

**INFLUENCE OF BIVALENT CATIONS ON INTERFACIAL
ACTIVE COMPONENTS OF CRUDE OIL EMULSIONS**

BY

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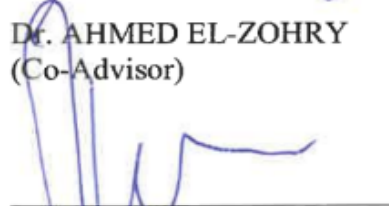
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To the greatest man in my life (*my father*) may Allah grant him Jannat AL Ferdous.

To my biggest supporter and my first teacher (*my mother*).

To my brothers and sisters who made this journey easier for me.

To all my family...

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LIST OF ABBREVIATIONS

W/O	:	Water in Oil Emulsion
O/W	:	Oil in Water Emulsion
DI	:	Deionized Water
CaCl₂	:	Calcium Chloride
ZnCl₂	:	Zinc Chloride
KOH	:	Potassium Hydroxide
PSD	:	Particle Size Distribution
PIP	:	Phase Inversion Point
IFT	:	Interfacial Tension
DE	:	Dehydration Efficiency
TAN	:	Total Acid Number

ABSTRACT

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A main step in oil production and transportation is the formation of water/oil emulsions. Since emulsion formation poses a costly operational challenge in oil production, there is a persistent need for the development of novel and effective demulsification methods. However, the absence of a fundamental understanding of the chemistry controlling the formation of this crude oil emulsion and the different factors governing its stability especially the water composition, makes this process very challenging. In this study, a systematic investigation of the influence of bivalent cations that are present in the seawater environment in the Gulf area on crude oil emulsion was conducted. Our focus was on two specific bivalent cations, calcium (Ca^{2+}), and zinc (Zn^{2+}), since they display varied chemical properties due to the difference in their electronic configurations. The primary objective of this study was to examine how bivalent cations present in the seawater environment of the Gulf area impact the interfacial active substances responsible for stabilizing the water-oil interface. Furthermore, the emulsion stability and rheological properties were evaluated using a variety of techniques, including optical microscopy, droplet size analysis and interfacial force densitometry, upon forming emulsions in the absence and the presence of these selective cations. The results were explained in terms of the chemical interactions between the bivalent cations such as Ca^{2+} and surface-active components. While other mechanisms are proposed for the case of using Zn^{2+} cations.

Finally, our experimental results demonstrated the promising potential of zinc chloride (ZnCl_2) as an additive to enhance the separation efficiency of crude oil and water phases in stiff emulsion.

الخلاصة

الاسم الكامل: غدير غنام الحربي

عنوان الرسالة: تأثير الكاتيونات ثنائية التكافؤ على المكونات النشطة البيئية لمستحلبات النفط الخام

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من المشاكل الرئيسية أثناء إنتاج ونقل النفط الخام، تشكلُ مُستحلبات الماء في الزيت غير المرغوب فيها. وبما أن تكوين المستحلب أثناء إنتاج النفط يُمثل مشكلة تشغيلية مكلفة للغاية، فإن هناك طلبًا مستمرًا لتطوير تقنيات تفكيك الاستحلاب الجديدة والفعالة. ومع ذلك، فإن الافتقار إلى الفهم الأساسي للكيمياء وراء تكوين هذا المستحلب والعوامل المختلفة التي تتحكم في استقراره، يزيد من تعقيد فهم عملية التفكك. تم في هذه الدراسة إجراء بحث منهجي لتأثير الكاتيونات ثنائية التكافؤ الموجودة في بيئة مياه البحر في منطقة الخليج على مُستحلب النفط الخام. إنصَب التركيز على اثنين من الكاتيونات ثنائية التكافؤ، هما الكالسيوم والزنك، وذلك بسبب اختلاف خصائصهما وتوزيعاتهما الإلكترونية. وكان الهدف الأساسي من هذه الدراسة هو دراسة كيفية تأثير الكاتيونات ثنائية التكافؤ الموجودة في بيئة مياه البحر في منطقة الخليج على المواد الفعالة السطحية المسؤولة عن استقرار الحاجز بين الماء والزيوت. بالإضافة إلى ذلك، تم تقييم استقرار المستحلب والخصائص الريولوجية باستخدام مجموعة مُتنوعة من التقنيات، بما في ذلك الفحص المجهرى الضوئي وتحليل حجم القطرة. بالإضافة إلى ذلك، تم أيضًا قياس تأثير الأملاح ثنائية التكافؤ على التوتر السطحي بين الزيت والماء. وتم شرح النتائج من حيث التفاعلات الكيميائية بين الكاتيونات ثنائية التكافؤ والمركبات النشطة سطحيا. وأخيرا، أظهرت نتائجنا التجريبية الإمكانات الواعدة لكوريد الزنك ($ZnCl_2$) كمادة مضافة لتعزيز كفاءة فصل مستحلب الزيت والماء في المستحلبات المستقرة.

CHAPTER 1

INTRODUCTION

Emulsions are mixture of two immiscible fluids, such as water and oil, in which one fluid is dispersed in the form of tiny droplets throughout the other fluid [1]. Emulsions can be classified into oil-in-water (O/W), water-in-oil(W/O) and multiple emulsions [2]. The emulsions formation process is known as emulsification, involving the application of sufficient agitation to interface, leading to the breakdown of large water droplets into smaller ones [3]. Emulsions are considered to be thermodynamically unstable owing to the high interfacial tension between the oil phases and the water phase. Because of that, emulsion formation is normally associated with surface-active components or stabilizers such as a surfactant or solid particles (Pickering emulsion) [4]. Emulsions are important due to their unique physicochemical properties, versatility, and widespread applications such as pharmaceutical [5], drug delivery [6], cosmetics [7], [8], food [9]–[12], agriculture [13], [14], energy [15], [16], and petroleum [17]. In these industries, emulsions are desirable for obtaining specific properties. However, in the oil industry, despite some useful applications of emulsions such as displacement fluid during enhanced oil recovery (EOR) process [18], heavy crude oil transportation [19], and alternative fuel [20], [21], emulsions formed during oil production is an expensive problem [17], because of the need for emulsion separation before transporting crude oil [22], as well as the potential for corrosion in the transportation system. The separation process can require the use of emulsion breakers, heat, and mechanical energy, and this can significantly increase both complexity and operational cost [2]. The intensive mixing of the formation water in the

reservoir and the natural emulsifiers in crude oil will cause eventually the formation of emulsions [2]. The emulsion stability remarkably varies from a couple of minutes up to several years [23]. Due to the considerable expenses associated with emulsion formation during oil production, there is a continuous need for the development of innovative and effective demulsification methods. The separation of emulsions is essential prior to crude oil transportation, aiming to meet the quality standards for water ratio, typically set at less than 1% [17], [22]. Over time, various techniques have been developed to separate crude oil emulsions, including [24], [25], mechanical [26], [27], biological [28], [29], electrical [30], [31], and thermal (conventional and microwave) [32]–[34] processes, in addition to ultrasonic [35]–[37] and membranes [38], [39]. Chemical approaches, are the most commonly used and reported in the literature [40]. Many demulsifier types have been developed and assessed for their effectiveness in demulsification, such as ionic [25], nonionic [41], and polymeric demulsifiers [42]. However, in order to select the best demulsification method for each type of emulsion, it is very crucial to have some understanding of the chemistry behind it and the internal mechanism of the active components occurring at the water and oil interface, and the different parameters affecting it. The presence of specific ion effects in colloidal systems has been known for a long period [43]. Seawater in the Gulf area typically contains a variety of cations, including divalent cations (such as Ca^{2+} , Mg^{2+} and Zn^{2+}) the concentrations of these cations are listed in **Table. 1** [45][44]. Nevertheless, a full understanding of how different cations impact emulsion formation remains unreached. The influence of salinity on emulsification has been subject of study for decades. Despite the wide investigation of the effect of salinity on emulsification, a comprehensive comprehension is still incomplete. Salt composition (specifically in terms of cationic composition) lacks understanding. In this work, a

systematic investigation of the influence of bivalent cations that are present in the seawater environment at the Gulf area on crude oil emulsion has been conducted. The focus is on the effect of these bivalent cations on the interfacial active substances stabilizing the water/oil interface. These findings will provide insight into the mechanisms that govern the stability of crude oil emulsions and can result in a better understanding of factors that are effective in controlling emulsion formation and stability during oil production.

Table 1 Seawater composition of divalent cations in the Gulf area.

(mg/L)		
Ca^{2+}	Mg^{2+}	Zn^{2+}
423-650	1512-2355	0.17-8.28

CHAPTER 2

Literature Survey

2.1 Mechanism of Emulsification

Researchers have extensively studied and reviewed the process of emulsion formation, reaching a general consensus on its mechanisms. Their findings consistently indicate that emulsion formation is predominantly influenced by the composition of the oil, particularly the presence of asphaltenes and resins [46]–[48]. According to Schubert and Armbruster [49] three key factors are crucial for the formation of crude oil emulsions. First, the interaction of immiscible liquids that don't naturally mix, typically oil and water. Second, the existence of surface-active substances, which serve as emulsifying agents, like asphaltenes and resins. The third requirement underscores the need for an adequate level of mixing energy to disperse one liquid phase into the other. This facilitates the formation of tiny liquid droplets suspended within a continuous liquid phase. Asphaltenes and resins, which are natural components of crude oil, act as emulsifying agents. They play a crucial role in preventing water droplets from coalescing in emulsion formation. These natural emulsifying agents attach themselves to the surface of water droplets, creating a barrier that resists rupture and coalescence [50]. Canevari, Fingas, and Ortiz have consistently found that the presence of asphaltenes and resins in crude oil is the primary factor contributing to the emulsion formation and stabilization [50]–[52]. Asphaltenes are particularly responsible for stabilizing water in oil (W/O) emulsions, while resins solvate

the asphaltenes. Additionally, asphaltenes tend to form a strong film at the interface of emulsions, further preventing coalescence [2].

Asphaltene is a natural surfactant in crude oil, which is an amphiphilic macromolecule, with polar hydrophilic groups mainly include $-\text{OH}$, $-\text{NH}_2$ and $-\text{COOH}$. And non-polar lipophilic groups mainly complex aromatic rings, cycloalkanes. The occurrence of natural emulsifiers in crude oil which simultaneously has hydrophilic and hydrophobic groups will lead to their accumulation at the oil-water interface. The hydrophilic heads of the surfactants are oriented toward the water phase, while the hydrophobic tails face away from the water and into the oil phase. This arrangement allows the surfactant molecules to effectively reduce the interfacial tension between the two phases and can stabilize the emulsion [53]. This reduction of the interfacial tension enables easier interaction of the fluids. Moreover, emulsifiers offer steric stabilization, wherein these molecules create a protective barrier around the water droplets. This protective layer inhibits the close proximity of the droplets, avoiding their coalescence and ensuring the stability of the water/oil emulsion [54].

Numerous factors influence the formation and properties of the emulsion. The factors influencing emulsions can be classified into two main groups: internal and external factors. External factors typically include water ratio, pH, shear rate, salinity, and temperature [55], while internal factors involve the occurrence of natural surfactants in crude oil, for example, asphaltene and resin, [56]. Additionally, acids in crude oil have a significant impact on the crude oil's interfacial properties. These acidic compounds, are collectively referred to as petroleum acids. Petroleum acids are primarily made of carboxylic acids, such as naphthenic acids. It's worth noting that the polar components in different crude oils have different structure and composition [46]. In broad terms, it is commonly believed

that small surface components in crude oil serve to reduce the interfacial tension, while larger components control the stability of the interfacial film [54]. Nevertheless, achieving a complete understanding of the internal mechanisms remains a formidable challenge, primarily due to the complexity of the crude oil system. Furthermore, the exact workings of these mechanisms are not yet fully understood.

2.2 Classification of Crude Oil Emulsion

Based on the type of dispersed phase and continuous phase, emulsions can be classified into three types, water in oil (W/O), oil in water (O/W) and multiple emulsions (W/O/W) [57], see **Fig 1**.

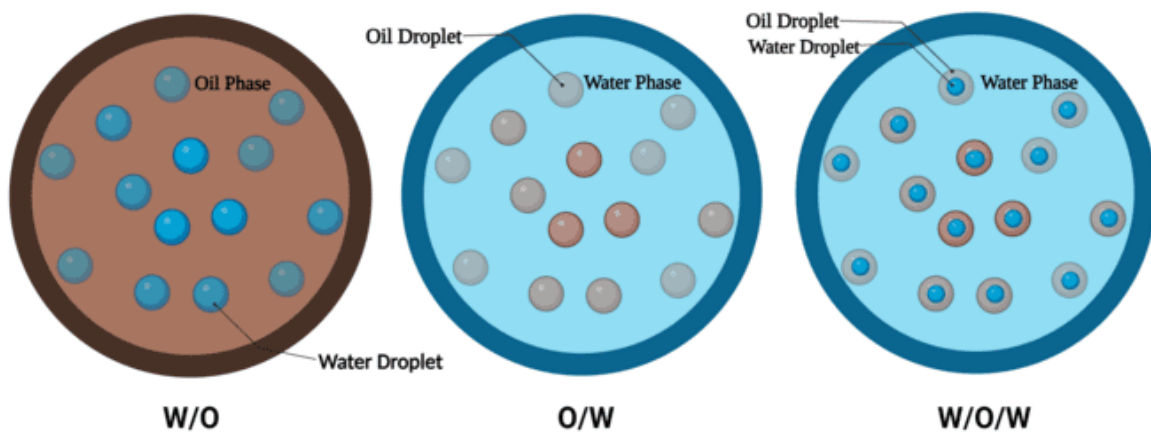


Figure 1. Various types of emulsion classifications.

1. Water in oil emulsion (W/O): In this type of emulsion, droplets of water are dispersed within the continuous oil phase. This is the most common type of crude oil emulsion.

2. Oil in water emulsion (O/W): it's also named "Inverted emulsion" since the continuous phase is the opposite of what is typically expected. In this type of emulsion, oil droplets are dispersed within the continuous water phase.

3. Multiple emulsion (W/O/W): This type of emulsion consists of water in oil and oil in water emulsions occurring simultaneously. It can have multiple layers of emulsion within the system.

2.3 Emulsion Stability

Various aspects can affect the emulsion stability such as: the volume of the internal phase, the distribution of drop sizes, and the chemical composition of both the oil and water. These factors have a significant impact on emulsion properties and stability, there is a strong motivation to investigate these factors [58].

2.3.1 Effect of Water Ratio

Water ratio in a water/crude oil emulsion can have a significant impact on emulsion stability, property, and behavior, in addition to the effectiveness of demulsification processes. According to the Einstein viscosity formula Eq. (1).

$$\eta_r = \eta_0 \left(\frac{1}{1 - (h\varphi)^{1/3}} \right) \quad (1)$$

where η_r and η_0 are the reduced viscosity and intrinsic viscosity of the emulsion respectively (mPa.s); φ is the volume fraction of internal phase (%); h is the volume fraction of the emulsion. The emulsion viscosity is closely related to the internal phase volume. As the internal phase ratio increases the viscosity increases as well. There are several attempts to study how the water ratio is affecting the emulsion properties and stability. For example, in 2018 a study was conducted to investigate the impact of water on emulsion viscosity. They observed a direct correlation between emulsion viscosity and water ratio [59]. Firstly, in the range of 10% to 60% water ratio, the viscosity increased with an increase of water content, until the maximum emulsion viscosity was observed at

a water ratio of 60%. On the other hand, they observed that the viscosity decreased drastically in the range of 70% to 90% water ratio. Evidently, there is a critical point in water-oil emulsions where saturation occurs when the water cut reaches 60%. After this saturation point, the emulsion viscosity decreases considerably. They define this point as the phase transition point, where the emulsion changes from water in oil emulsion to oil in water emulsion. To summarize their findings, it is clear that prior to reaching the phase transition point which in their case is 60% water ratio, the emulsion exhibits an increase in viscosity as the water cut increases. However, once the phase transition point is surpassed, the viscosity of the emulsion begins to decrease as the water cut exceeds this critical value. Moreover, in 2003 a study was conducted to investigate the impact of water ratio on seven different crude oils at different water ratio from 10% to 90% [60]. The trend in viscosity of all their samples were similar to the pervious mentioned study; as the water content increases from 10% to 60% the viscosity increases. The difference in viscosity between the seven crude oils were not significant for water cuts lower than 60% to 70%; there is small variation in viscosity for a certain water cut. However, the saturation limit for each crude oil was different. For instance, the lowest saturation point was at 60% water cut while the highest was at 90% water cut. Similar to the previous reported one, the trend of viscosity after the maximum point was reversed as the water content increases the viscosity decreases. There is usually seen to be a very robust increase in viscosity for high water cuts, up to nearly 95% in extreme cases [60]. The author gave possible reasons for the significant variations between different crude oil samples at higher water ratios; (1) the partial separation of the water and oil phases, (2) the inversion of emulsion from water in oil to oil in water, (3) dispersions being in an ambivalent state between oil- and water-continuous, and finally (d) the impact of variations in droplet size distribution is expected

to be more pronounced at higher water cuts. According to the literature, it is well-established that a phase inversion will take place when water content increases, from water in oil to oil in water. This phase inversion point is referred to as the phase inverse point (PIP) [61]. Krieger and Dougherty [62] developed an empirical model where they assumed that maximum packing of droplets occurs at the inversion point of the emulsion and proposed the following correlation for emulsion viscosity ratio Eq. (2).

$$\eta_r = \left(1 - \frac{\varphi_{int}}{\varphi_{pack}}\right)^{-2.5\varphi_{pack}} \quad (2)$$

where η_r is the viscosity of the emulsion, φ_{pack} is the volume fraction of the dispersed phase at close packing, and φ_{int} is the water cut. This equation could be used to determine at which water cut the inversion point takes place.

2.3.2 Effect of Water Droplet Size

The size of the dispersed droplets in an emulsion is a critical factor that affects the stability of the emulsion and its ability to be separated into its water and oil phases [63]. According to Stoke's law, the particle size of the dispersed phase has a direct impact on the stability of the emulsion system Eq. (3).

$$v_{stokes} = -2gr^2 \frac{(\rho_2 - \rho_1)}{9\eta_1} \quad (3)$$

In the equation, v_{Stokes} represents the creaming velocity, r is the droplet radius, g is the acceleration due to gravity, ρ_1 and ρ_2 are the density of two phases, and η_1 is the shear viscosity. Based on Stoke's law, as the droplet size decreases, the stability of the emulsion increases. The importance of droplet size role in emulsion stability can be seen when comparing between microemulsions [64], and conventual emulsions (macroemulsions). Microemulsions are thermodynamically stable with spontaneous formation. Their unique

characteristics, including tiny droplet size, and uniformity, has a profound effect on their stability [65]. The small droplets minimize the potential for coalescence, ensuring that the system remains thermodynamically stable over time. In contrast, macroemulsions, characterized by larger droplets, are kinetically stable but more prone to phase separation and coalescence. The difference in droplet size is a key factor in determining the long-term stability of these colloidal systems, making microemulsions ideal for applications that demand precise control and sustained stability of dispersed phases. Therefore, to have a more stable emulsion that resists creaming, it is important for the droplets to be small and evenly distributed with minimal variation, which is known as particle size distribution (PSD). Creaming arises when the droplets combine and rise to the top of an emulsion sample [63]. Furthermore, emulsification procedures have a vital role in controlling the droplets' size and their distribution. For example, the amount and type of emulsification energy applied in addition to the duration of emulsification can impact the droplet size of the internal phase, and further the stability of the emulsion. The study conducted by Ghannam [66] investigated the effect of mixing speed on emulsion stability, investigated a range of mixing speeds from 500 to 2000 rpm for a period of 30 minutes. Increasing the rpm results in improved stability of the emulsion. Their results clearly indicate that higher mixing speeds lead to a significant decrease in droplet diameter, ultimately improving the overall stability of the emulsion. On the other hand, some researchers claim the opposite. According to [67], the study found that increasing the mixing speed from 700 to 1000 rpm resulted in an increase in droplet size of microemulsion from 9.79 to 24.4 nm. This increase in the size of droplets may be attributed to the re-coalescence of microemulsion droplets. Previous studies have also reported that increasing the speed from 200 to 800 rpm led to a decrease in droplet size [68]. Similarly, when investigating the effect of mixing time,

similar results were observed. Increasing the mixing duration from 2 to 3 hours, the size of the droplets increased from 20.7 to 64.5 nm. This increase in droplet size could be attributed to re-coalescence, leading to an overall increase in droplet size.

2.3.3 Effect of Oil Composition

Crude oil is a complex mixture which is primarily made up of hydrocarbons, with up to 90% being hydrocarbons. The SARA Analysis is a way to categorize crude oil based on its composition. It considers the percentage of saturated compounds, aromatic compounds, resins, and asphaltenes present in the oil. The composition of crude oil, including the occurrence of natural emulsifiers like asphaltenes, naphthenic acids, and resins, as well as the number of aromatic components, has a large impact on the formation and the stability of the emulsion [58]. The primary role of surface-active materials is two-fold. Firstly, they reduce the interfacial tension between water and crude oil, leading to water in oil emulsion formation. Secondly, these materials play a crucial role in maintaining the stability of water droplets within the oil phase, thereby preventing the coalescence of water droplets. This buildup of surface-active material happens at the interface between water droplets and crude oil, successfully stabilizing the emulsion [69]. It is believed by many researchers that the main surface-active materials that stabilize the emulsion are of asphaltenes, resins, and solids [70]. Asphaltenes are complicated polyaromatic hydrocarbons that are made up of aromatic rings, aliphatic chains, and several heteroatoms. Resin molecules, on the other hand, have lower molar mass, lower heteroatom content and higher hydrogen/carbon ratio. Both asphaltenes and resins exhibit predominantly hydrophobic structures with some hydrophilic groups. Asphaltene and resin are generally categorized based on their solubility in a specific organic solvent [71]. Consequently, they possess the capability to accumulate

at the interface of water/oil. However, the behavior of asphaltenes and resins within crude oil remains partly understood. In crude oil, asphaltenes are recognized for their propensity to self-associate, forming colloids or micelles. In contrast, resins are known to strongly inhibit asphaltene association, and owing to resins small size and less complexity, it can dissolve the asphaltene [46]. Various earlier studies stated that resins by itself could not serve as an emulsion stabilizer, whereas the occurrence of resins could affect the ability of asphaltenes to stabilize the emulsion significantly [72]. Naturally, the polar bonding and π - π stacking interactions between asphaltenes are interrupted by interaction with resins, leads to decreased aggregate of asphaltenes and enhance its solubility [73]. Furthermore, acidic components present in emulsions (such as carboxylic acids, naphthenic and aromatic acids) have the capacity to anchor themselves to the interface through robust ionization, thereby enhancing emulsion stability [74]. These interface-active acids also engage with asphaltenes through mechanisms like hydrogen bonding or π - π stacking [75]. When organic acids such as sodium naphthenates reach a specific concentration threshold (known as the critical concentration), they can compete with asphaltenes at the oil/water interface, resulting in a decrease in the stability of the emulsions. Below this threshold, the interfacial film is exclusively comprised of asphaltenes and exhibits significant rigidity. Additionally, various other components within emulsions, such as silica, clay, and metal compounds, have been observed to participate in emulsion stability by interacting with the asphaltenes polar groups [76]. Wax and solid particles are examples of solid impurities present in crude oil. They have the capacity to adsorb onto the interface, thereby contributing to the emulsion's stability [77]. The process of stabilization of oil and water droplets by solid particles (particle-stabilized emulsions) are largely known as Pickering emulsions [78]. Furthermore, steric stabilization provided by this type of solid impurities can obstruct the

coalescence of the droplets, consequently enhancing the emulsion stability [79]. Hence, variations in crude oil compositions can lead to significant differences in emulsion behavior and stability.

2.3.4 Effect of Water Composition

Emulsion stability relies on several factors, for instance, the characteristics of the aqueous phase, thermodynamic characteristics, and salinity [80]. Ions presence in the brine has a significant contribute to the emulsion stability. Natural surface-active molecules such as asphaltene move toward the water/oil interface. Ions enhance the migration of asphaltenes to the interface of water and oil. Salts stabilize asphaltene molecules via various methods. First, by decreasing the IFT of water/oil, second, improving the adsorption of asphaltenes at the interface, third, decreases the size of droplets and, fourth, inhibits the attraction between droplets [80]. The viscosity of the emulsions will increase as a result of increasing salts concentration; it will lessen the quantity of separated water as well. The increase in the salinity of the brine will result in the improvement of the emulsions stability since ions will serve as barriers among the droplets. Similar observation has been reported that an increase in emulsion viscosity was associated with higher salinity of the aqueous phase. This phenomenon was correlated to the reduced interfacial tension between the oil and aqueous phases at higher aqueous salinity levels. It is understandable that at lower interfacial tensions smaller droplets of dispersed phase would form which would represent higher stability [80]. The salt effect on the stability and properties of emulsion has been investigated [81], [82]. The polar groups in asphaltene molecules lead them to be ionized and frequently neutral or negatively charged. (Ca, Mg, and other cations) present in water phase exert a significant impact on asphaltene molecules. For instance, these cations have

the ability to interact with asphaltene molecules, forming chelates that facilitate asphaltene adsorption at interface of water and oil [81]. Accordingly, an increase in salinity leads to an enhancement in the stability of emulsions [82]. Owing to the higher charge number of bivalent cations compared to monovalent cations, they can improve the asphaltene distribution at the interface further [83]. Moreover, magnesium ions contribute to the stability of an emulsion more than calcium ions because of the stronger charge density of magnesium ions compared to calcium. The interaction of these cations with the polar surface-active components, for instance naphthenic acids or asphaltenes, can maintain their distribution at the interface, which lead to enhance the rigidity of the interfacial film [84]. In addition, elevating temperature improved the strength and properties of this film. Addition of salts to the aqueous phase would lead to the migration of ions from the aqueous to the oil phase. Cations such as (Ca^{2+} and Na^+) will interact with the polar groups (O, N, S negatively charged in asphaltene molecules) present in crude oil. This interaction between polar sites and cations will lead to the neutralization of these sites and prevent asphaltenes aggregation. This interaction will help the asphaltenes to remain at the interface instead of the oil phase [80]. Increasing salt concentration initially improves the migration of asphaltene molecules from the bulk to the interface and the stability of the emulsion. This will increase the activity coefficient, causing ions to transfer from water to oil. Cations like Na^+ and Ca^{2+} neutralize polar sites of the polar compounds (O, S, N with anionic charge) [85], preventing asphaltene aggregation compared to when they are only in contact with water [86]. Asphaltenes bond with pure water forming larger aggregates, but increased salt concentration improves asphaltene stability, however, there comes a point at which an optimal salt concentration is reached. Beyond this threshold, water molecules become incapable of simultaneously accommodating the salts and asphaltenes. Salts can break the

hydrogen bonds between the polar components and water phase and further destabilize these polar molecules at the interface. Consequently, this leads to the occurrence of salting-out phenomena, where the polar groups migrate back to the bulk [80].

CHAPTER 3

PRESENT STATUS OF THE PROBLEM & OBJECTIVES

The presence of specific ion effects in colloidal systems has been known for a long period [43]. Nevertheless, a full understanding of how different cations impact emulsion formation remains unreached. The influence of salinity on emulsification has been the subject of study for decades. Despite the wide investigation of the effect of salinity on emulsification, a comprehensive comprehension is still incomplete. Salt composition (specifically in terms of cationic composition) lacks understanding. According to the available literature, there are contradictory opinions regarding the effect of salinity on the aqueous phase and the oil phase interfacial characteristics. This study aims to address this research gap by systematically investigating the influence of bivalent cations, specifically calcium and zinc that are present in sea water environment in the Gulf area, on the interfacial active components of crude oil emulsions. The focus is to investigate how each bivalent cation interacts with the interfacial active components stabilizing the water/oil interface in terms of viscosity, droplet size, and interfacial tension (IFT) of the synthetic crude oil emulsions.

The results will be explained in terms of the chemical interactions between the bivalent cations and the surface-active components. These findings will provide insight of how the particular characteristics and behaviors of each bivalent cation affect the formation and stability of crude oil emulsions.

CHAPTER 4

THE WORK PLAN

4.1. Methodology

Preparation of emulsion depends on various factors, thus, to be able to make reproducible emulsions various steps should be tested and verified. For instance, the effect of preparation conditions on the properties of lab-made emulsions, and the influence of time and speed of mixing on the droplet size and demulsification rate of crude oil emulsion will be investigated and constrained. All emulsions will be prepared using deionized (DI) water as the aqueous phase and Saudi crude oil as the oil phase. Three samples will be prepared using an overhead stirrer with a fixed speed of 1000 rpm at different times i.e., 10, 20, and 40 mins, respectively. On the other hand, the effect of mixing speed using the homogenizer will be evaluated using three samples, where the emulsion samples will be prepared at 1000, 3000, and 5000 rpm, respectively, for 40 mins. Images of the emulsions will be captured with an optical microscope to evaluate droplet properties. The freely available software ImageJ will be employed to determine the distribution of droplet sizes from the microscopic images. Three images for each sample will be used for the droplet size analysis to ensure the accuracy of the results. As a final step in this part, the influence of droplet size on the dehydration rate will be evaluated using the bottle test demulsification method. Then, lab-made emulsions at different water-to-oil ratios from 10% to 90% water content will be prepared using DI water as the aqueous phase and Saudi crude oil as the oil phase, via the optimized procedures. The viscosity of the prepared emulsions will be examined using a Rheometer after 24 h of the preparation. Samples will be shaking before transforming 20 ml of the sample to the analysis cell at the range of 0.1 to 1000 shear rate

at room temperature. A minimum of three samples for each water cut will be prepared on different days to ensure reproducibility. Furthermore, the impact of water content on the droplet size of the dispersed phase will be evaluated using the optical microscope. After that, the effect of each bivalent cations such as Ca^{2+} on the crude oil emulsions of different water to oil ratio from 10% to 90% at different concentrations 500, 10000, 30,000 ppm will be investigated via analyzing the impact of bivalent cations on the emulsion viscosity and the dispersed droplet size using Rheometer and the dynamic light scattering respectively. The droplet size analysis will be conducted at least three times for each sample and the average size will be used. Same procedures will be followed for the emulsion preparation, and the viscosity analysis. Additionally, the effect of bivalent cations on the interfacial tension (IFT) of water and oil phase will be investigated using the pendant drop method to explain the interaction of bivalent cations and the active components of the crude oil at the interface. Moreover, to study how the bivalent cations effects are controlled by the acids present in crude oil, and to further propose mechanism of bivalent cations interaction with the surface-active components, the bivalent cations effect will be investigated in the absence of acidic components in crude oil. Therefore, acidic active components will be extracted from crude oil using the procedures of liquid-liquid extraction developed by Colati et al [87]. This will involve the performance of five successive extractions of 125 ml portions of crude oil with a mixture of ethanol/water in a ratio of 7:3 totaling 250 ml. The extraction of acidic components will be performed at a pH 14; sodium hydroxide will be used to adjust the pH. Emulsions formation will result from the mixing of the two liquids in a separatory funnel. The aqueous phases will be collected after the emulsion dispersed. Afterward, the combined phases will undergo four washes with 100-200 ml of petroleum ether. Subsequently, will be evaporated using rotary evaporator. Concentrated HCl solution

will be used to adjust the pH before the next step. Four extractions with diethyl ether using 20 ml each time on the aqueous solution will be performed, and then drying using sodium sulfate before filtration. Characterization of the acidic extract using FTIR will be conducted. Furthermore, the role of bivalent cations in emulsion dehydration will be tested using the bottle test demulsification method. Finally, all formed emulsions will be classified as W/O or O/W based on the droplet test method results. The repeatability and reproducibility of emulsions analysis will be assessed.

Materials

Two Saudi Arabian crude oils from the Uthmania (Uth) reservoir will be used. SARA analysis (crude oils are separated into saturate, aromatic, resin and asphaltene fractions) of the crude oils are presented in **Tables 2** and **3**. Deionized water (DI) obtained from the Milli-Q system will be used in emulsion preparation. Calcium chloride (CaCl_2) and Zinc chloride (ZnCl_2) were purchased from Sigma Aldrich.

Techniques:

Iatroscan (TLC-FID) for the SARA analysis. IKA overhead stirrer (EUROSTAR 20 digital). Optical microscope (Olympus BX51, Olympus Stream Essential software). Imaging processing through the open-source software ImageJ. Attension Theta Optical Tensiometer instrument from Biolin Scientific for Interfacial tension Analysis (IFT). Viscosity measurements using Discovery Hybrid Rheometer (TA Instruments, DHR 3). Droplet size measurements were performed by Zetasizer Nano ZS90 (Malvern Instruments Ltd.). Fourier transforms infrared spectroscopy FTIR will be recorded using Bruker INVENIO Series IR spectrometer. UV–vis spectroscopy will be recorded using Ocean Optics HDX-XR UV–vis spectroscopy. ICP-OES

Table 2 SARA analysis of crude oil A.

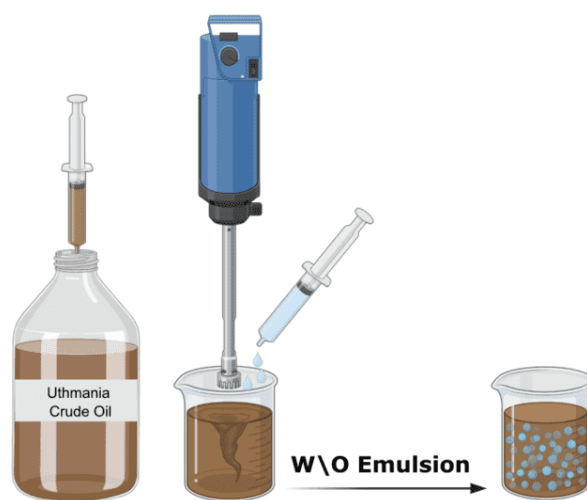
Viscosity (mPa.s)	Content (wt%)			
15.1	Aromatics	Saturates	Asphaltenes	Resins
	33.18	40.18	11.27	15.37

Table 3 SARA analysis of crude oil B.

Viscosity (mPa.s)	Content (wt%)			
38	Aromatics	Saturates	Asphaltenes	Resins
	55.44	13.06	15.54	15.96

Emulsion preparation

The synthesis of crude oil emulsions involved the following steps: Initially, the crude oil was transferred to a 50 ml beaker, and DI water was added drop by drop at varying ratios ranging from 10% to 90%. After allowing sufficient time for mixing, the emulsion was left undisturbed for 24 hours to achieve stability before proceeding to the characterization step, as illustrated in **Fig 2**.

**Figure 2.** Schematic representation for the Emulsion preparation steps.

Droplet test analysis

In order to determine the type of the emulsion, droplet test analysis can be conducted to determine whether it is water in oil (W/O) or oil in water (O/W) emulsion. The procedure is as follows: first, two beakers are used; the first one is filled with 20 ml of water, the second one is filled with 20 ml of diesel. After that, 1 ml of the emulsion sample is added to 20 ml of diesel if the emulsion is spread in the diesel (miscible) that indicates W/O emulsion, if not it is O/W emulsion. In the second beaker, 1 ml of emulsion is added to 20 ml of water, if the emulsion is suspended (immiscible) in the water, that indicates W/O emulsion if not it is O/W emulsion. As demonstrated in **Fig 3**.

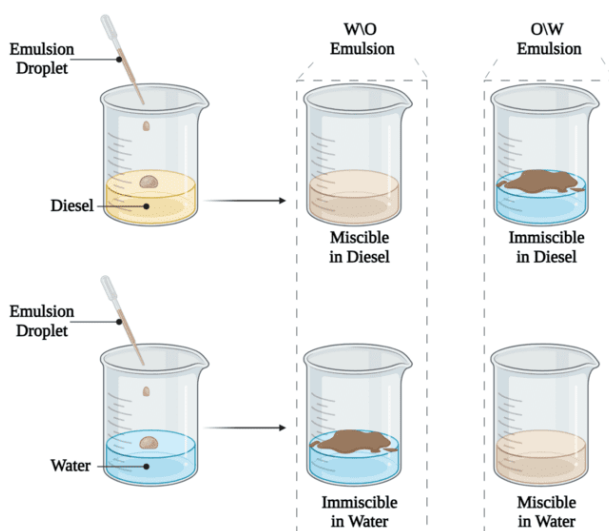


Figure 3. Schematic illustration of droplet test analysis.

Usually, a conductivity test is used along with the droplet test method to confirm the results of the droplet test. Using a conductivity meter, we measure the emulsion conductivity. If the sample conductivity is equal to zero that indicates that the outer phase of the emulsion is oil not water since oil has no conductivity, and it is (W/O) emulsion. On the other hand,

if the conductivity was higher than zero, that indicates that the outer phase is water, and it is (O/W) emulsion.

Demulsification experiment

Demulsification experiments were conducted as per the following procedure: 4–5 ml of the emulsion was transferred to a 15 ml tube, and an equal volume of demulsifier solution in xylene was added. Subsequently, the tube was manually shaken to guarantee full distribution of the demulsifier within the emulsion, and the separation of W/O was observed at room temperature. A blank was also prepared to illustrate the demulsification effect for comparative analysis. The dehydration efficiency (DE%) was computed using Eq. (4).

$$DE \% = (V / V_0) \times 100 \quad (4)$$

Here, V represents the volume of water separated from the emulsion, and V_0 indicates the initial volume of water.

The influence of preparation conditions on crude oil emulsion

Six crude oil emulsion samples were synthesized via the previously explained procedure **Fig 2**. In this set of experiments, a fixed ratio of 60/40 (Oil /DI water) was used. Different samples were prepared via different preparation conditions. After the emulsion formation, characterization and demulsification were performed after 24 hours as shown in **Fig 4**.

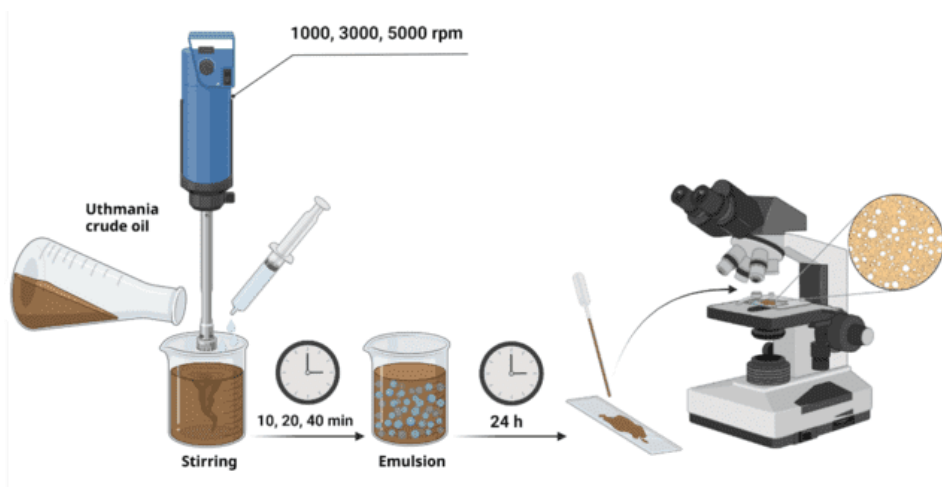


Figure 4. Schematic illustration of emulsion preparation and characterization.

Influence of mixing time on droplet size

Images from the microscope of samples (**10–40 min**) are shown in **Fig 5a–c**. Interestingly, an increase in mixing time, ranging from 10 to 40 minutes, leads to a significant reduction in water droplet size. For example, **10 min** exhibits a non-uniform droplet size distribution, ranging from 7 to 27 μm , with the maximum intensity at 7 μm as shown in **Fig 5d**. Nevertheless, when the mixing time was increased to **20 min**, a significant change in droplet size distribution compared to **10 min** was observed, with sizes ranging from 8 to 20 μm and a maximum at 8 μm . Remarkably, further increase in the mixing time to **40 min** displays a uniform droplet size distribution, ranging from 7 to 12 μm .

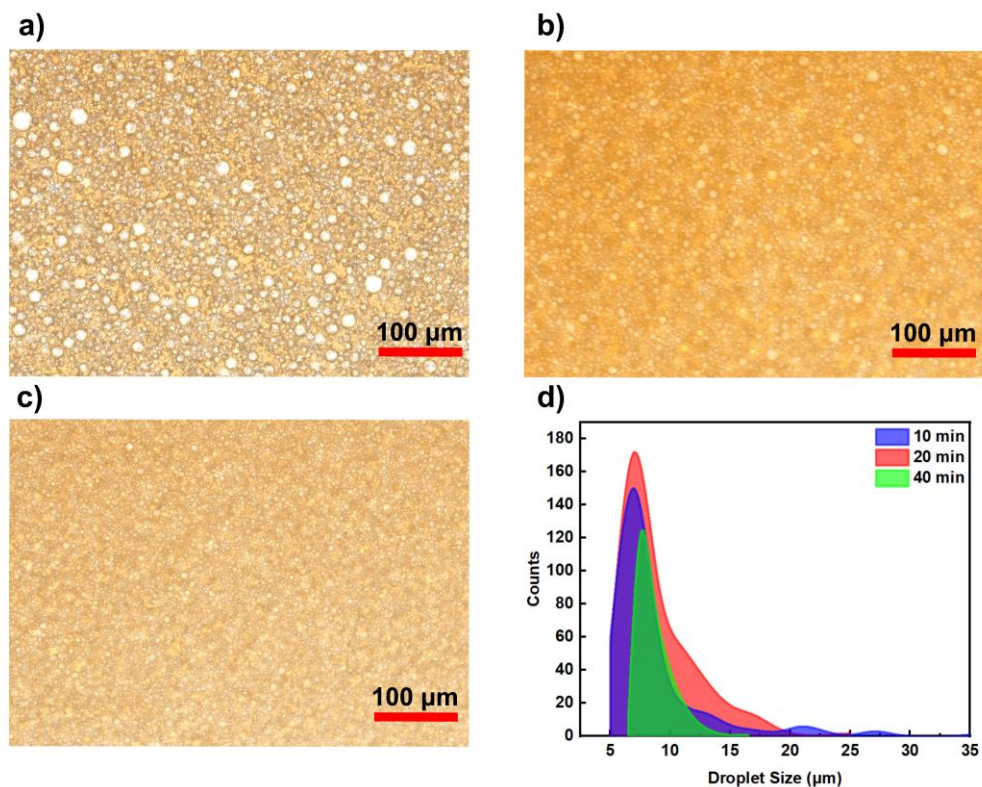


Figure 5. Images from the microscope of emulsion prepared at 60% water cut and at different time a) **10 min**, b) **20 min**, and c) **40 min**, d) droplet size distribution of **10–40 min**.

Influence of mixing speed on droplet size and demulsification

Moreover, an investigation was conducted to assess the impact of varying mixing speeds on the distribution of droplet sizes. Consequently, three emulsions labeled as **1000**, **3000** and **5000** were formed with varying speeds of **1000**, **3000**, and **5000 rpm**, respectively, using a homogenizer for a duration of 40 minutes. **Fig 6.** displays the images of the emulsions from the microscope, and the distribution of droplet size.

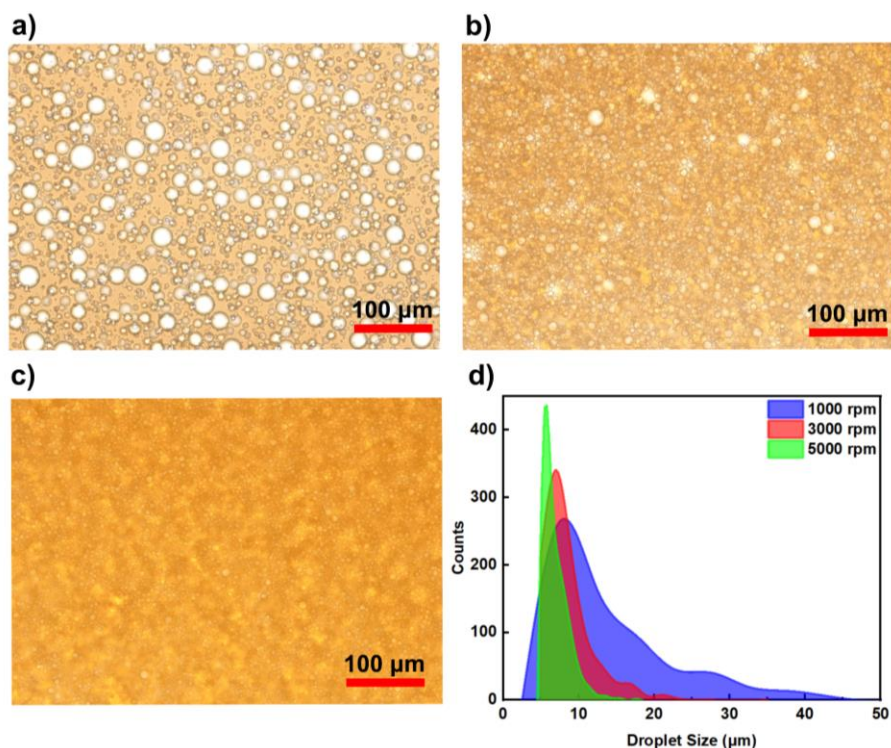


Figure 6 Images from the microscope of emulsion prepared at 60% water cut and at different speeds a) **1000 rpm**, b) **3000 rpm**, and c) **5000 rpm**, d) droplet size distribution of **1000–5000 rpm**.

Samples mixed at a speed of **1000 rpm** exhibited a wide-ranging droplet size distribution from 3 to 45 μm , with the majority of water droplets falling around 3 and 15 μm (**Fig 6a, d**). Multimodal distribution in **1000** indicates an uneven distribution of water droplets. As the speed increased to **3000 rpm**, the image demonstrated a large reduction in droplet size with a more limited range between 8 and 25 μm compared to **3000 rpm** (**Fig 6b, d**). Moreover, when the mixing speed reached to **5000 rpm**, fragmentation into tiny ones was observed, leading to a uniform distribution (**Fig 6c, d**). **5000 rpm** droplet size lies in a range of 5-12 μm , demonstrating a significant reduction compared to the droplet size observed in **1000 rpm**.

To assess the influence of droplet size on the hydration rate, we conducted bottle test demulsification of samples **1000**, **3000**, and **5000 rpm** using a 100 ppm demulsifier as

shown in **Fig 7**. Droplet size appears to play a crucial role in the rate of dehydration, with emulsions having larger droplet sizes exhibiting faster separation. These findings align with Stoke's law, where the emulsion breakdown process begins with sedimentation or creaming, followed by flocculation and coalescence, ultimately leading to phase separation. This entire process is highly dependent on the droplet size of the dispersed phase [3].

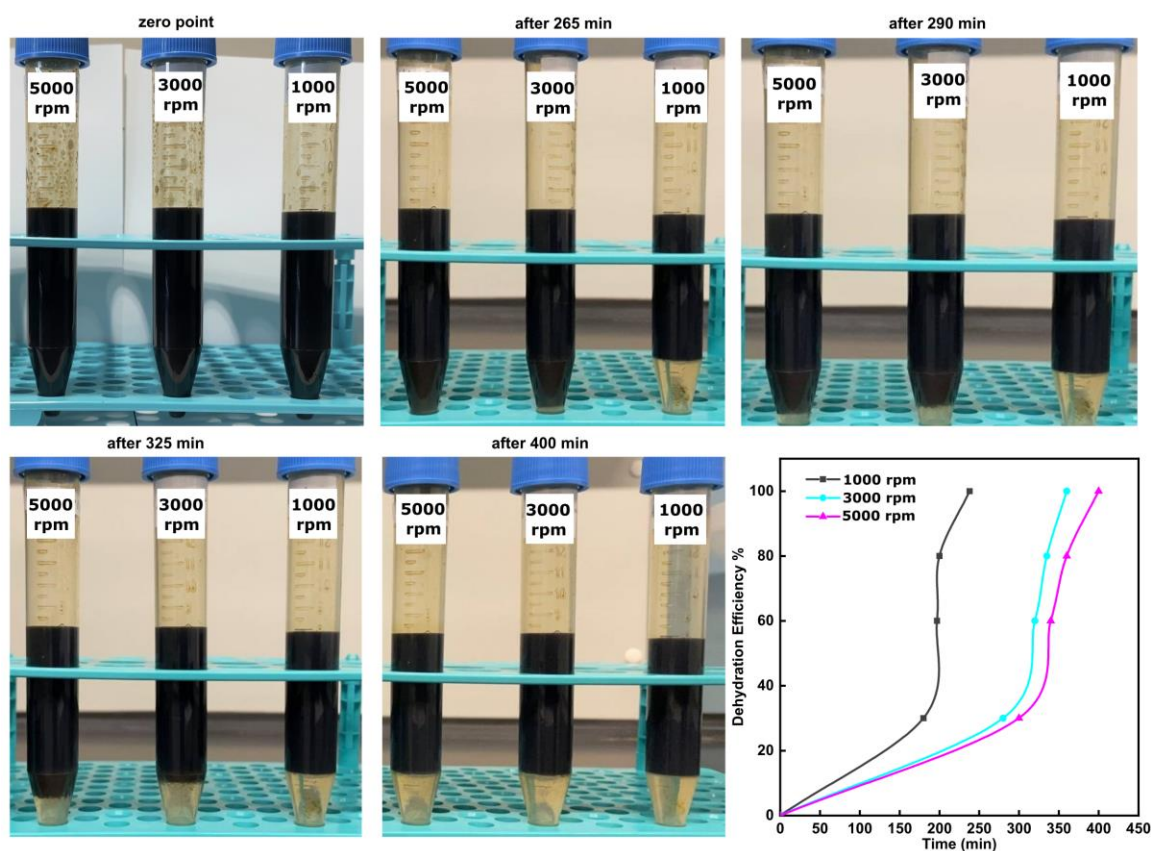


Figure 7. Effect of droplet size on the rate of dehydration for emulsions prepared at different speeds: **1000, 3000, and 5000 rpm**.

Considering the factors associated with emulsion preparation and the confirmed influence of preparation parameters, such as the time of mixing and speed, on emulsion properties, specifically the size of emulsion droplets and their consequential impact on emulsion stability, it became crucial to establish a standardized procedure for the preparation of lab-

made emulsion. Consequently, in this study, a fixed time of 20 minutes and a speed of 700 rpm were implemented for all emulsion samples to ensure consistency and uniformity in the experimental conditions.

Extraction of Acidic Components

liquid-liquid extraction of acidic compounds from crude oil was successfully accomplished. Acidic isolates were extracted at pH 14 from crude oil using the procedures previously explained. **Fig 8a** demonstrates the first step of the extraction (emulsion formation) using ethanol\water mixture after that, the aqueous phases were collected as shown. Afterward, the combined phases underwent four washes with 100-200 ml of petroleum ether **Fig 8b**. Subsequently, ethanol was evaporated using rotary evaporator. Concentrated HCl solution was used to adjust the pH before the next step. Four extractions with diethyl ether using 20 ml each time on the aqueous solution was carried out **Fig 8c**, and then drying using sodium sulfate before filtration Fig. 13d. Acidic material was obtained as oily tarlike residues as shown in **Fig 8e**.

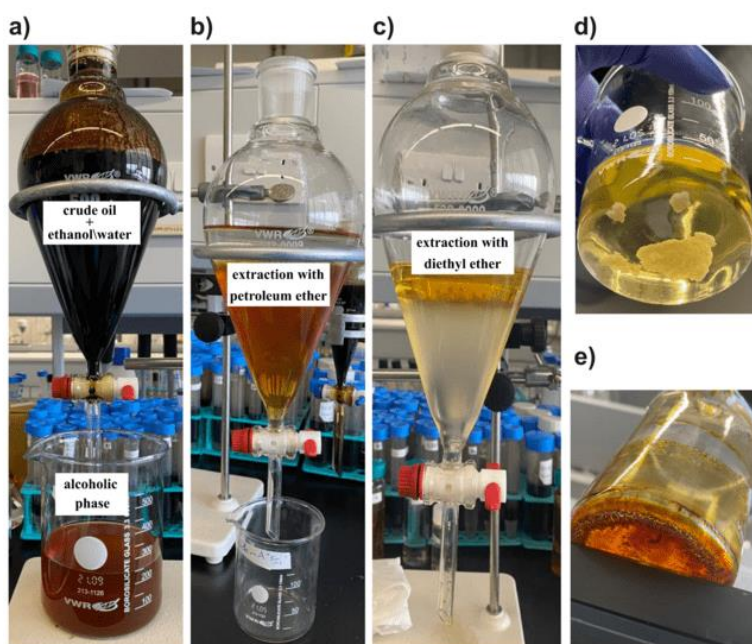


Figure 8. liquid-liquid extraction of acidic components from crude oil (a-c) extraction steps; (d) drying using sodium sulfate; (e) acidic extract.

CHAPTER 5

RESULTS AND DISCUSSION

5.1 Effect of water ratio

Two crude oils with different viscosity 15 and 39 mPa.s for crude oil A and crude oil B, respectively, were used to prepare 18 emulsion samples **S10–S90**. In this set of experiments, each 20 ml of emulsion sample was prepared with different DI water ratios ranging from 10%-90%. Emulsions were prepared using the previously explained procedure; see **Fig 2**. The viscosity of the samples was measured at a fixed shear rate of 400 s^{-1} , and at room temperature. Our results show an increase in the emulsion viscosity as the water ratio increases. In the range of 10%-40% water content, the increase in viscosity is minor, though a significant increase in the viscosity can be observed from 50% until it reaches a maximum increase at 70% water content as shown in **Fig 9a, b**. This could be explained in terms of droplet distribution within the continuous phase. For instance, at a low water content of 10% to 40%, the space between the water droplets is larger than the space between the water droplets at a higher water content of 50% to 70%. When the droplets are more compacted and closer to each other, the movement of the droplets becomes more restricted and as a result the resistance to flow increases. In addition, the surfactants at the droplet surface could interact with each other and enhance the movement restriction of water droplets when the droplets are close enough, which lead eventually to a more pronounced increase in the viscosity. On the other hand, as the water content exceeded 70% the trend is reversed. For example, the viscosity of oil A at 80% water cut was lower than the viscosity at 60% as can be seen in **Fig 10a**. This observation is similar

to what was reported in the literature [59]. This substantial decrease in viscosity at these high-water ratios (80%-90%) could be attributed to the destabilization of the emulsion system; see **Fig 10**. Free water can be seen in the emulsion samples which were prepared at these high-water contents. Similar conclusions can be reached from the two types of crude oil. However, emulsions samples prepared using crude oil B had a larger increase in their viscosity compared to crude oil A as shown in **Fig 9a, b**. Additionally, the influence of the water ratio on the droplet size of the crude oil emulsion was studied through the optical microscope. **Fig 9c-e**. show a decrease in water droplet as the water ratio increases until the maximum was reached at 70% water ratio. On the other hand, after the water ratio is increased from 70% to 90%, an increase in the water droplet can be observed.

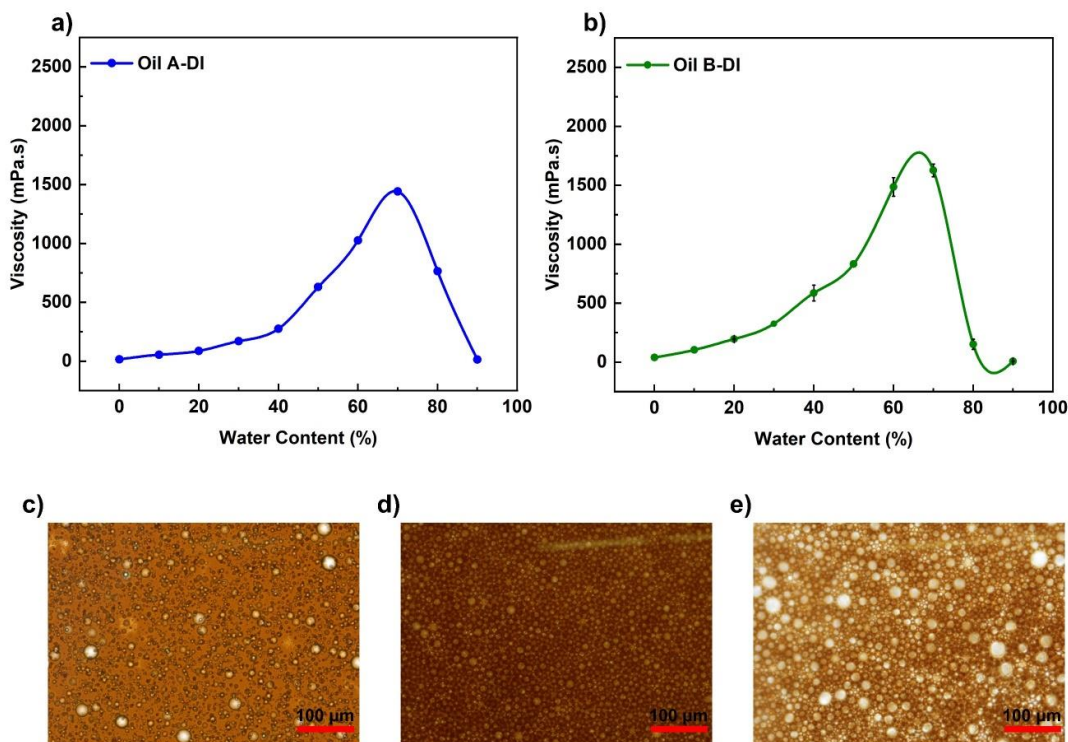


Figure 9. Effect of water content on a) viscosity of emulsions **S10–S90**. Microscopic images at different water cut of oil A c) 30%, d) 70% and e) 90%.

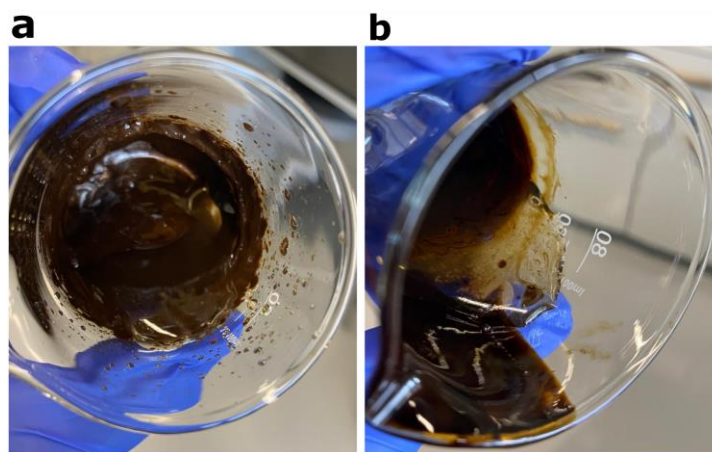


Figure 10. Unstable emulsions at high water ratio a) 80% b) 90%

To examine the influence of water content on the determination of the emulsion type, we present the results of droplet test analysis (using DI only) on three emulsion samples with different water % (10, 30, and 70); **Fig. 11a-c**. Since all emulsions appear to be immiscible with the water, this indicates water in oil emulsions. No phase inversion was observed.

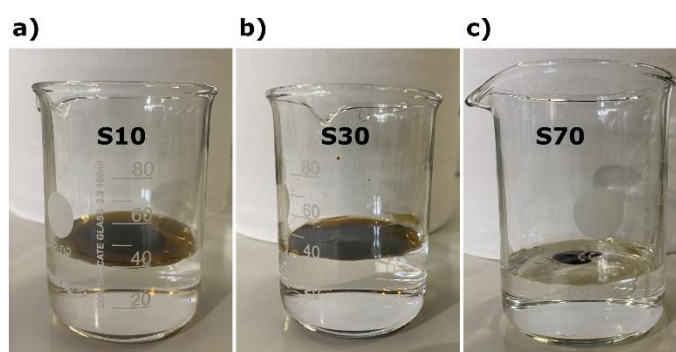


Figure 11. DI emulsion droplet test analysis in water at different water cut a) 10%, b) 30%, and c) 70%.

5.2 Effect of adding CaCl_2

The investigation of different CaCl_2 concentrations is crucial for a comprehensive understanding of the influence of calcium chloride on crude oil emulsions. Through systematic testing, a detailed assessment of the relationship between CaCl_2 concentration and key emulsion characteristics, including viscosity and droplet size can be obtained. In this set of experiments, nine emulsion samples (**C10-C90**) of crude oil were prepared. Each

20 ml emulsion sample was created using different brine ratios ranging from 10% to 90%, while maintaining a fixed CaCl_2 concentration of 500 ppm. The emulsions were prepared following a previously explained procedure depicted in **Fig 2**.

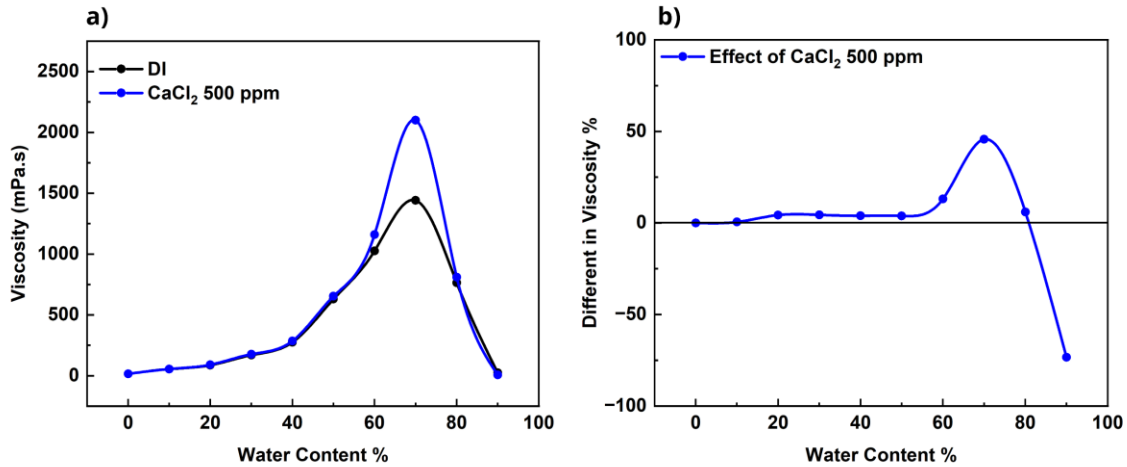


Figure 12. Effect of 500 ppm of CaCl_2 at room temperature and 400 shear rate on a) emulsion viscosity, b) percentage increase in viscosity.

The results obtained from these experiments demonstrate an interesting relationship between the brine ratio and the viscosity of the emulsion. Our findings reveal that as the brine ratio increases, the viscosity of the emulsion also increases as can be seen **Fig 12**. However, it is worth noting that the increase in viscosity is relatively minor within the range of 10%-50% brine content. Remarkably, a significant rise in viscosity is observed from 60% brine content onwards, with the maximum increase occurring at 70% brine content, as depicted in **Figure 12a**. This observation suggests that there is a critical brine ratio at which the viscosity of the emulsion experiences a substantial enhancement. Similar observation was found by other researchers [88] where their emulsion samples exhibit a pronounced increase at the same brine ratio (70%) only, while minor effect on viscosity was observed for the remaining brine ratios. This phenomenon could be related to the fact that at this specific high ratio of the internal phase, the compactness of the droplet can

enhance the attraction of the Ca^{2+} at the interface and the active components in the oil phase (i.e. forced interaction). This interaction between Ca^{2+} cations and polar groups present in the active components of crude oil, such as asphaltenes and petroleum acids can increase the viscosity considerably. These interactions promote the retention of these components at the interface, leading to stronger interactions between water droplets and the active components in the crude oil. Ultimately, these interactions contribute to the overall increase in the viscosity of the emulsion. For higher water ratio beyond 70%, the overall viscosity decreases to be lower than the viscosity of 60% water cut. This decrease in emulsion viscosity after the saturation ratio (70%) could be also related to the breakage of the emulsion, and the instability of the system. In addition to the viscosity analysis, the study also examined the influence of CaCl_2 on determining the emulsion type. This was achieved through a droplet test analysis, specifically using deionized water (DI) on three emulsion samples with varying brine percentages (10%, 30%, and 70%), as shown in **Figure 13**.

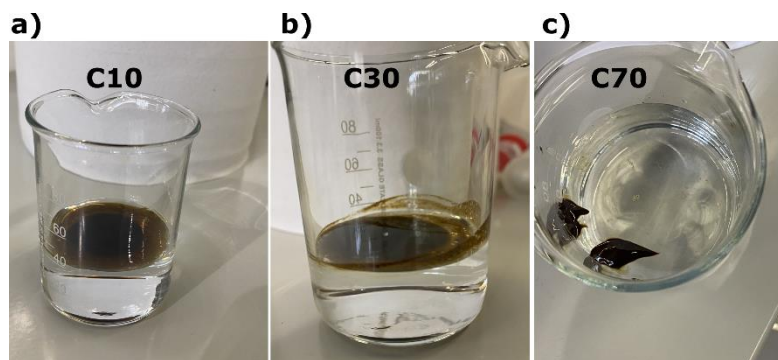


Figure 13. CaCl_2 emulsion droplet test analysis in water at 500 ppm at different water cut a) 10%, b) 30%, and c) 70%.

The results of the droplet test analysis revealed that all three emulsion samples exhibited immiscibility with water, indicating that they are water-in-oil emulsions. It is worth noting that no phase inversion was observed in any of the samples; further confirming the water-in-oil nature of the emulsions. This additional analysis provides valuable insights into the

emulsion type and demonstrates that the presence of CaCl_2 did not induce any phase inversion.

5.3 Effect of CaCl_2 concentration on emulsion viscosity and droplet size

In this experiment, emulsion samples were prepared with nine different brine ratios ranging from 10% to 90%. For each emulsion ratio, three different concentrations of calcium chloride (CaCl_2) were used: 500, 10,000, and 30,000 ppm (see **Fig 14**). This allowed for a comprehensive analysis of the effect of CaCl_2 concentration on the viscosity of the emulsion across a wide range of brine ratios.

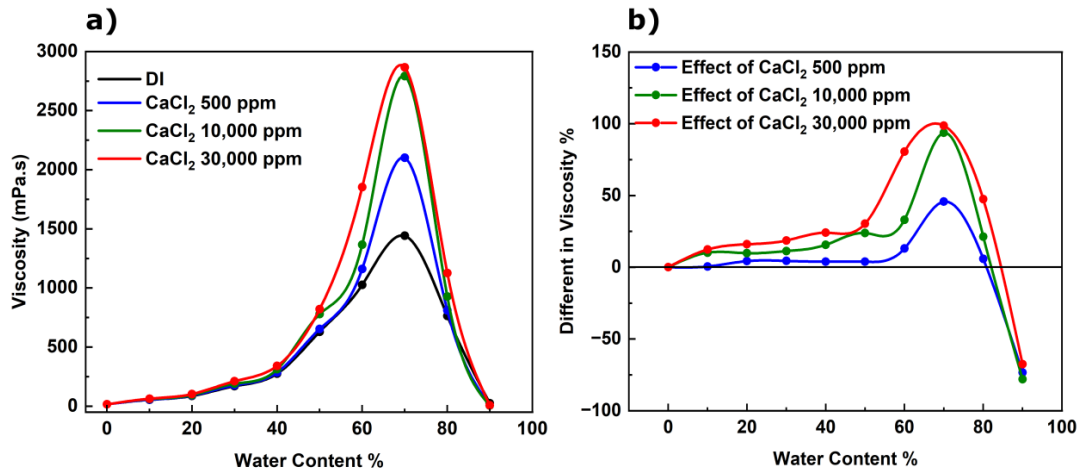


Figure 14. Effect of different CaCl_2 concentrations at room temperature and 400 shear rate on a) emulsion viscosity b) percentage increase in viscosity.

Upon examining the results, a few interesting trends can be observed. Firstly, at lower water content percentages (10% and 20%), the increases in viscosity caused by CaCl_2 are relatively modest across all concentrations. For instance, at 10% water content, the maximum increase in viscosity is 12 % with 30,000 ppm CaCl_2 . This suggests that the effect of CaCl_2 on viscosity is minimal when the water content is low. However, as the water content percentage rises, the influence of CaCl_2 on viscosity becomes more

pronounced. At 50% water content, the increase in viscosity ranges from 3 % for 500 ppm CaCl_2 to 30% for 30,000 ppm CaCl_2 . This demonstrates a substantial impact, with higher CaCl_2 concentrations leading to more significant increases in viscosity. Furthermore, at higher water content percentages (60% to 90%), the impact of CaCl_2 on viscosity becomes even more substantial. For example, at 70% water content, the increase in viscosity reaches 98 % with 30,000 ppm CaCl_2 . This indicates a strong correlation between water content, CaCl_2 concentration, and viscosity increase. Overall, the effect of CaCl_2 on increasing viscosity is generally more pronounced in high brine ratio conditions compared to low brine ratio conditions. Higher CaCl_2 concentrations tend to have a more significant influence on viscosity in the high brine ratio range, resulting in higher viscosity values across a range of water content percentages. The increase in viscosity with higher concentrations of CaCl_2 in the emulsion can be attributed to several possible mechanisms. Firstly, CaCl_2 can act as an emulsifier, promoting the formation of stable droplets within the emulsion. As the concentration of CaCl_2 increases, more Ca^{2+} ions are available to interact with the emulsion components, leading to stronger interfacial interactions and tighter packing of the droplets. This modification of interfacial tension can promote the breakup of larger droplets into smaller ones, which increases the overall surface area and contributes to a thicker and more viscous emulsion. With this fact in mind, we proceeded to study the effect of CaCl_2 concentrations on the droplet size of crude oil emulsion and the results are presented in **Fig 15**.

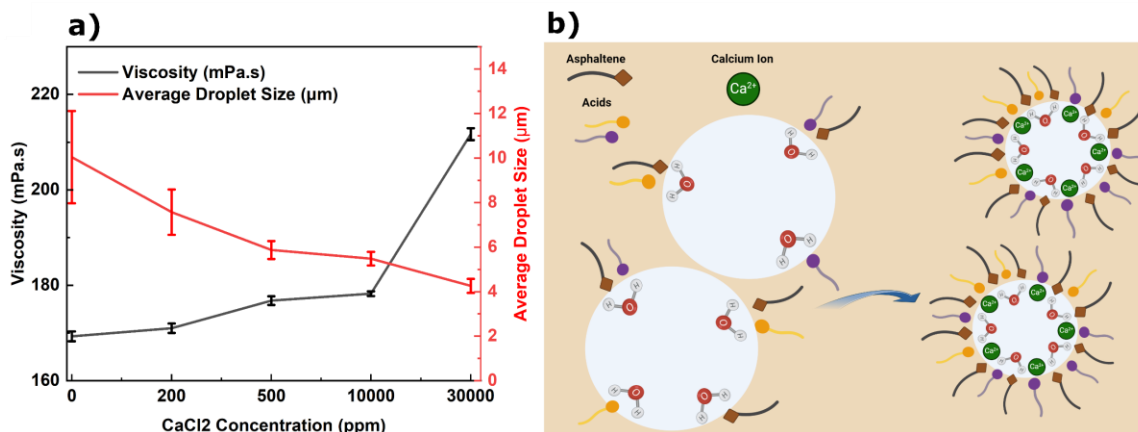


Figure 15. a) Effect of different concentrations of CaCl_2 on emulsion droplet size vs viscosity at 30% water cut emulsions b) Schematic illustration of the effect of CaCl_2 on emulsion droplet size.

The results show the relationship between the concentration of calcium chloride CaCl_2 , the viscosity of the emulsion, and the average droplet size of the emulsion. At a CaCl_2 concentration of 0 ppm, the viscosity of the emulsion was measured to be 169.3 mPa.s, and the average droplet size was 10.04 μm . When the CaCl_2 concentration was increased to 500 ppm, the viscosity slightly increased to 176.78 mPa.s, while the average droplet size decreased to 5.87 μm . This suggests that the addition of CaCl_2 at this concentration had a limited effect on reducing the droplet size and resulted in a slight increase in viscosity. At a higher CaCl_2 concentration of 10,000 ppm, the viscosity further increased to 178.25 mPa.s, and the average droplet size decreased to 5.48 μm . This indicates that the addition of CaCl_2 at this concentration had a slightly more pronounced effect on reducing the droplet size while increasing the viscosity. The highest CaCl_2 concentration tested was 30,000 ppm, which resulted in a significant increase in viscosity to 211.67 mPa.s. Additionally, the average droplet size decreased further to 4.26 μm . These findings suggest that the higher concentration of CaCl_2 led to a more substantial reduction in droplet size and a significant increase in viscosity. Higher CaCl_2 concentrations were associated with more

pronounced reductions in droplet size and substantial increases in viscosity. This highlights the crucial role of CaCl_2 in preventing droplet coalescence through two primary mechanisms. Firstly, higher concentrations of CaCl_2 leads to a stronger interaction between the active components of crude oil and the Ca ions at the interface, consequently, a more rigid film is formed around the water droplets, preventing their coalescence, and resulting in smaller and more stable emulsion droplets. This formation of a protective interfacial film surrounding the droplets will serve as a robust barrier that hinders direct contact and coalescence. Secondly, CaCl_2 effectively facilitates the migration of the active components from the bulk to the oil/ water interface, which results in enhancing the emulsion's viscosity. The resulting higher viscosity limits droplet movement and collision, leading to a significant decrease in the probability of coalescence. Overall, the results indicate that as the concentration of CaCl_2 increased, the emulsion's viscosity generally increased, while the average droplet size decreased. This suggests that the addition of CaCl_2 has a stabilizing effect on the emulsion.

5.4 Effect of CaCl_2 on interfacial tension

In this test, the effect of three concentrations starting from 500 ppm up to 10,000 ppm and 30,000 ppm of CaCl_2 on the interfacial tension (IFT) of crude oil and brine (CaCl_2 solution) were examined, as shown in **Fig 16**. Literature shows that the IFT of crude oil and CaCl_2 decreases with increasing CaCl_2 concentration [89]. Similarly, our results reveal a comparable pattern, showing lower IFT values for higher CaCl_2 concentrations. The results show that the IFT between crude oil and brine decreases as the concentration of CaCl_2 increases from 500 to 30,000 ppm (**Fig 16**). The results show valuable insights into the impact of CaCl_2 concentration on the interfacial tension (IFT) between crude oil and

Deionized (DI) water. Initially, the IFT value for the crude oil versus DI water stands at approximately 24.6 mN/m at time 0 seconds. However, as time progresses, the IFT values gradually decrease, demonstrating a natural reduction in interfacial tension between the crude oil and water phases. This reduction in the interfacial tension within time is a sign of interfacial activity between the active components of the crude oil and the water molecules. Interestingly, when the IFT of crude oil was measured against 500 ppm of CaCl_2 , the initial IFT value at time 0 seconds was 22.5 mN/m and it kept decreasing over time, reaching 19.5 mN/m after 10 minutes. This gives an indication of enhancing the stability of the active components at the interface, which lead to the reduction in the IFT. Furthermore, higher concentrations of CaCl_2 10,000 and 30,000 ppm resulted in more pronounced reduction of the IFT reaching 19 and 16 mN/m respectively.

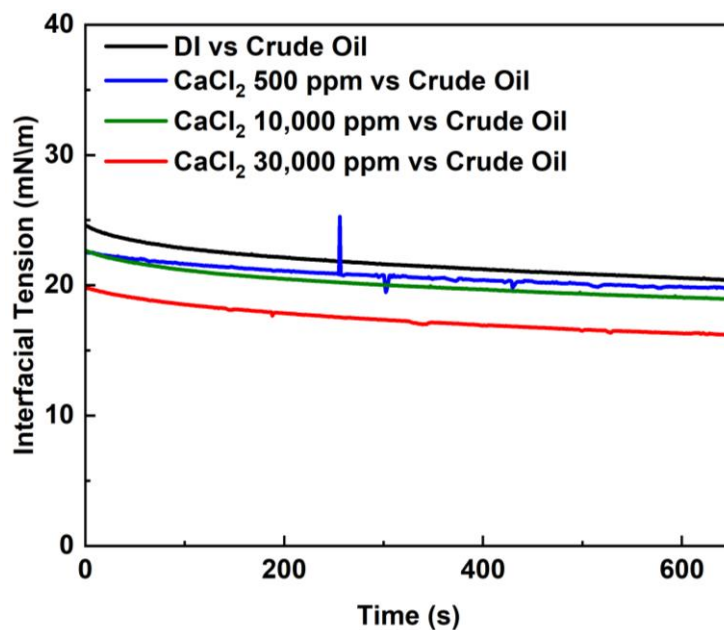


Figure 16. IFT results for Crude oil vs different concentrations of brine (CaCl_2 solutions).

This indicates that the presence of Ca^{2+} ions in the aqueous phase have the ability to facilitate the migration of the active component from the bulk of the crude oil to the interface, by interacting with the negatively charged components (**Fig 18**).

5.5 Effect of CaCl₂ on emulsion viscosity after acids removal.

An experimental study was conducted to examine the effect of CaCl₂ on emulsion viscosity in the absence of acidic components. The objective was to understand the role of CaCl₂ in emulsion properties when acidic components are not present. The acidic components were removed from the crude oil using Liquid-Liquid (L-L) extraction. This technique involves selectively extracting the acidic compounds from the crude oil using the procedures of developed by Colati et al [87]. To confirm the complete removal of acidic components from the crude oil, the experiment included conducting Total Acid Number (TAN) analysis. TAN analysis is a common analytical technique used to quantify the acidic content of crude oil. It measures the concentration of acidic compounds, such as naphthenic acids, in terms of their equivalent mass of potassium hydroxide (KOH) required to neutralize the acids present. The TAN of the crude oil before the acid removal was (0.28 mg-KOH g⁻¹), while after the removal of the acids, no endpoint was detected, which confirms the successful removal of the acidic compounds in the crude oil. Moreover, characterization of the acidic extract using Fourier transfer infrared spectroscopy FTIR was conducted (see **Fig 17**).

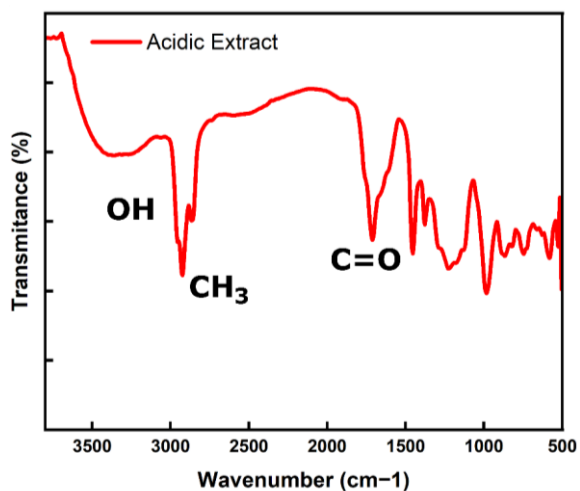


Figure 17. FTIR spectra for acidic extract.

From the FTIR spectra, we can confirm the acidic nature of the extract. For instance, the broad band in the range of $3200\text{--}3600\text{ cm}^{-1}$ displayed the --OH absorption band, resulting from --COOH . Moreover, the absorption band of carbonyl group (from --COOH) was obtained at 1730 cm^{-1} . After the acid's removal step, emulsion samples were prepared using the acid-depleted crude oil at 70% brine ratio, with varying concentrations of CaCl_2 , 500, 10,000, and 30,000 ppm, and their viscosities were evaluated. These samples were then compared to the emulsion samples prepared using crude oil before the removal of the acids as shown in **Fig 18**.

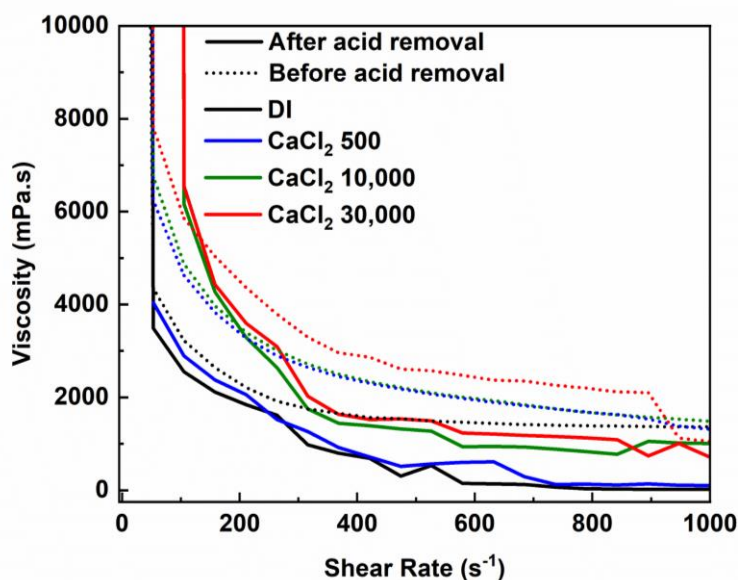


Figure 18. Effect of acids removal on emulsion viscosity at 70% water cut and different shear rates.

For instance, at low shear rate of 52.7 s^{-1} , the viscosity after acid removal of emulsion prepared with DI water only (DI) was measured to be 3492 mPa.s, which was lower than the viscosity before acid removal (DI) at 4353 mPa.s. Acids present in crude oil can interact with both water and oil phases in the emulsion, affecting their interfacial properties and the overall stability of the emulsion. The strong bonding between water droplets and oil phase,

which cause the increase in emulsion viscosity due to the formation of smaller and more closely packed droplet structures is now decreased due to the absence of these interfacial active acidic components. By removing the acids from the crude oil, the interfacial interactions between water droplets and oil are weakened. This weakened interaction contributes to a decrease in viscosity. Furthermore, the viscosity values after acid removal were examined for different calcium concentrations. At the same shear rate of 52.7 s^{-1} , the viscosities after acid removal were 4038.9, 519930, and 561220 mPa.s for Ca 500, Ca 10,000, and Ca 30,000, respectively. The remaining effect of Ca^{2+} ions in enhancing the emulsion viscosity could be related to the interaction with other active components in the crude oil such as asphaltene. However, in comparison, the corresponding viscosities before acid removal were 6768.2, 6250.3, and 7822.3 mPa.s. These results highlight the significant impact of acidic components on the emulsion viscosity across different calcium concentrations. Moving to a higher shear rate of 474 s^{-1} , the viscosity after acid removal (DI) was measured to be 306.47 mPa.s; significantly lower than the viscosity before acid removal (DI) at 1540.3. Similarly, the viscosities after acid removal for Ca 500, Ca 10,000, and Ca 30,000 were 516.17, 1321.7, and 2179.3, respectively, while the viscosities before acid removal were 2211.1, 1534.9, and 2609.3. These results further support the consistent trend of decreased viscosity after acid removal, emphasizing the correlation between the decrease in viscosity and the absence of acids in crude oil which can be attributed to the reduced interactions between water droplets and oil in the emulsion. At an even higher shear rate of 895 s^{-1} , the viscosity after acid removal (DI) was measured to be 22.635 mPa.s, significantly lower than the viscosity before acid removal (DI) at 1375. Similarly, the viscosities after acid removal for Ca 500, Ca 10,000, and Ca 30,000 were 135.65, 1053.7, and 1534 mPa.s, respectively, while the corresponding viscosities before acid removal

were 1574.6, 742.85, and 2102.7mPa.s. Overall, the experimental results consistently demonstrate a decrease in viscosity after acid removal across different shear rates and for different calcium concentrations. The results of these tests indicated that, in the absence of acidic components, which are known to contribute to emulsion stability and viscosity, the addition of CaCl_2 did not lead to a substantial increase in emulsion viscosity. The findings suggest that the observed increase in viscosity when CaCl_2 is added to emulsions is primarily due to the interaction between CaCl_2 and acidic components present in the crude oil. In the absence of these acidic components, the mechanisms by which CaCl_2 typically affects emulsion viscosity, such as stabilization and reduction of both droplet size and interfacial tension, were not prominent. These results highlight the importance of considering the presence or absence of acidic components when assessing the impact of CaCl_2 on emulsion properties in crude oil systems. Specifically, in crude oil systems that have undergone acid removal processes or exhibit low acid content, the influence of CaCl_2 on emulsion viscosity may be limited.

These experimental observations suggest an ongoing interaction between the interfacial active components of the crude oil and the Ca^{2+} ions in the water phase. Herein, we propose a mechanism of the interaction happening at the interfaces, see the illustration in **Fig 19**.

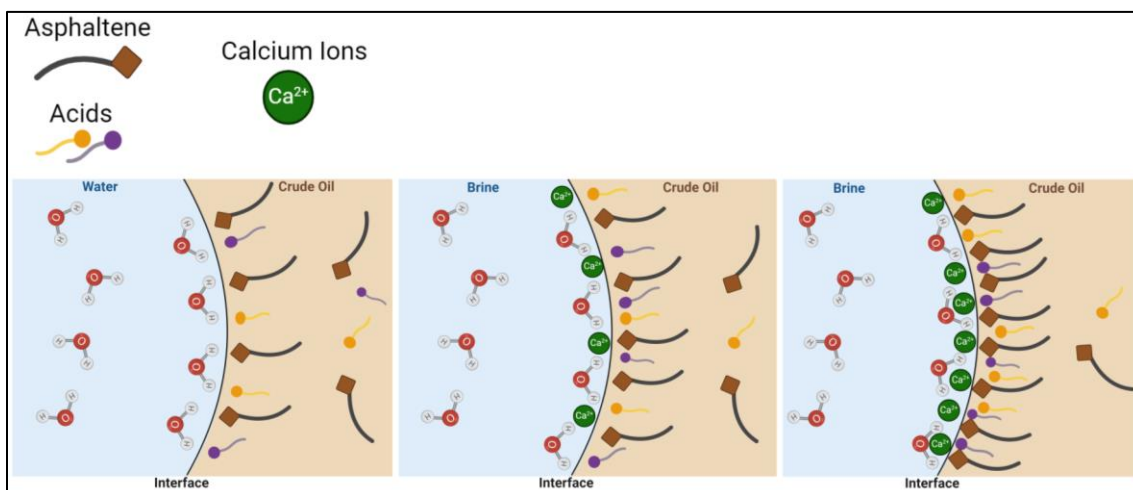


Figure 19. Schematic illustration for the proposed mechanism of IFT decrease by adding CaCl_2 to water-oil emulsion.

The data support the idea that increasing the concentration of CaCl_2 results in a more significant reduction in interfacial tension, leading to improved emulsion stability. This indicates that the presence of a higher concentration of CaCl_2 leads to a stronger interaction between the active components of crude oil and the Ca^{2+} ions at the interface (see **Fig 18.**)

5.6 Effect of ZnCl_2 concentrations on emulsion viscosity and droplet size

Here, we investigate the influence of ZnCl_2 concentrations on emulsion viscosity and the average droplet size. Three different ZnCl_2 concentrations were employed: 500, 10,000, and 30,000 ppm, with nine different brine ratios ranging from 10% to 90% as shown in **Fig 19**. We can observe that as the concentration of ZnCl_2 increases, there is a corresponding decrease in the viscosity of the emulsion. For instance, at low water content levels (10-20%), ZnCl_2 at different concentrations does not have a significant impact on viscosity. For example, at a concentration of 500 ppm, the viscosity decreases by only -1.7% to -2.5%.

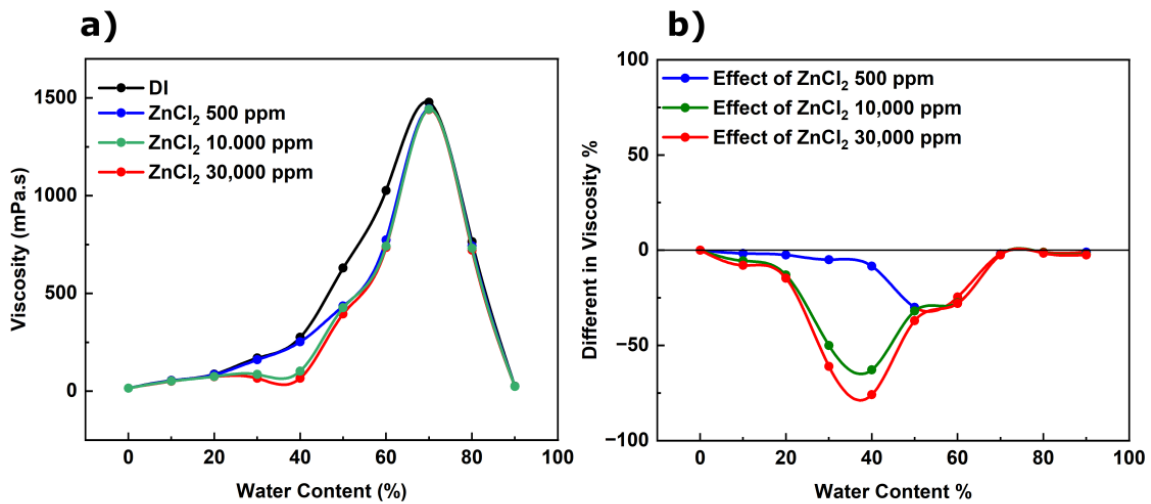


Figure 20. Effect of different ZnCl_2 concentrations at room temperature and 400 shear rate on a) emulsion viscosity (b) percentage increase in viscosity.

In contrast, higher concentrations of ZnCl_2 (10,000 ppm and 30,000 ppm) result in more substantial decreases, ranging from -5.6% to -13% and -8% to -14.7%, respectively. As we move to higher water content levels (30-40%), the effect of ZnCl_2 concentration becomes more pronounced. The greatest viscosity reduction is observed with higher concentrations of ZnCl_2 (10,000 ppm and 30,000 ppm). At 30% water content, the viscosity decreases by -50% to -61%; at 40% water content, the decrease ranges from -62.8% to -75.9%. On the other hand, ZnCl_2 at 500 ppm only produces a maximum decrease of -8.4% at these water content levels. Interestingly, at intermediate water content levels (50-60%), the effect of ZnCl_2 at 500 ppm becomes more significant with increasing water content. For instance, at 50% water content, the viscosity decreases by -30%, while at 60% water content, the decrease is -24.6%. However, for higher ZnCl_2 concentrations (10,000 ppm and 30,000 ppm), the viscosity reduction diminishes as the water content increases. At 50% water content, the decrease is -32% to -37%, and at 60% water content, it is -27.7% to -28%. At high water content levels (70-90%), the effect of ZnCl_2 on viscosity becomes negligible across all concentrations, there is minimal impact observed on viscosity reduction. Therefore, the influence of ZnCl_2 on viscosity reduction depends on the concentration and water content levels. At low water content, the effect is not significant, but it becomes more pronounced at moderate water content levels, particularly with higher ZnCl_2 concentrations. At high water content, the effect of ZnCl_2 on viscosity is minimal. This suggests an inverse correlation between the concentration of ZnCl_2 and the viscosity of the emulsion. The addition of ZnCl_2 to the emulsion can decrease the intermolecular interactions, potentially reducing the strength of the bonds and the resistance to flow, resulting in a decrease in viscosity. Furthermore, we have examined the relationship between ZnCl_2 concentration and the average droplet size of the emulsion. The data

indicates that as the ZnCl_2 concentration increases, the average droplet size tends to increase as well, **Fig 21a**.

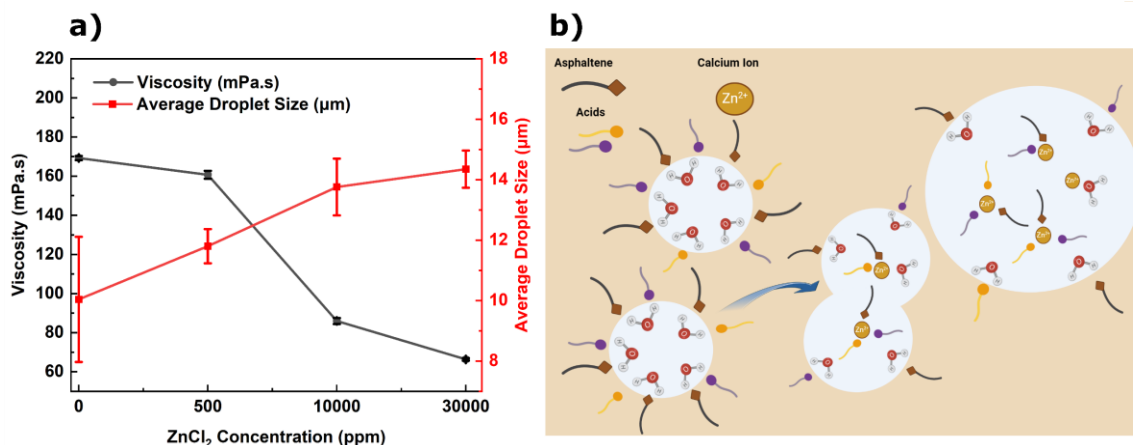


Figure 21. a) Effect of different concentrations of ZnCl_2 on emulsion droplet size vs viscosity at 30% water cut emulsions b) Schematic illustration of the effect of ZnCl_2 on emulsion droplet size.

The decrease in viscosity and the increase in droplet size can be attributed to the low interaction of Zn ions with the active components of crude oil at the interface of crude oil. The proposed mechanism is illustrated in **Figure 21b**. At 0 ppm of ZnCl_2 , the viscosity of the emulsion is 169.3 mPa.s, and the average droplet size is 10.04 μm . Without the presence of zinc ions, the water molecules primarily hydrate the active components of the crude oil at the interface. However, as the ZnCl_2 concentration increases to 500 ppm, the viscosity decreases to 160.73 mPa.s, while the average droplet size increases to 11.8 μm . The higher concentration of ZnCl_2 promotes the preferential hydration of zinc ions by water molecules, in addition to the removing of the active components from the interface by the zinc ions towards the water phase, weakening the film around the water droplets and making them more prone to coalescence. Consequently, the droplets agglomerate and become larger. Moreover, at a ZnCl_2 concentration of 10,000 ppm, the viscosity further decreases to 85.948 mPa.s, and the average droplet size increases to 13.76 μm . More removal of the

active components from the interface by the zinc ions intensifies the weakening of the film around the droplets, resulting in a more significant increase in droplet size. Finally, at a ZnCl_2 concentration of 30,000 ppm, the viscosity decreases to 66.287 mPa.s, and the average droplet size further increases to 14.35 μm . The higher concentration of ZnCl_2 continues to enhance the migration of those active components from the interface to the water phase, leading to greater weakening of the film around the droplets and promoting coalescence, which results in larger droplets. Therefore, based on our experimental results there is a clear correlation between the decrease in viscosity and the increase in droplet size. The high interaction between Zn ions and the active components of crude oil causes the removal of these active components from the interface. This preference weakens the film around the water droplets, leading to droplet coalescence and an increase in droplet size. As the droplets agglomerate and become larger, the overall viscosity of the system decreases. This suggests a positive correlation between the concentration of ZnCl_2 and the average droplet size. The addition of ZnCl_2 to the emulsion may promote droplet coalescence, leading to larger average droplet sizes. ZnCl_2 can affect the interfacial tension between the oil and water phases, potentially reducing the stability of the emulsion and resulting in larger droplet sizes.

5.7 Effect of ZnCl_2 on interfacial tension of crude oil

This part investigated the influence of three concentrations of ZnCl_2 starting from 500 ppm and increasing to 10,000 ppm and 30,000 ppm on the interfacial tension (IFT) between crude oil and brine (ZnCl_2 solution), as depicted in **Figure 22**. The IFT values demonstrate that the presence of ZnCl_2 leads to an increase in interfacial tension compared to pure water (DI Water). For instance, the IFT values for crude oil vs DI at time 0 seconds is around

24.6 mN/m, while for ZnCl_2 at different concentrations of 500 ppm, 10,000 ppm, and 30,000 ppm are measured at 27.972 mN/m, 28.980 mN/m, and 33.097 mN/m, respectively. These values indicate that even a low concentration, ZnCl_2 can significantly affect the interfacial tension, resulting in reduced miscibility and increased resistance to mixing between crude oil and water. After 5 minutes, the IFT values continue to show a similar trend. The interfacial tension for DI water is measured at 21.6 mN/m, whereas the IFT values for ZnCl_2 500 ppm, ZnCl_2 10,000 ppm, and ZnCl_2 30,000 ppm are 25.402 mN/m, 25.8 mN/m, and 28.8 mN/m, respectively. These values suggest that the presence of ZnCl_2 , even at lower concentrations, contributes to an increase in the interfacial tension between crude oil and brine compared to pure water. At the end of the measurement period (approximately 7 minutes), the IFT values are approximately 24.8 mN/m for ZnCl_2 500 ppm, 25.3 mN/m for ZnCl_2 10,000 ppm, and 28.3 mN/m for ZnCl_2 30,000 ppm, while it is 21 mN/m for DI.

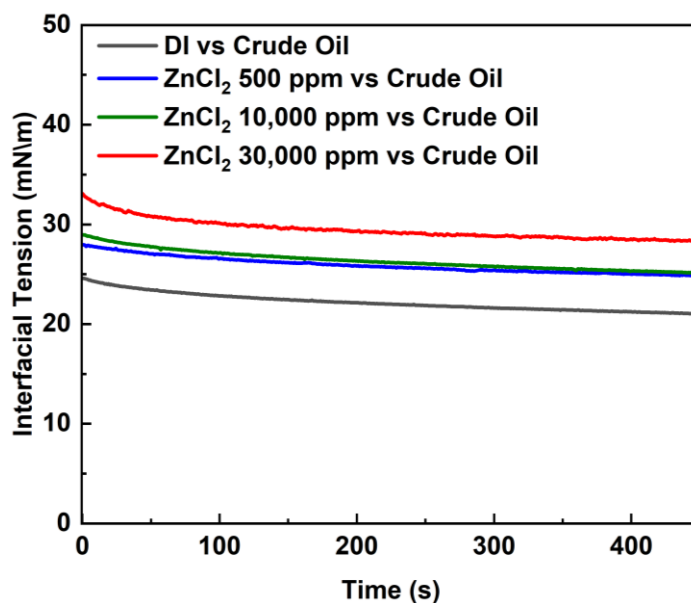


Figure 22. IFT results for Crude oil at different concentrations of brine (ZnCl_2 solutions).

Similar to the proposed mechanism in the previous section (**Figure 21**), we explain this trend of increasing in IFT in the presence of ZnCl_2 by assuming that zinc ions present in

the water phase can remove the active components from the interface and form complexes in the water phase. Consequently, the film between the oil and the water weakens, leading to the reduction of the stability of the active components at the water/oil interface, as described in **Fig 23**. As a result, the interfacial tension between crude oil and water increases.

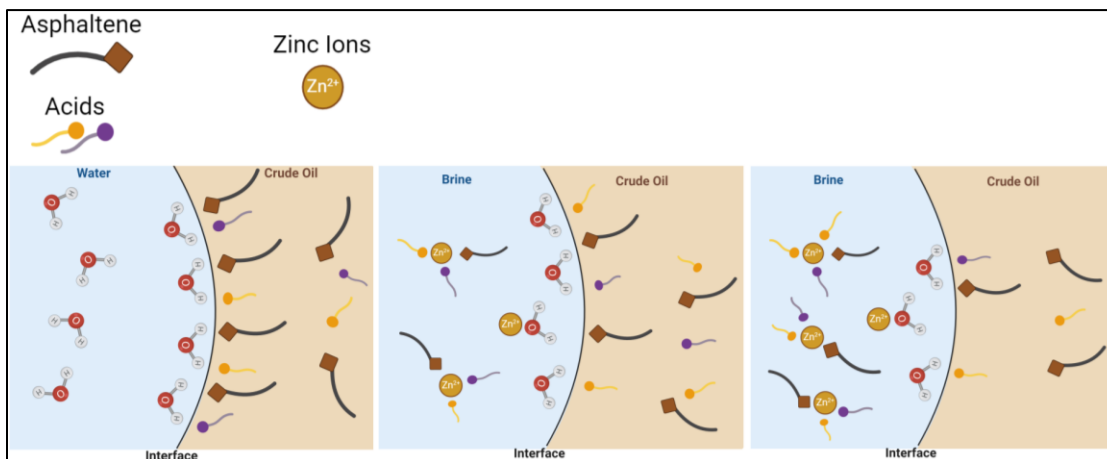


Figure 23. Schematic illustration for the proposed mechanism of IFT increase by adding $ZnCl_2$ to water-oil emulsion.

Moreover, the increase in interfacial tension becomes more prominent with higher concentrations of $ZnCl_2$. Higher concentrations of zinc ions, such as those represented by $ZnCl_2$ at 10,000 ppm or 30,000 ppm, result in a more significant increase in interfacial tension. This is because a larger number of zinc ions are available to enhance the migration of the active molecules from the interface to the water phase, which ultimately increases the IFT. Additionally, the trend of interfacial tension increasing over time aligns with the proposed explanation. The IFT values for $ZnCl_2$ concentrations remain higher than those for pure water, indicating a sustained influence on the interfacial properties between crude oil and the water phase.

5.8 Using ZnCl_2 to enhance the demulsification.

The first demulsification experiment aimed to examine the impact of ZnCl_2 on separating crude oil emulsions without any addition of demulsifiers. To conduct this experiment two lab-made emulsions were prepared at 30% water cut, In the demulsification experiment, the emulsion was subjected to high temperature, where one emulsion sample contains 30,000 ppm of ZnCl_2 and the second one was free of ZnCl_2 . The temperature was maintained at approximately 70 °C **Fig 24**.

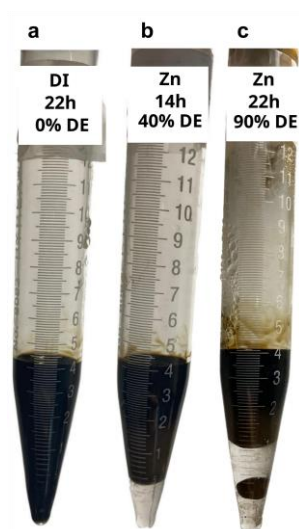


Figure 24. Emulsion dehydration at 30% water cut at high temperature of 70 °C and a) 2 hours b) 14 hours c) 22 hours. Sonication for a) 2 hours b) 30 minutes c) 2 hours.

After heating the emulsion for 14 hours at this temperature and applying 30 minutes of sonication, around 40% dehydration was achieved. Subsequently, by prolonging the heating time to 22 hours and increasing the sonication duration to 2 hours, nearly 100% dehydration was accomplished as could be seen in **Fig 24**. These findings further support the conclusion that the presence of zinc chloride destabilized the emulsion, facilitating its separation and dehydration. To further validate the proposed mechanism (as depicted in **Fig 23**) of how ZnCl_2 destabilizes crude oil emulsions, we conducted an additional

analysis. The separated water from the demulsification step was tested for the presence of Zn^{2+} ions using ICP technique. Remarkably, the results revealed that all Zn^{2+} ions initially injected were detected solely later on in the water phase. This finding strongly supports the notion that Zn^{2+} ions remain predominantly in the water phase during the emulsion destabilization. Furthermore, we tested the hypothesis of the migration of the active components from the interface to the water phase by analyzing the separated water using UV-VIS spectroscopy. Interestingly, we can see the absorption below 300 nm. This absorption indicates the presence of some organic compounds transferred to the water phase by reacting with the Zn^{2+} (see **Fig 25**).

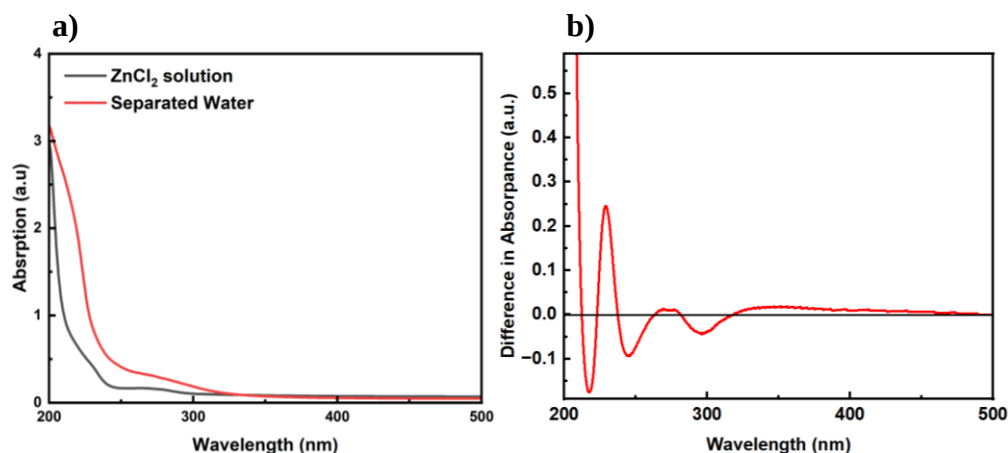


Figure 25. UV-VIS spectra of a) the separated water from the demulsification experiment compared to the solution of ZnCl_2 in DI, b) difference in absorbance.

To accelerate the performance of demulsification of crude oil emulsion by the ZnCl_2 , we conducted another experiment in the presence of a demulsifier provided by Halliburton, without heating or sonication. where four lab-made emulsions with different ZnCl_2 concentrations of 200, 500, 10,000 and 30,000 ppm were prepared along with a benchmark sample with DI only as shown in **Fig 26**. A full phase separation of emulsion was achieved within 4 min only for ZnCl_2 of 10,000 ppm sample, where ZnCl_2 of 30,000 ppm reached

complete dehydration after 12 min. Although the lower concentration of ZnCl_2 of 500 ppm took longer time to separate, around 3 h and 30 min it was still faster than the DI-only emulsion which demulsified completely after an additional hour. Moreover, it seems 200 ppm of ZnCl_2 is not enough to accelerate the emulsion separation.



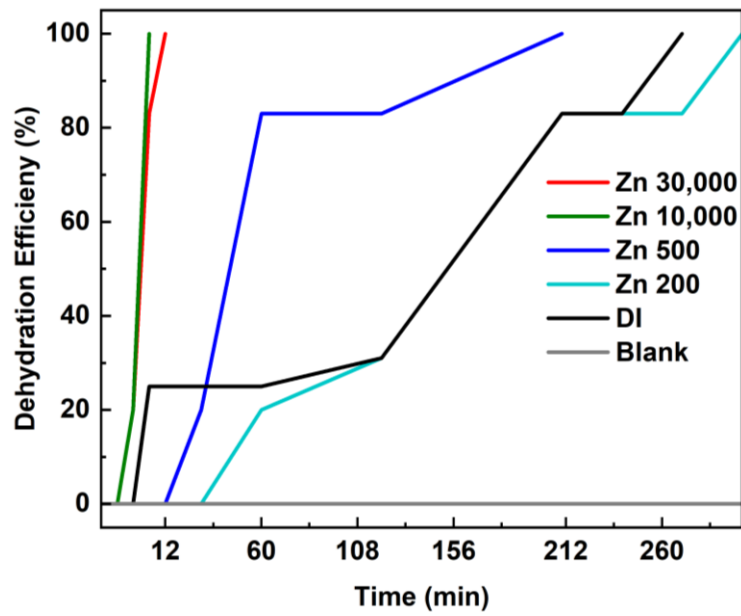


Figure 26. Photo images of emulsion samples under demulsification with different ZnCl_2 concentrations 0-30,000 ppm, in the presence of demulsifier and at 60% water cut (top). Extracted data (bottom).

CHAPTER 6

CONCLUSIONS AND RECOMENDATIONS

Conclusions

The thesis primarily focused on investigating the impact of selective bivalent cations on the active components of crude oil emulsion at the interface. The main objective of the study was to comprehend the role of calcium and zinc cations, which are commonly found in seawater in the Gulf area, in relation to the stability and properties of crude oil emulsions. By employing a systematic research approach, the study examined various factors that influence emulsion stability, including water ratio, droplet size, oil composition, and water composition. Furthermore, the study investigated the effects of different concentrations of calcium chloride (CaCl_2) and zinc chloride (ZnCl_2) on emulsion viscosity, droplet size, and interfacial tension. The findings revealed that the presence of bivalent cations, particularly CaCl_2 and ZnCl_2 , had significant impacts on the properties of the emulsion. These two ions affected the viscosity, droplet size, and interfacial tension of the crude oil emulsion in distinct ways. The Ca^{2+} cations appeared to stabilize the emulsion by interacting with the surfactants at the water-oil interface, while the Zn^{2+} cations seemed to destabilize the formed emulsion by interacting with water molecules and removing surfactants from the interface. One possible explanation for these contrasting effects is the influence of the presence or absence of electrons in the d orbital on the reactivity of calcium (II) and zinc (II). Calcium (II), with an empty d orbital, exhibits high reactivity and tends to form stable complexes at the interface. On the other hand, Zinc (II), with a filled d orbital, is less reactive in terms of complex formation at the interface. This disparity can account for the

different behavior of calcium ions towards the active components at the interface and their role in stabilizing these components. Additionally, the research outcomes have implications for the development of effective demulsification techniques for crude oil emulsion using ZnCl_2 , with the aim of addressing the operational challenges associated with emulsion formation during oil production and transportation. In conclusion, this study provides valuable insights into the influence of selective bivalent cations on the interfacial active components of crude oil emulsion and offers potential solutions for improving the management of emulsion-related issues in the oil industry.

Recommendations

1. Investigate and compare the effects of monovalent and bivalent ions on the interfacial active components.
2. Conduct a comprehensive study on different types of crude oil, focusing on variations in oil composition.
3. Test the effects of bivalent cations on different crude oils with varying levels of acidity. This investigation will shed light on the interaction between cations and acidic components, allowing for a better understanding of how these factors influence emulsion properties.
4. Conduct theoretical calculations to deeply understand the contrast differences between Ca^{2+} and Zn^{2+} .

By addressing these recommendations, future research can advance our understanding of emulsion behavior and contribute to the development of more effective strategies for controlling and managing emulsions in the oil and gas industry.

Thesis Outcomes

- 1- Patent titled “Enhanced Demulsification Performance of Crude Oil Emulsions using Bivalent Cations” has been filed.
- 2- Abstract for ADIPEC Downstream 2024 conference has been submitted.
- 3- Abstract to IPTC 2025 has been submitted.

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