80	71	72	78
S9+Formation water	77	78	78	79	65	67	68	69	35	37	37	40	78	67	37
S10+Formation water	0	0	0	0	72	73	73	73	20	23	25	32	0	73	25
S11+Formation water	45	46	48	48	60	61	62	64	0	0	0	0	47	62	0
S12+Formation water	0	0	0	0	70	72	74	75	68	69	71	71	0	73	70

Table 11: ESI for Formation Water

	Base Line				Demulsifier 1				Demulsifier 2				Emulsion Separation Index, %		
	Volume of water separated with time, cc				Volume of water separated with time, cc				Volume of water separated with time, cc						
	5 mins	10 mins	15 mins	20 mins	5 mins	10 mins	15 mins	20 mins	5 mins	10 mins	15 mins	20 mins	Base line	Type 1	Type 2
S1+Seawater	70	70	71	72	73	73	74	74	0	0	0	0	71	74	0
S2+Seawater	40	53	57	65	75	77	78	78	0	0	0	0	54	77	0
S4+Seawater	65	65	68	70	63	65	65	68	25	27	30	30	67	65	28
S5+Seawater	41	43	44	47	70	70	73	75	0	0	0	0	44	72	0
S7+Seawater	45	45	49	50	75	77	79	79	0	0	0	0	47	78	0
S9+Seawater	38	39	43	45	68	70	72	73	0	0	0	0	41	71	0
S10+Seawater	52	52	53	53	75	77	77	79	73	75	78	80	53	77	77
S11+Seawater	69	70	73	75	74	77	78	79	0	0	0	0	72	77	0
S12+Seawater	34	36	39	40	74	75	79	79	0	0	0	0	37	77	0

Table 12: ESI for Seawater

In formation water, Type 1 demulsifier efficiency remains stable despite the increase in asphaltene content or resin content as shown in **Figure 26** and **Figure 27**. On the other hand, Type 2 demulsifier efficiency decreases as asphaltene or resin content increases.

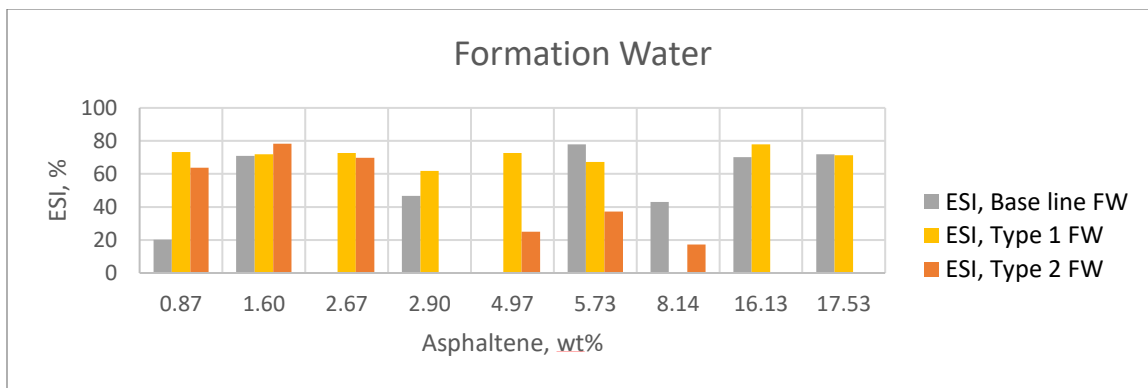


Figure 26: Formation Water Emulsion Separation Index vs Asphaltene

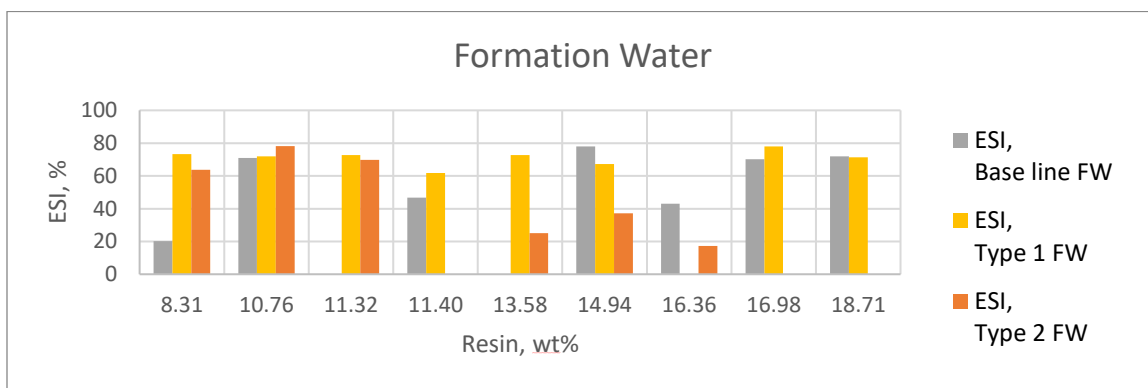


Figure 27: Formation Water Emulsion Separation Index vs Resin

In formation water, Type 1 demulsifier efficiency remains stable despite the increase in density or viscosity as shown in **Figure 28** and **Figure 29**. On the other hand, Type 2 demulsifier efficiency fluctuates as density or viscosity increases.

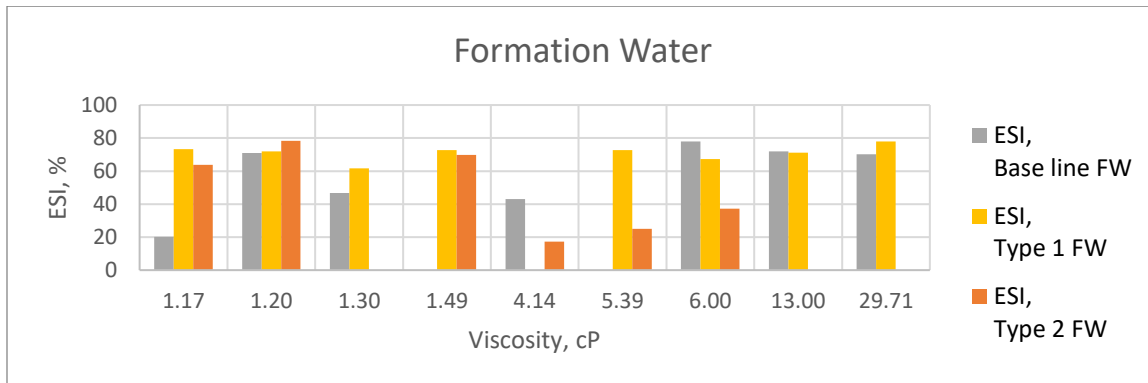


Figure 28: Formation Water Emulsion Separation Index vs Viscosity

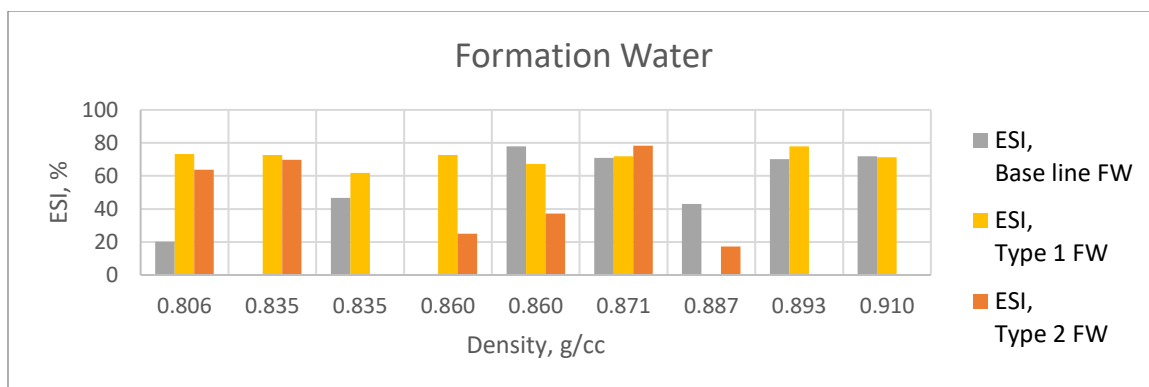


Figure 29: Formation Water Emulsion Separation Index vs Density

In seawater, Type 1 demulsifier efficiency remains stable despite the increase in asphaltene content or resin content as shown in **Figure 30** and **Figure 31**. On the other hand, Type 2 demulsifier efficiency was very low for all samples as asphaltene or resin content increases except Sample 10.

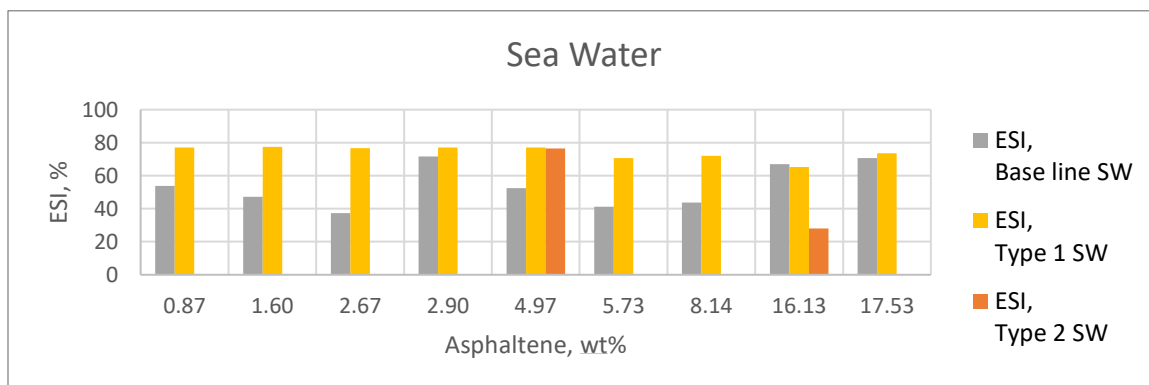


Figure 30: Seawater Emulsion Separation Index vs Asphaltene

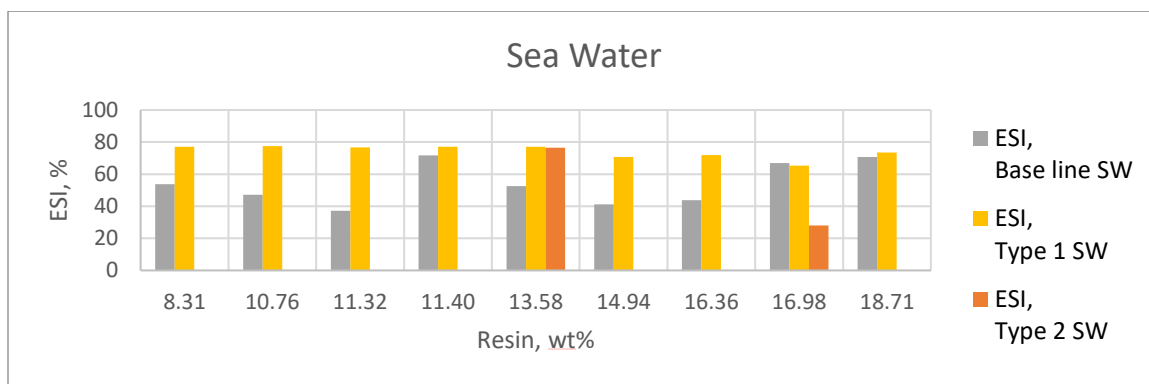


Figure 31: Seawater Emulsion Separation Index vs Resin

In seawater, Type 1 demulsifier efficiency remains stable despite the increase in density or viscosity as shown in **Figure 32** and **Figure 33**. On the other hand, Type 2 demulsifier efficiency is low as crude oil viscosity or density increases except Sample 10.

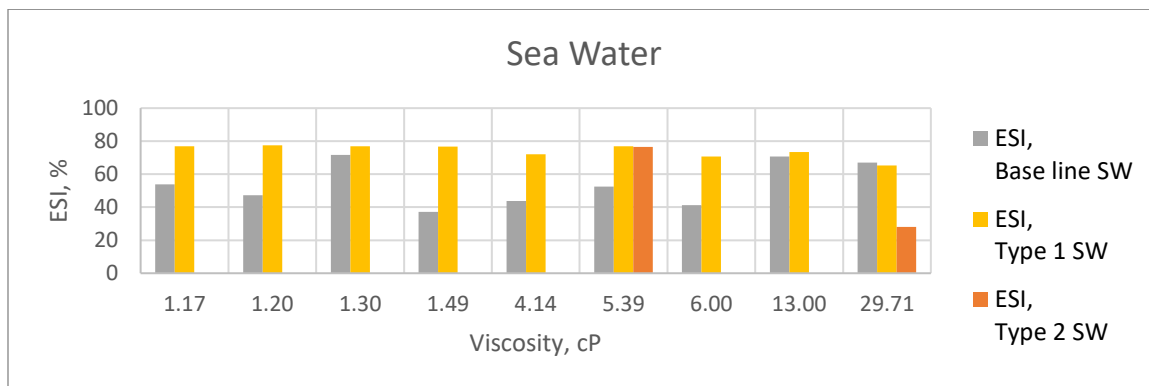


Figure 32: Seawater Emulsion Separation Index vs Density

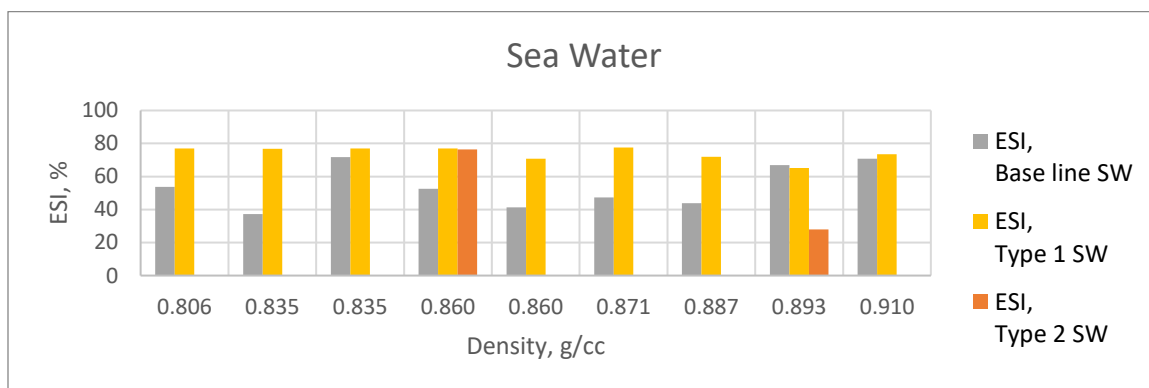


Figure 33: Seawater Emulsion Separation Index vs Viscosity

5.4 Demulsifier Analysis

Table 13 shows a summary for demulsifier types in terms of ionic charge, ability to ionize water, and sensitivity to pH and water hardness.

	Anionic Demulsifier	Cationic Demulsifier	Nonionic Demulsifier	Amphoteric Demulsifier
Charge on surface active part	-	+	No charge	- & +
Water ionization	Yes	Yes	No	Yes
pH	Sensitive	Sensitive	Insensitive	Sensitive
Presence of mineral	Sensitive	Sensitive	Insensitive	Sensitive
Water hardness	Sensitive	Sensitive	Insensitive	Sensitive

Table 13: Demulsifier Types

Table 14 shows the demulsifier analysis for Type 1 and Type 2. It is clear that Type 1 demulsifier is mostly made of non-ionic surfactants with a small percent of cationic surfactant as shown in **Table 6**. On the other hand, Type 2 is mostly made of non-ionic and anionic surfactants as shown in **Table 7**.

	Type 1	Type 2
Solvent used	• Methanol (large %) • Naptha (small %)	• Methanol (small %) • Morpholine (small %)
Surfactant types	Large % • Non-ionic: Oxyalkylated Alkyl Alcohol • Non-ionic: Oxyalkylated Alcohol (2) Small % • Non-ionic: Oxyalkylated Alcohol (1) • Cationic: Quaternary ammonium compounds	Large % • Non-ionic: Oxyalkylated alcohols • Anionic: Organic sulfonic acid amine salt

Table 14: Demulsifier Analysis

5.5 Root Cause of Demulsifier Ineffectiveness

By looking at **Figure 34** and **Figure 35**, it is clear that there are variations in the calculated ESI due to variations in oil composition, water composition, and demulsifier types. Furthermore, the addition of demulsifier reduced ESI in some samples, which is an indication of incompatibility.

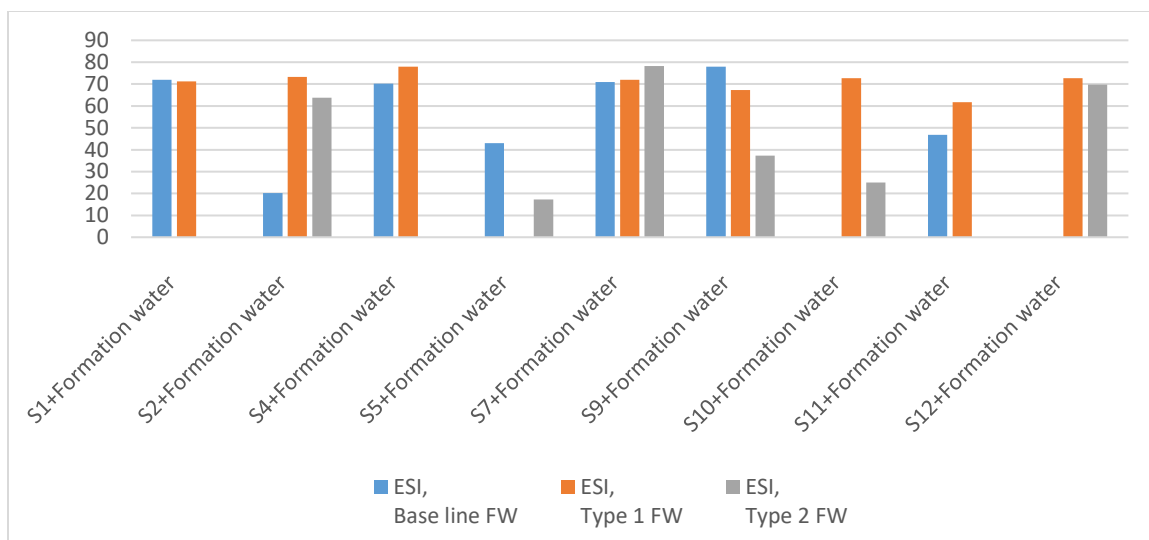


Figure 34: Emulsion Separation Index: Formation Water

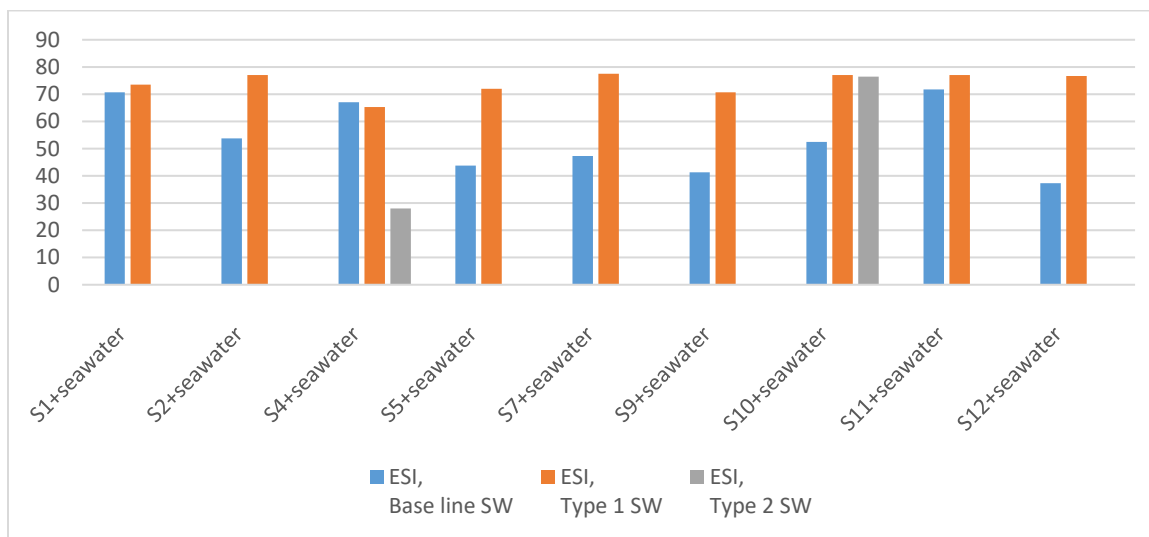


Figure 35: Emulsion Separation Index: Seawater

Type 1 demulsifier showed a better performance in both formation water and seawater based emulsions (mostly made of non-ionic surfactant). On the contrary, Type 2 demulsifiers showed a very poor performance in seawater based emulsions (mostly made of a non-ionic surfactant and anionic surfactants). Type 1 demulsifier showed a better performance than Type 2 in formation water and seawater and while using different oils due to the resistance of non-ionic surfactant to salinity, polarity, and water hardness.

CHAPTER 6

CONCLUSIONS AND RECOMMENDATIONS

This thesis aims to investigate the root causes of demulsifier ineffectiveness. This work tries to incorporate science to help select the optimum demulsifier type and eliminate random selection. Also, it stresses the importance of analyzing all the components involved in the formation and breakage of emulsions. These include oil, water, emulsion, and demulsifier. In this thesis work, two demulsifiers made of different functional groups and surfactants (Type 1 and Type 2) were evaluated for their emulsion breakage ability. Nine oil samples with different fluid properties fields were mixed with formation water in the first round and with seawater in the second one. To mimic high water cut well or invert emulsions, the water-oil ratio of 80:20 was achieved using a blender for 1.5 minutes at 300 RPM. Saturates, Aromatics, Resins, and Asphaltene (SARA), viscosity, density, and sulfur content were determined for all oil samples as shown in **Table 8**. Furthermore, water chemical analysis was conducted on all water samples to determine the concentration of anions and cations as shown in **Table 10**. After applying both demulsifiers at the same concentration (1% of total volume), volumes of water separated were measured at 5, 10, 15, and 20 minutes and used in calculating the emulsion separation index (ESI).

The main conclusions of this study include:

- Oil density and viscosity along with sulfur content all increase as asphaltene or resin content increase as shown in **Figures 21-25**.
- Formation water has a higher salinity, polarity, water hardness than seawater.
- Type 1 demulsifier showed a better performance than Type 2 in formation water and seawater while using different oils due to the resistance of non-ionic surfactant to salinity, polarity, and water hardness as shown in **Figure 34** and **Figure 35**.
- Type 1 demulsifier also showed stability in its performance despite increases in asphaltene, resin, density, and viscosity.
- The possibility of re-emulsification through improper selection of demulsifier as

shown in **Figure 34** and **Figure 35**.

The outcomes of this research may help in developing an automated workflow to select the proper demulsifier based on oil, water, and emulsion analysis. For future work, the below tests are suggested:

- Oil tests: Total Acid Number (TAN), wax content, High-Performance Liquid Chromatography (HPLC), zeta potential, and presence of organic scale with their respective wettability.
- Water tests: the presence of inorganic scale with their respective wettability
- Emulsion: droplet size distribution and emulsion type

References

1. Explore the new oilfield glossary. (n.d.). Retrieved April 16, 2021, from <https://www.glossary.oilfield.slb.com/en/Terms/e/emulsion.aspx>
2. Kokal, S. (2002, September 29). Crude Oil Emulsions: A State-Of-The-Art Review. All Days. SPE Annual Technical Conference and Exhibition. <https://doi.org/10.2118/77497-ms>
3. Dosunmu, A. ., Otikiri, A. E., & Fekete, P. O. (2012, August 6). Evaluation of Emulsion Treatment Using Different De-emulsifiers. All Days. Nigeria Annual International Conference and Exhibition. <https://doi.org/10.2118/162969-ms>
4. Saad, M. A., Kamil, M., Abdurahman, N. H., Yunus, R. M., & Awad, O. I. (2019). An Overview of Recent Advances in State-of-the-Art Techniques in the Demulsification of Crude Oil Emulsions. *Processes*, 7(7), 470. <https://doi.org/10.3390/pr7070470>
5. Poteau, S., Argillier, J.-F., Langevin, D., Pincet, F., & Perez, E. (2005). Influence of pH on Stability and Dynamic Properties of Asphaltenes and Other Amphiphilic Molecules at the Oil–Water Interface†. *Energy & Fuels*, 19(4), 1337–1341. <https://doi.org/10.1021/ef0497560>
6. Kokal, S., & Al-Juraid, J. (1999, October 3). Quantification of Various Factors Affecting Emulsion Stability: Watercut, Temperature, Shear, Asphaltene Content, Demulsifier Dosage and Mixing Different Crudes. All Days. SPE Annual Technical Conference and Exhibition. <https://doi.org/10.2118/56641-ms>

7. Salgado, Hernando & Pecheco, Rosangela & Marino, Luis. (2014). Overcoming tight emulsion problems (separation of an oil-water-caustic emulsion by membrane coalescence). *Petroleum Technology Quarterly*. 19. 31.
8. Gold, V. (Ed.). (2019). *The IUPAC Compendium of Chemical Terminology*. International Union of Pure and Applied Chemistry (IUPAC).
<https://doi.org/10.1351/goldbook>
9. Yahaya Khan, M., Abdul Karim, Z. A., Hagos, F. Y., Aziz, A. R. A., & Tan, I. M. (2014). Current Trends in Water-in-Diesel Emulsion as a Fuel. *The Scientific World Journal*, 2014, 1–15. <https://doi.org/10.1155/2014/527472>
10. Agrawal, A., Kulkarni, S., & Sharma, S. (2016). Recent advancements and applications of multiple emulsions. *International Journal of Advances in Pharmaceutics*, 4(6), 94-103. <https://doi.org/10.7439/ijap.v4i6.2648>
11. Tadros, T. F. (2013). Emulsion Formation, Stability, and Rheology. In *Emulsion Formation and Stability* (pp. 1–75). Wiley-VCH Verlag GmbH & Co. KGaA.
<https://doi.org/10.1002/9783527647941.ch1>
12. Kokal, S. L. (2005). Crude Oil Emulsions: A State-Of-The-Art Review. *SPE Production & Facilities*, 20(01), 5–13. <https://doi.org/10.2118/77497-pa>
13. Jiao, J., & Burgess, D. J. (2003). Rheology and stability of water-in-oil-in-water multiple emulsions containing Span 83 and Tween 80. *AAPS PharmSci*, 5(1), 62–73. <https://doi.org/10.1208/ps050107>
14. Kibbe, A. H. (n.d.). Laboratory 7 - characteristics of surfactants and emulsions. Retrieved April 17, 2021, from <https://web.wilkes.edu/arthur.kibbe/lab7.html>
15. Tambe, D. E., & Sharma, M. M. (1995). Factors Controlling the Stability of

- Colloid-Stabilized Emulsions. *Journal of Colloid and Interface Science*, 171(2), 456–462. <https://doi.org/10.1006/jcis.1995.1202>
16. Schramm, L. L. (Ed.). (1992). Emulsions. In *Advances in Chemistry*. American Chemical Society. <https://doi.org/10.1021/ba-1992-0231>
 17. Kestens, V., Conneely, P., & Bernreuther, A. (2008). Vaporisation coulometric Karl Fischer titration: A perfect tool for water content determination of difficult matrix reference materials. *Food Chemistry*, 106(4), 1454–1459. <https://doi.org/10.1016/j.foodchem.2007.01.079>
 18. ASTM International. (2016) ASTM D4007-11(2016)e1, Standard Test Method for Water and Sediment in Crude Oil by the Centrifuge Method (Laboratory Procedure), ASTM International, West Conshohocken, PA, 2016, [DOI:10.1520/d4007-11r16e01](https://doi.org/10.1520/d4007-11r16e01),
 19. Hill, P. J., & Ng, K. M. (1996). Statistics of multiple particle breakage. *AIChE Journal*, 42(6), 1600–1611. <https://doi.org/10.1002/aic.690420611>
 20. Liao, Y., & Lucas, D. (2009). A literature review of theoretical models for drop and bubble breakup in turbulent dispersions. *Chemical Engineering Science*, 64(15), 3389–3406. <https://doi.org/10.1016/j.ces.2009.04.026>
 21. Sleicher, C. A. (1960). *Rheology: Theory and Applications*. Vol. III. Edited by F. R. E. IRICH. New York and London: Academic Press, 1960. 680 pp. \$12.00. *Journal of Fluid Mechanics*, 9(01), 158. <https://doi.org/10.1017/s0022112060230983>
 22. Manning, F., & Thompson, R. (1995). *Oilfield Processing of Petroleum: Oilfield Processing*, Vol. 2: Crude Oil (Volume 2). PennWell Corp.

23. Kokal, S. L., & Sayegh, S. G. (1995, March 11). Asphaltenes: The Cholesterol Of Petroleum. All Days. Middle East Oil Show. <https://doi.org/10.2118/29787-ms>
24. Speight, J. G., & Long, R. B. (1996). The Concept of Asphaltenes Revisited. Fuel Science and Technology International, 14(1–2), 1–12.
<https://doi.org/10.1080/08843759608947559>
25. Elkahky, S., Lagat, C., Sarmadivaleh, M., & Barifcani, A. (2019). A comparative study of density estimation of asphaltene structures using group contribution methods and molecular dynamic simulations for an Australian oil field. Journal of Petroleum Exploration and Production Technology, 9(4), 2699–2708.
<https://doi.org/10.1007/s13202-019-0641-x>
26. Nascimento, P. T. H., Santos, A. F., Yamamoto, C. I., Tose, L. V., Barros, E. V., Gonçalves, G. R., Freitas, J. C. C., Vaz, B. G., Romão, W., & Scheer, A. P. (2016). Fractionation of Asphaltene by Adsorption onto Silica and Chemical Characterization by Atmospheric Pressure Photoionization Fourier Transform Ion Cyclotron Resonance Mass Spectrometry, Fourier Transform Infrared Spectroscopy Coupled to Attenuated Total Reflectance, and Proton Nuclear Magnetic Resonance. Energy & Fuels, 30(7), 5439–5448.
<https://doi.org/10.1021/acs.energyfuels.6b00523>
27. Mitchell, D. L., & Speight, J. G. (1973). The solubility of asphaltenes in hydrocarbon solvents. Fuel, 52(2), 149–152. [https://doi.org/10.1016/0016-2361\(73\)90040-9](https://doi.org/10.1016/0016-2361(73)90040-9)
28. Leontaritis, K. J. (1989). Asphaltene Deposition: A Comprehensive Description of Problem Manifestations and Modeling Approaches. SPE Production

Operations Symposium. SPE Production Operations Symposium.

<https://doi.org/10.2118/18892-ms>

29. Strassner, J. E. (1968). Effect of pH on Interfacial Films and Stability of Crude Oil-Water Emulsions. *Journal of Petroleum Technology*, 20(03), 303–312.

<https://doi.org/10.2118/1939-pa>

30. El-Sayed, M. (2012). Factors Affecting the Stability of Crude Oil Emulsions. In *Crude Oil Emulsions- Composition Stability and Characterization*. InTech.

<https://doi.org/10.5772/35018>

31. Menon, V. B., & Wasan, D. T. (1987). Particle—fluid interactions with applications to solid-stabilized emulsions Part III. Asphaltene adsorption in the presence of quinaldine and 1,2-dimethylindole. *Colloids and Surfaces*, 23(4),

353–362. [https://doi.org/10.1016/0166-6622\(87\)80276-7](https://doi.org/10.1016/0166-6622(87)80276-7)

32. Kokal, S., & Al-Juraid, J. (1998, September 27). Reducing Emulsion Problems By Controlling Asphaltene Solubility and Precipitation. All Days. SPE Annual

Technical Conference and Exhibition. <https://doi.org/10.2118/48995-ms>

33. Jones, T. J., Neustadter, E. L., & Whittingham, K. P. (1978). Water-In-Crude Oil Emulsion Stability And Emulsion Destabilization By Chemical Demulsifiers.

Journal of Canadian Petroleum Technology, 17(02). <https://doi.org/10.2118/78-02-08>

34. Kimbler, O. K., Reed, R. L., & Silberberg, I. H. (1966). Physical Characteristics of Natural Films Formed at Crude Oil-Water Interfaces. *Society of Petroleum*

Engineers Journal, 6(02), 153–165. <https://doi.org/10.2118/1201-pa>

35. Kokal, S., & Wingrove, M. (2000, October 1). Emulsion Separation Index: From

- Laboratory to Field Case Studies. All Days. SPE Annual Technical Conference and Exhibition. <https://doi.org/10.2118/63165-ms>
36. ASTM International. (2016) ASTM G205-16, Standard Guide for Determining Emulsion Properties, Wetting Behavior, and Corrosion-Inhibitory Properties of Crude Oils, ASTM International, West Conshohocken, PA, 2016, <https://doi.org/10.1520/g0205-16>
 37. ASTM International. (2015) ASTM F3045-15e1, Standard Test Method for Evaluation of the Type and Viscoelastic Stability of Water-in-oil Mixtures Formed from Crude Oil and Petroleum Products Mixed with Water, ASTM International, West Conshohocken, PA, 2015, <https://doi.org/10.1520/f3045-15e01>
 38. Al-Ghamdi, A., & Kokal, S. (2003, June 9). Investigation of Causes of Tight Emulsions in Gas Oil Separation Plants. All Days. Middle East Oil Show. <https://doi.org/10.2118/81508-ms>
 39. Ellison, B. T., Gallagher, C. T., Frostman, L. M., & Lorimer, S. E. (2000, May 1). The Physical Chemistry of Wax, Hydrates, and Asphaltene. All Days. Offshore Technology Conference. <https://doi.org/10.4043/11963-ms>
 40. Wiehe, Irwin & Kennedy, Raymond. (1999). The Oil Compatibility Model and Crude Oil Incompatibility. Energy & Fuels - ENERG FUEL. 14. <https://doi.org/10.1021/ef990133+>
 41. Smith, H. V., & Arnold, K. E. (1987, January 1). Crude Oil Emulsions (1987 PEH Chapter 19). Society of Petroleum Engineers.
 42. Petsev, D. N. (2004). Theory of emulsion flocculation. In Interface Science and

- Technology (pp. 313–350). Elsevier. [https://doi.org/10.1016/s1573-4285\(04\)80010-3](https://doi.org/10.1016/s1573-4285(04)80010-3)
43. Bobra, M. (1990). A Study of the Formation of Water-in-Oil Emulsions,” Proc., 1990 Arctic and Marine Oil Spill Program Technical Seminar
 44. Spasic, A. M. (2018). Rheology of emulsions: Electrohydrodynamics principles. London: Academic Press an imprint of Elsevier.
 45. Gbadamosi, A. O., Junin, R., Manan, M. A., Agi, A., & Yusuff, A. S. (2019). An overview of chemical enhanced oil recovery: recent advances and prospects. International Nano Letters, 9(3), 171–202. <https://doi.org/10.1007/s40089-019-0272-8>
 46. Rogel, E. (2000). Simulation of Interactions in Asphaltene Aggregates. Energy & Fuels, 14(3), 566–574. <https://doi.org/10.1021/ef990166p>
 47. Banki, R., Hoteit, H., & Firoozabadi, A. (2008). Mathematical formulation and numerical modeling of wax deposition in pipelines from enthalpy–porosity approach and irreversible thermodynamics. International Journal of Heat and Mass Transfer, 51(13–14), 3387–3398. <https://doi.org/10.1016/j.ijheatmasstransfer.2007.11.012>
 48. Doshi, B., Sillanpää, M., & Kalliola, S. (2018). A review of bio-based materials for oil spill treatment. Water Research, 135, 262–277. <https://doi.org/10.1016/j.watres.2018.02.034>
 49. Piacentini, E. (2016). Emulsion. In Encyclopedia of Membranes (pp. 679–682). Springer Berlin Heidelberg. https://doi.org/10.1007/978-3-662-44324-8_1066
 50. Griffin, W.C. (1949) Classification of Surface-Active Agents by “HLB”. Journal

- of Cosmetic Science, 1, 311-326.
51. Fink, J.K. (2003) Oil Fields Chemicals. Gulf Professional Publishing, New York.
 52. Abed, S. M., Abdurahman, N. H., Yunus, R. M., Abdulbari, H. A., & Akbari, S. (2019). Oil emulsions and the different recent demulsification techniques in the petroleum industry - A review. IOP Conference Series: Materials Science and Engineering, 702, 012060. <https://doi.org/10.1088/1757-899x/702/1/012060>
 53. Ben Mya, O., Houga, S., Chihouba, F., & Asla, B. (2018). Treatment of Algerian crude oil using REB09305 OS demulsifier. Egyptian Journal of Petroleum, 27(4), 769–773. <https://doi.org/10.1016/j.ejpe.2017.11.004>
 54. Yau, Y., Rudolph, V., Ho, K., Lo, C. C., & Wu, K. (2017). Evaluation of different demulsifiers for Marpol oil waste recovery. Journal of Water Process Engineering, 17, 40–49. <https://doi.org/10.1016/j.jwpe.2017.02.013>
 55. Liu, J., Wang, H., Li, X., Jia, W., Zhao, Y., & Ren, S. (2017). Recyclable magnetic graphene oxide for rapid and efficient demulsification of crude oil-in-water emulsion. Fuel, 189, 79–87. <https://doi.org/10.1016/j.fuel.2016.10.066>
 56. Hippmann, S., Ahmed, S. S., Fröhlich, P., & Bertau, M. (2018). Demulsification of water/crude oil emulsion using natural rock Alginite. Colloids and Surfaces A: Physicochemical and Engineering Aspects, 553, 71–79. <https://doi.org/10.1016/j.colsurfa.2018.05.031>
 57. Almohsin, A. M., Alabdulmohsen, Z., Bai, B., & Neogi, P. (2018). Experimental Study of Crude Oil Emulsion Stability by Surfactant and Nanoparticles. SPE EOR Conference at Oil and Gas West Asia <https://doi.org/10.2118/190440-MS>
 58. Hazrati, N., Miran Beigi, A. A., & Abdouss, M. (2018). Demulsification of water

- in crude oil emulsion using long chain imidazolium ionic liquids and optimization of parameters. *Fuel*, 229, 126–134. <https://doi.org/10.1016/j.fuel.2018.05.010>
59. Udumbasseric, C. (2015, July 17). Demulsifiers-Specialty oilfield chemicals. Retrieved April 17, 2021, from <https://www.scribd.com/document/464772411/Demulsifiers-Specialty-oilfield-chemicals>
60. Udumbasseric, C. (2015, July 19). Demulsifier -Bottle testing and information collection. Retrieved April 17, 2021, from <https://www.slideshare.net/ChandranUdumbasseri1/demulsifier-bottle-testing-and-information-collection-m>
61. Abdurahman H., N. & M. Nuraini. (2010). Chemical Destabilization On Water In Crude Oil Emulsions. Zenodo. <https://doi.org/10.5281/ZENODO.1328522>
62. Oil analysis services - LUBRICANT Monitoring | CPI Fluid engineering. (2020, June 29). Retrieved April 17, 2021, from <https://www.cpifluideng.com/oil-analysis-services/>
63. Speight, J. G. (1999). The chemistry and technology of petroleum. New York: Marcel Dekker.
64. SLB, (2016). Maze Microfluidic SARA Analysis. Retrieved April 17, 2021, from <https://www.slb.com/-/media/files/testing-services/product-sheet/microfluidic-sara-analysis-ps.ashx>
65. Fondriest (2019, January 23). Conductivity, salinity & total dissolved solids. Retrieved April 17, 2021, from <https://www.fondriest.com/environmental-measurements/parameters/water-quality/conductivity-salinity-tds/>

66. Wu, J., Xu, Y., Dabros, T., & Hamza, H. (2005). Effect of EO and PO positions in nonionic surfactants on surfactant properties and demulsification performance. *Colloids and Surfaces A: Physicochemical and Engineering Aspects*, 252(1), 79–85. <https://doi.org/10.1016/j.colsurfa.2004.09.034>
67. Urdahl, O., Brekke, T., & Sjöblom, J. (1992). ¹³C n.m.r. and multivariate statistical analysis of adsorbed surface-active crude oil fractions and the corresponding crude oils. *Fuel*, 71(7), 739–746. [https://doi.org/10.1016/0016-2361\(92\)90122-5](https://doi.org/10.1016/0016-2361(92)90122-5)
68. Spiecker, P. M., Gawrys, K. L., Trail, C. B., & Kilpatrick, P. K. (2003). Effects of petroleum resins on asphaltene aggregation and water-in-oil emulsion formation. *Colloids and Surfaces A: Physicochemical and Engineering Aspects*, 220(1–3), 9–27. [https://doi.org/10.1016/s0927-7757\(03\)00079-7](https://doi.org/10.1016/s0927-7757(03)00079-7)
69. Kim, Y.-H., Nikolov, A. D., Wasan, D. T., Diaz-Arauzo, H., & Shelly, C. S. (1996). DEMULSIFICATION OF WATER-IN-CRUDE OIL EMULSIONS: EFFECTS OF FILM TENSION, ELASTICITY, DIFFUSIVITY AND INTERFACIAL ACTIVITY OF DEMULSIFIER INDIVIDUAL COMPONENTS AND THEIR BLENDS. *Journal of Dispersion Science and Technology*, 17(1), 33–53. <https://doi.org/10.1080/01932699608943487>
70. Fang, C. S., Lai, D. M. C., Chang, B. K. L., & Klaila, W. J. (1989). Oil recovery and waste reduction by microwave radiation. *Environmental Progress*, 8(4), 235–238. <https://doi.org/10.1002/ep.3300080416>
71. Al-Sabagh, A. M., Kandile, N. G., & Noor El-Din, M. R. (2011). Functions of Demulsifiers in the Petroleum Industry. *Separation Science and Technology*,

- 46(7), 1144–1163. <https://doi.org/10.1080/01496395.2010.550595>
72. Porter, M. R. (1991). Use of surfactant theory. In *Handbook of Surfactants* (pp. 24–48). Springer US. https://doi.org/10.1007/978-1-4757-1293-3_4
73. Al-Sabagh, A.M.; Zaki, N.N. (1997) De-emulsifiers for water-in-crude oil-emulsions. *Tenside Surfactants and Detergents*, 34 (1): 554–1559.
74. De Gennes, P. G., & Taupin, C. (1982). Microemulsions and the flexibility of oil/water interfaces. *The Journal of Physical Chemistry*, 86(13), 2294–2304. <https://doi.org/10.1021/j100210a011>
75. H. Nour, A., Mohd. Yunu, R., & Anwaruddin, H. (2007). Water-in-Crude Oil Emulsions: Its Stabilization and Demulsification. *Journal of Applied Sciences*, 7(22), 3512–3517. <https://doi.org/10.3923/jas.2007.3512.3517>
76. Kim, Y. H., Wasan, D. T., & Breen, P. J. (1995). A study of dynamic interfacial mechanisms for demulsification of water-in-oil emulsions. *Colloids and Surfaces A: Physicochemical and Engineering Aspects*, 95(2–3), 235–247. [https://doi.org/10.1016/0927-7757\(94\)03032-u](https://doi.org/10.1016/0927-7757(94)03032-u)
77. Wanli, K., Yi, L., Baoyan, Q., Guangzhi, L., Zhenyu, Y., & Jichun, H. (2000). Interactions between alkali/surfactant/polymer and their effects on emulsion stability. *Colloids and Surfaces A: Physicochemical and Engineering Aspects*, 175(1–2), 243–247. [https://doi.org/10.1016/S0927-7757\(00\)00461-1](https://doi.org/10.1016/S0927-7757(00)00461-1)
78. Mukherjee, S., & Kushnick, A. P. (1989). Effect of Demulsifiers on Interfacial Properties Governing Crude Oil Demulsification. In *ACS Symposium Series* (pp. 364–374). American Chemical Society. <https://doi.org/10.1021/bk-1989-0396.ch019>

79. Kim, B.-Y., Moon, J. H., Sung, T.-H., Yang, S.-M., & Kim, J.-D. (2002). Demulsification of water-in-crude oil emulsions by a continuous electrostatic dehydrator. *Separation Science and Technology*, 37(6), 1307–1320.
<https://doi.org/10.1081/ss-120002613>
80. Papirer, E., Bourgeois, C., Siffert, B., & Balard, H. (1982). Chemical nature and water/oil emulsifying properties of asphaltenes. *Fuel*, 61(8), 732–734.
[https://doi.org/10.1016/0016-2361\(82\)90248-4](https://doi.org/10.1016/0016-2361(82)90248-4)
81. Lichaa, P. M., & Herrera, L. (1975, January 13). Electrical and Other Effects Related to the Formation and Prevention of Asphaltene Deposition Problem in Venezuelan Crudes. All Days. SPE Oilfield Chemistry Symposium.
<https://doi.org/10.2118/5304-ms>
82. Krawczyk, M. A., Wasan, D. T., & Shetty, C. (1991). Chemical demulsification of petroleum emulsions using oil-soluble demulsifiers. *Industrial & Engineering Chemistry Research*, 30(2), 367–375. <https://doi.org/10.1021/ie00050a014>
83. Umar, A. A., Saaid, I. B. M., Sulaimon, A. A., & Pilus, R. B. M. (2018). A review of petroleum emulsions and recent progress on water-in-crude oil emulsions stabilized by natural surfactants and solids. *Journal of Petroleum Science and Engineering*, 165, 673–690. <https://doi.org/10.1016/j.petrol.2018.03.014>
84. Migahed, M. A., & Al-Sabagh, A. M. (2009). BENEFICIAL ROLE OF SURFACTANTS AS CORROSION INHIBITORS IN PETROLEUM INDUSTRY: A REVIEW ARTICLE. *Chemical Engineering Communications*, 196(9), 1054–1075. <https://doi.org/10.1080/00986440902897095>
85. Nakama, Y. (2017). Surfactants. In *Cosmetic Science and Technology* (pp. 231–

- 244). Elsevier. <https://doi.org/10.1016/b978-0-12-802005-0.00015-x>
86. Raya, S. A., Mohd Saaid, I., Abbas Ahmed, A., & Abubakar Umar, A. (2020). A critical review of development and demulsification mechanisms of crude oil emulsion in the petroleum industry. *Journal of Petroleum Exploration and Production Technology*, 10(4), 1711–1728. <https://doi.org/10.1007/s13202-020-00830-7>
87. Salager, J.-L., & Forgiarini, A. M. (2012). Emulsion Stabilization, Breaking, and Inversion Depends upon Formulation: Advantage or Inconvenience in Flow Assurance. *Energy & Fuels*, 26(7), 4027–4033. <https://doi.org/10.1021/ef3001604>
88. Matijasevic, B., & Banhart, J. (2006). Improvement of aluminium foam technology by tailoring of blowing agent. *Scripta Materialia*, 54(4), 503–508. <https://doi.org/10.1016/j.scriptamat.2005.10.045>
89. Xiangling, K. & Ohadi, M. Applications of Micro and Nano Technologies in the Oil and Gas Industry-An Overview of the Recent Progress. Abu Dhabi International Petroleum Exhibition and Conference, <https://doi.org/10.2118/138241-MS>
90. Zolfaghari, R., Fakhru'l-Razi, A., Abdullah, L. C., Elnashaie, S. S. E. H., & Pendashteh, A. (2016). Demulsification techniques of water-in-oil and oil-in-water emulsions in petroleum industry. *Separation and Purification Technology*, 170, 377–407. <https://doi.org/10.1016/j.seppur.2016.06.026>
91. Grenoble, Z., & Trabelsi, S. (2018). Mechanisms, performance optimization and new developments in demulsification processes for oil and gas applications. *Advances in Colloid and Interface Science*, 260, 32–45.

<https://doi.org/10.1016/j.cis.2018.08.003>

92. Mat, Hanapi & Samsuri, Ariffin & Rahman, Wan & Othman, Norasikin & Chieng, Yu & Jong, Siaw & Zulkania, Ariany. (2021). Study on demulsifier formulation for treating Malaysian crude oil emulsion.
93. Anton Paar. (n.d.). Kinematic viscometer: Svm. Retrieved April 17, 2021, from <https://www.anton-paar.com/corp-en/products/details/svm-series/>
94. Elementar. (n.d.). MACRO ANALYZER. Retrieved April 17, 2021, from <https://www.elementar.com/en/products/organic-elemental-analyzers/vario-macro-cube>

APPENDICES

Appendix A: Bottle Test³⁵

The bottle test is a screening test for commercial demulsifiers made of the below steps.

- Remix emulsion samples using a bottle shaker for 2 minutes
- Transfer the emulsion sample to 100 ml standard centrifuge tubes.
- Heat the tubes by placing them in a water bath for a minimum of half an hour
- Add a dose of demulsifier to the tubes
- Shake the tubes a couple of times then place them back again in the water bath
- Measure and record the amount of separated water with respect of the different period of time
- Lastly, calculate The Emulsion Separation Index (ESI) is from the recorded data to characterize the tightness of produced oil-field emulsions and evaluate the effectiveness of different demulsifiers by looking at how much water got separated, precipitation of sediment/sludge, and effluent water quality. ESI equation is shown below:

$$ESI = \frac{\sum \text{Water separation at a given demulsifier conc. and / or time (\%)}}{\sum \text{number of experiments}}$$

Appendix B: Common Chemical Demulsifiers ⁵¹

Demulsifier	Type	Demulsifier	Type of demulsifier
Blends containing (1) tannin or amino methylated tannin, (2) a cationic polymer, (3) polyfunctional amines	WiO		
Copolymer of diallyldimethyl ammonium chloride and quaternized amino alkylmethacrylates and (meth)acrylic esters (e.g., 2-ethylhexylacrylate)	OiW	Tannin-based blends	W/O
Amphoteric acrylic acid copolymer	OiW	Ethoxylated or epoxidized PAG	W/O
Branched polyoxyalkylene copolyesters	OiW	Oxalkylated poly(alkylene) poly(amine)s	W/O
Copolymer of esters of acrylic acid and the respective acids, methacrylic acid ^a	WiO	Polythioalkyloxides	W/O
Copolymer of polyglycol acrylate or methacrylate esters	OiW	Poly(ether) poly(urethane)	W/O
Poly(1-acryloyl-4-methyl piperazine and copolymers of 1-acryloyl-4-methyl piperazine quaternary salts with acrylamide quaternary salts)	OiW	Diallyl dimethyl ammonium chloride polymer	O/W
Copolymers of acrylamidopropyltrimethyl ammonium chloride with acrylamide	OiW	Amphoteric acrylic acid (AA) copolymer	O/W
Vinyl phenol polymers ^b	OiW	Copolymer of polyglycol acrylate	O/W
Ethoxylated or epoxidized polyalkylene glycol	WiO	Poly(1-acryloyl-4-methyl piperazine	O/W
Polymers from dimethylaminoethyl methacrylate, dimethylaminopropyl methacrylamide	OiW	Vinyl phenol polymers	O/W
Polymer of monoallylamine	OiW	Poly(dimethyl diallyl ammonium chloride)	O/W
Copolymers of allyl-polyoxyalkylenes with acrylics		Cross-linked oxalkylated poly(alkylene) poly(amine)s	O/W
Copolymer of diallyldimethyl ammonium chloride and vinyl trimethoxysilane	WiO	Dithiocarbamates	O/W
Cationic amide-ester compositions	OiW	Sulfonated poly(styrene)s	O/W
Polyalkylenepolyamides-amines	OiW, WiC	Acid-modified polyol	LS
Fatty acid N,N-dialkylamides ^c	OiW		
Diamides from fatty amines ^d	WiO		
Polycondensates of oxalkylated fatty amine ^d	OiW		
Poly(diallyldimethyl ammonium chloride)	OiW		
Alkoxylated fatty oil			
Oxalkylated polyalkylene polyamines	WiO		
Crosslinked oxalkylated polyalkylene polyamines	OiW		
Phenol-formaldehyde resins, modified with benzylamine ^e			
Alkoxylated alkylphenol-formaldehyde resins	WiO		
Phenol-formaldehyde polymer modified with ethylene carbonate	WiO		
Modified phenol-formaldehyde resins			
Polyalkylene polyamine salts	OiW		
Dithiocarbamate of bis-hexamethylenetriamine	OiW		
Di- and tri-dithiocarbamic acid compounds			
Polythioalkyloxides	WiO		
Polyether/polyurethanes	WiO		
Polyurea-modified polyetherurethanes	WiO		
Sulfonated polystyrenes	OiW		

LS liquid-solid separation, O/W oil-in-water use, W/O water-in-oil use

Appendix C: Summary of the recent studies on chemical demulsifiers⁵²

Type of emulsion	Type of demulsification	Emulsifier/ demulsifier concentration	Ratio & effect of demulsifier on separation	Year of study	Ref.
W/O	REB09305 OS demulsifier	5-40 ppm	100% demulsification ratio achieved at the process condition of demulsifier dose 20 ppm, ambient temperature, centrifugation speed 1200 rpm, and contact time of 45 min	2017	53
W/O	Anionic, cationic and nonionic.		Anionic and nonionic surfactants performed best after 30 h at 70oC.	2017	54
O/W	Magnetic graphene oxide	0.04-0.25 wt%,	99.98% demulsification efficiency achieved at an optimal dosage.	2017	55
W/O	Alginate	0.5 wt. %	The water removal capacity was >98%.	2018	56
WACO	Polyether	50-150 mg/L	laboratory test showed 91.7% demulsification efficiency within 90 min and 97.9% within 45 min on an offshore platform.	2018	57
W/O	Ionic liquids	500-3500 ppm	86–95% water separation efficiency achieved within 24 h.	2018	58

Appendix D: Common Chemical Demulsifiers Suppliers ⁵⁹

AKZO-NOBEL	Baker Petrolite	BASF
Brentag	Buckman	CECA
Cochran	Clariant	Croda
Dorf Ketal	Dow	Eonchemicals Putra
Hydrates chemical Co	Instral BV	Halliburton
Schlumberger	Nalco Champion	NCPI
REDAOilfield	Scharer & Schlaofer AG	UNIVAR
PCC EXOL		

Appendix E: List of Demulsifiers with their solubility ⁶¹

Group	Demulsifier	Solubility
Amine	Pentylamine	Oil soluble
	Hexylamine	Oil soluble
	Octylamine	Oil soluble
	Dioctylamine	Oil soluble
Alcohol	Methanol	Water soluble
	Ethanol	Water soluble
	Propanol	Water soluble
	Butanol	Water soluble
Polyhydric Alcohol	PEG 300	Water soluble
	PEG 400	Water soluble

Vitae

- Name: Ali Ridha Altowilib
- Nationality: Saudi
- Date of Birth: 11/09/1991
- Academic Background: BS in Petroleum Engineering from Louisiana State University in 2014
- Work Experience: Reservoir Engineer at Saudi Aramco in EXPEC ARC (2014-Present)
- Work address: Building 2291 R&DC, Dhahran 31311, Saudi Arabia
- Home Address: Building 8435 Aljarodiah, Qatif 32652, Saudi Arabia
- Email: ali.altowilib@gmail.com
- Publications:
 - Reservoir Fluid Sample Decontamination: Application Example
 - <https://doi.org/10.2118/196394-MS>
 - SARA-Based Lumping Scheme: An Application
 - <https://doi.org/10.2118/198015-MS>
 - Reserves Estimation for Coalbed Methane Reservoirs: A Review
 - <https://doi.org/10.3390/su122410621>