Destabilization and Treatment of Produced Oil-Water Emulsions from EOR Application Using Dissolved Air Flotation Technique

BY

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This work is dedicated to my family, my dear parents, faithful wife, my sweet daughter, brother and sister for their unconditional and continuous support. May Allah continues blessing all of us and my son in heaven

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ABSTRACT

Full Name : [Ma He]

Thesis Title : [Destabilization and Treatment of Produced Water-Oil Emulsions from EOR Application using Dissolved Air Flotation Technique]

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Surfactant and polymer flooding technology can greatly enhance the oil recovery through the expansion of sweeping and displacing efficiency. The recovered oil from surfactant and polymer flooding emulsifies the residual chemical, which makes the separation of water from oil quite difficult, yet the impact of the enhanced oil recovery (EOR) chemicals on the produced water cycle is generally neglected in chemically-based EOR studies. This includes compatibility of EOR chemicals with the additives used to pre-treat the injected water or change reservoir wettability and result in producing oil/water emulsion after EOR breakthrough.

The largest waste produced in oil and gas industries is believed to be the produced water, as it contains different types of organic and inorganic admixture. The discharging of produced water contaminates not only the water, both surface and underground, but also the soil. There are a number of treatment methods available for produced water. To separate water from oil in a much efficient manner and to reach the emission standard, a new class of water soluble polymer of polyacrylamides (PAMs) was used as destabilizing agents for water-oil emulsions, which have been stabilized by surfactant (Tallowamine Acetate).

The impact of the surface charge, and the charge density of polyacrylamides in turbidity reduction, zeta potential, COD and viscosity of separated water were explored in this study.

Different anionic polyacrylamide of different surface charge density and molecular weight were evaluated. Different anionic polyacrylamides and chelating agent were utilized, and optimum dosage have been investigated.

Above all, anionic AN 934 PAM at its optimum concentration was proved as the best way to reduce the residual turbidity and increase the volume of separated water compared with other PAMs mentioned in this research. The results also showed that the W/O emulsion stability related with its salinity, while the optimum concentration of demulsifier are same at both high and low salinity. The effects of electrolytes such as aluminum sulphates and ferrous sulphate on produced water degree of flocculation in the existence of anionic polyacrylamide were investigated in terms of turbidity reduction and volume of separated water after jar test. The results showed that the volume of separated water increased more than 25% compared when only PAMs were used, and the turbidity and COD reduction of separated water improved significantly. The chelating agent (HEDTA) used as demulsifier and parameters such as concentration and pH were investigated, when only at concentration at 10 wt% of HEDTA was used which gave us efficient separation and turbidity reduction, and separation only took place at high pH such as 12.2 rather than at lower pH values.

ABSTRACT (ARABIC)

ملخص الرسالة

الاسم الكامل: ما هي

عنوان الرسالة: زعزعة الاستقرار و معالجة لمستحلبات المياة في الزيت الناتجة من تطبيقاتEOR باستخدام تقنية تعويم الهواء المحلول

التخصص: هندسة البترول

تاريخ الدرجة العلمية: مايو 2015

تقنيتا يتم استخدام المؤثر السطحي (السيرفكتنت) و البوليمر لتحسين استخراج النفط بصورة ملحوظة من خلال زيادة فعالية الازاحة .النفط المستخرج من خلال هذه التقنيات تقوم باستحلاب المواد الكيميائية المتبقية، مما يجعل فصل الماء من النفط بدرجة عالية من التعقيد، على الرغم من ذلك تأثير المواد الكيميائية المستخدمة في استخراج النفط المدعم على دورة انتاج المياة الحقلية تم تجاهله في الدراسات السابقة المعنية باستخدام المواد الكميائية لاستخراج النفط المدعم. هذا يتضمن توافقية هذه المواد الكيميائية مع المواد التي يتم اضافتها لمعالجة المياة المستخدمة (المحقونة) قبل استخدامها او تغير تبللية المكمن مما ينتج عنه مستحلب زيت (نفط) في ماء بعد تنفيذ تقنية استخراج النفط المدعم.

يعتقد ان الماء المنتج اكبر (فايض) منتج من حقول النفط و الغاز، لاحتوايه على عدة انواع من المواد العضوية و غير العضوية. عند (اطلاق) المياة المنتجة لا ينجم عنه فقط تلويث المياة السطحية و الجوفية، بل يؤدي الى تلوث التربة كذلك. هنالك عدة طرق متوفرة لمعالجة المياه المنتجة. لفصل الماء من النفط بأسلوب فعال و لتحقيق و الوصول لمستويات انبعاث الاوكسجين المسموح بها (COD)، فئة جديدة من البولميرات الذائبة في الماء (بولي اكريلي مايد) تم استخدامها كعامل مثبط للاستقرارية لمستحلبات الماء في النفط ، و التي تم تحقيقه استقراريتها باستعمال العامل السطحي (تالوامين استيت).

تاثيرالشحنة و الكثافة السطحية لالبولي اكريلي مايدات في تقليل العكورة وجهد زيتا و كيميائةة سماحية الاوكسجين و لزوجة المياة المنفصلة تم دراستها.عدة بولي اكريلي مايد (سالبة الشحنة) ذات شحنة كثافة سطحية و وزن مولي مختلفة تم استخدامها. عدة بولي اكريلي مايد (سالبة الشحنة) و عامل العزل عند التركيز المناسب تم استخدامة.

بصورة خاصة, يعتبر البولي اكريلي مايد AN 934 ذو الايونية السالبة عند تركيزه المناسب وجد انه افضل طريقة لخفض العكورة و زيادة كمية الماء المنفصل مقارنة بالبولي اكريلي مايدات الاخرى التي تم زكرها في هذا البحث. في هذه الدراسة تم ايضا ملاحظة ارتباطية ثباتية مستحلب الماء في الزيت بالملوحة الماء المستخدم ، بينما بقي التركيز المناسب لعامل زعزعة الستحلاب ثابت في حالتي الملوحة العالية و القليلة. تاثير الالكترولايت مثل المونيوم سالفيت في درجة التجمعية للبولي اكريلي مايد في المياة المنتجة تم دراستها من ناحية تقليل العكورة و حجم الماء المنفصل من اختبار الجرة. النتائج تظهر ان حجم الماء المنفصل زادة اكثر من 25% مقارنة بما نتج عندما تم استخدام البولي اكريلي مايدات. كما لوحظ تحسن بصورة عالية في مستويات خفض العكورة و انبعاث الاوكسجين المسموح بها COD . عامل العزل (HEDTA) تم استخدامه كلعامل لزعزعة الاستحلاب تم دراسة اثرعوامل مثل التركيز و pH.عندما تم استخدام التركيز 10 wt% من HEDTA ادى معدل فصل و خفض عكورة عالي، الانفصال حدث فقط في حالة pH العالية مثل 12.2 مالم يتم ملاحظته عند pH المنخفضة.

CHAPTER 1

INTRODUCTION

Produced water-oil emulsion from EOR application is very large waste stream generated in oil and gas industries. Produced water-oil emulsion contains different inorganic compounds and organic and mixture of both of them. Discharged produced water-oil emulsion will pollute earth surface and soil and underground water. There are some methods available for treating produced water-oil emulsion. However, each method is limited in capability, depending on the condition and the organic concentration and inorganics in the produced water.

The ultimate aim of this study is to investigate experimentally the treatment of the waste produced in oil and gas industries which is believed to be the produced water, as it contains different sort of organic and inorganic admixture. The discharging of produced water contaminates not only the water, both surface and underground, but also the soil. There are a number of treatment methods available for produced water. To separate water from oil in a much efficient manner and to reach the disposal standard, a new class of water soluble polymer of polyacrylamides (PAMs) was used as destabilizing agents for water-oil emulsions, which have been stabilized by surfactant (Tallowamine Acetate).

From the literature review, no many researchers focus on studying the combination system of the electrolytes and polyelectrolyte, only one literature written by M. Karhu et al in 2014 mentioned about the using of the polyelectrolytes and some electrolytes; however M. Karhu et al also did not use the PAM (Polyacrylamide) that is going to be used in our research. So our study on produced water treatment methods are unique and can be summarized as follow:

1. PAM (Polyacrylamide) as flocculator will be used which have never been studied before according to the literature, to the best of our knowledge there is no research in the literature shows the use of different types of PAM (Polyacrylamide): Cationic, Anionic, Amphoteric in produced water treatment; in addition the effect of the salinity (salt content) of produced water will be evaluated using different electrolytes and polyelectrolyte with PAM as optimization.

2. There is no either literature shows the effects of the different types of polyelectrolyte in produced water treatment. Firstly different concentration of polyelectrolyte will be tested to find the optimal combinations. Secondly, three surface chargers density of polyelectrolyte from low to medium and high will be used to investigate the effects of these different charges in destabilization of emulsions.

3. It was noticed that the effect of salinity of produced water in emulsion destabilization was not studied previously, so the effects of salinity at optimal condition for high salinity in practice 57,000 ppm and 200,000 salt will be investigated.

4. The chelating agent (HEDTA) used as demulsifier and parameters such as concentration and pH were investigated.

From all above, the ultimate aim of this study is to investigate the treatment of the oilfield produced oil-water emulsion from EOR application.

The aims of the present work, can be divided into three parts. In part one, based on the characteristics of oil droplets in the produced water, flocculation and destabilization experiments using different polyelectrolytes and different charge density of PAM will be conducted to flocculate and destabilize the oil droplets in the produced water. The flocculation and destabilization characteristics will be investigated through jar tests, volume of separated water, viscosity, density, FTIR, turbidity, and zeta potential measurements. The dependence of the oil droplets charge and size on the solution surface chemistry such as concentration and type of coagulant and flocculants will be explored to find the optimum flocculants types, concentrations, and conditions.

In part two, the optimum polyacrylamides type and concentration will be used to further study with addition of electrolytes such as aluminum sulphate and ferrous sulphate, which was proved as the best way to reduce the residual turbidity compared with other additives mentioned in this research. The results showed that the volume of separated water increased more than 25% compared when only PAMs were used, and the turbidity and COD reduction of separated water improved significantly.

In part three, the chelating agent (HEDTA) used as demulsifier and parameters such as concentration and pH were investigated. Hence, the optimum concentration that would enhance the efficiency of the separation will be determined. In addition, a statistical analysis and optimization will be carried out to evaluate and correlate all the parameters such as pH, coagulant and flocculent concentrations on the performance of demulsifiers.

1.1 Oil in water emulsion

The content of oil is commonly divided into 4 categories based on physical property in **Table** 1 (Sangal et al., 2012):

1. Free oil: free oil rises very fast to the surface of water under inactivate condition.
2. Emulsified oil: emulsified oil has an assembly of their electrical charges to form fine droplets, but the surfactant is the main force to form the stable emulsion because of the interaction at the O/W interface.
3. Dispersed oil: dispersed oil has a close distribution same as emulsified oil whiles the stability of emulsion is not depending on the surfactants.
4. Dissolved oil: the oil itself is not showing in the visible droplets, while which is actually dissolved in fine droplets.

Table 1: O/W emulsions in drop size

Oil Type	Droplet diameter, Dp (μm)
Free oil	≥150
Emulsified oil	≤20
Dispersed oil	20−150
Dissolved oil	≤5

1.2 O/W and W/O emulsion

An emulsion is a mixture of two or more liquids that are usually immiscible (no mixable or unbendable). Actually, it is consisting of one immiscible at least to present as a heterogeneous system, the one phase usually dispersed in droplets and dissolved in another continuous phase. When a continuous water phase contain the oil droplets which can form the oil-in-water (O/W) emulsion, while in water-in-oil (W/O) emulsion a continuous oil phase with droplets of water contained. The emulsion can be only formed under some specific ranges of pressure, composition, and temperature.

A surfactant plays important role to establish some higher concentrations between the interfaces rather than in blank liquid. As we noticed the adsorption which relies on the concentration of certain surfactant. There is no any orientation at low concentration, and the surfactant lies on the molecular interface flatly. When we increased the concentration of surfactant, the molecules begin to arrange in their own way, while this arrangement base on the property of its interface and hydrophilic group. So this specified concentration is called critical micelle concentration (CMC). In this case when the increases concentration more, the extra surfactant molecules begin to aggregate, and then form 3 dimension structures and in orders which are called micelles [**Figure 1**]. The suspended oil droplets cover a layer was formed by the surfactant, avoiding them from coalescing and colliding. The shape and structure of micelles rely on the types of surfactant and certain temperature as well as its concentrations, the presence of water-soluble organic and other ions compounds in emulsion. According to these conditions, different shape such as rod-shaped, spherical and lamellar shapes micelles can be formed (Benito, 2011).

One of critical property of the surfactant that related to the structures of surfactant with its effectiveness to be emulsifiers, which is known as the hydrophilic-lipophilic balance (HLB), we can use this chemical structure to calculate the HLB of a surfactant, while this HLB could be used to characterize any naphtha-diluted bitumen phases and bituminous froth, froth components was extracted, and the froth emulsions was resolve by the commercial demulsifiers. The emulsification requires the classified the bitumen phases and diluted froth by the HLB in related of requiring HLB valves. Somehow the classification like this was that effective to detecting the gross movements in the bitumen phase and diluted froth of the interfacial components, meaningful HLB values were obtained for the water soluble natural surfactants (HLB 16 ± 1) and asphaltenes (HLB 11 ± 1) isolated from the froth. The HLB values for three commercial demulsifies were found to change depending on the delivery medium, from 12 ± 1 if the demulsifier was dissolved in naphtha to 7 ± 1 if the demulsifier was dissolved in water. This difference in apparent HLB may arise from differences in interfacially active components in the diluent. It appears that demulsifier components delivered in naphtha and the water-soluble natural surfactants will seek to form O/W emulsions and, therefore, act to destabilize the W/O froth emulsions. Conversely, demulsifier components delivered in water and naturally occurring asphaltenes will act to stabilize the W/O froth emulsions. The surfactant classification according to HLB values as in **Figure 2**.

Emulsions are usually not stable due to the high surface energy and large interfacial zone, which is proportional to its surface energy. If there is some changes happening in system where could reduce all surface energy and cause the emulsion become more stable. All surface energy is decreased when there are droplets coalesce in emulsion. When the total surface charge energy of the emulsion system reduces will increase the stability of systems by using surfactant (Hayatdavoudi and Louisiana, 2006).

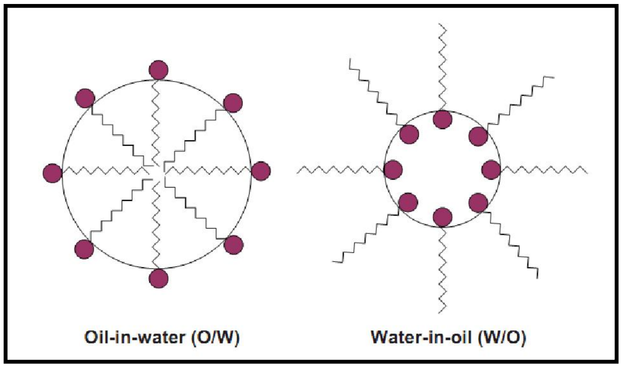


Figure 1: Surfactant stabilized micelles

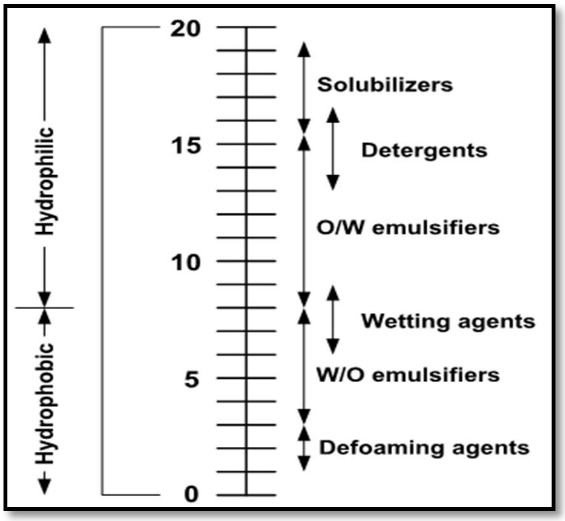


Figure 2: surfactant types based on HLB values

1.3 Destabilization of emulsion in water

Elements of coagulation theory include: (1) characterizing the colloids and the action of the coagulant chemicals, (2) elucidating the chemistry of metal coagulants in water, and (3) describing the characteristics of polymers and the mechanisms of their actions.

There are four important processes to be controlled well so that we can prepare the stable emulsion system: flocculation, creaming, coalescence, and ripening. The flocculation is interaction distance between these droplets because of net attraction strongly depends on these droplets, where all the droplets keep their identification individually. The creaming is the process the form the formation of a concentrated gradient droplet inside of the emulsion. While the coalescence is the process which allows the elimination of the liquid film, and separated the dispersed droplets from closed array. The last process called ripening which is a common phenomenon in emulsion polydisperse such as the smaller droplets form the larger droplets (Sjsblom et al., 1992).

1.4 Stability of emulsion in water

There are some usual stability methods have been developed for counteract the process above. Electrostatic stabilization is duo to the double layers repulsion force between two droplets adjacently with the equivalent charges (Benito, 2011). Particle stabilization is that the solid particles incorporation took place into the emulsion droplets interface zone, and a deeper change based on the properties of interface itself. While the steric stabilization is based on polymeric interfaces overlap on the droplets of emulsion. These different formations of multilayer structures of surfactants are going to increase the stability at the oil-water interface against coalescence drastically (Sjsblom et al., 1992).

The key to an understanding of the stability/destabilization is a realistic model of the W/O interface, and the processes taking place there upon addition of chemicals. Therefore we summarize our information about the interfacial zone as follow: interfacial properties; destabilization of the oil emulsion, which is dependent on the coalescence rate of the dispersed droplets. This rate can be accelerated by chemical additives. And also the chemical composition, molar mass, solubility, ionic character etc. are all parameters of importance for the destabilization process.

There are some properties are very critical for oil/water emulsion stability, for analyzing this process of potential separation it is necessary to measure those properties. In details, those properties as follow: zeta potential, contact angle, interfacial and surface tension, as well as droplets size distribution.

1.5 Statement of problem

From the literature review, no many researchers focus on studying the combination system of the electrolytes and polyelectrolyte except the work of Karhu et al. (2014) which was first to report the use of polyelectrolytes and some electrolytes with Dissolved air flotation (DAF) unit, however the polyelectrolyte used was PolyDADMAC (polydiallyldimethylammonium chloride) . Therefore, our study on produced water treatment methods are unique and can be summarized as follow:

1. PAM (Polyacrylamide) as flocculator will be used which, to the best of our knowledge, have not been reported in the literature. There is also no published work showing the use of the different types of PAM (Polyacrylamide): Cationic, Anionic, Amphoteric in produced water treatment; in addition the effect of the salinity (salt content) of produced water will be evaluated using different electrolytes and polyelectrolyte with PAM as optimization.

2. The effect of surface charger density of polyelectrolyte from low to medium and high has not been considered in earlier work and will be used in this study to investigate the effects of charges on destabilization of emulsions.

3. It has been observed that there is limited work on the effects of salinity of produced water and its impact on emulsions destabilization. Therefore, the effects of salinity at real condition of 200,000 and 57,000 ppm multi-ion salt will be investigated.

4. The effect of using chelating agent (HEDTA) as an alternative additive will be studied for optimal condition.

1.6 Thesis objectives

From all above, the ultimate aim of this study is to investigate the treatment of the oilfield produced oil/water emulsion from EOR application. The objectives of the present work can be divided into three parts.

1. Based on the characteristics of oil droplets in the produced water, flocculation and destabilization experiments using different polyelectrolytes and different charge density of will be conducted to flocculate and destabilize the oil droplets in the

produced water. The flocculation and destabilization characteristics will be investigated through jar tests, volume of separated water, viscosity, density, FTIR, turbidity and zeta potential measurements. The dependence of the oil droplets charge and size on the solution surface chemistry such as concentration and type of coagulant and flocculants will be explored to find the optimum flocculants types, concentrations and conditions.

2. The optimum polyacrylamides type and concentration will be used to further study on addition of electrolytes such as aluminum sulphate and ferrous sulphate, which was proved as the best way to reduce the residual turbidity compared with other additives mentioned in this research. The results showed that the volume of separated water increased more than 25% compared when only PAMs were used, and the turbidity and COD reduction of separated water improved significantly.
3. The destabilized produced water will be used chelating agent HEDTA to investigate the effect of the parameters including concentration, pH. Hence, the optimum concentration that would enhance the efficiency of the separation will be determined. In addition, a statistical analysis and optimization will be carried out to evaluate and correlate all the parameters such as pH, coagulant and flocculent concentrations on the performance of demulsifiers.

CHAPTER 2

LITERATURE RIVEW

Surfactant and polymer flooding technology can greatly enhance the oil recovery through the expansion of sweeping and displacing efficiency. The recovered oil from surfactant and polymer flooding emulsifies the residual chemical, which makes the separation of water from oil quite difficult, yet the impact of the enhanced oil recovery (EOR) chemicals on the produced water cycle is generally neglected in chemically-based EOR studies. This includes compatibility of EOR chemicals with the additives used to pre-treat the injected water or change reservoir wettability and result in producing oil/water emulsion after EOR breakthrough.

2.1 Destabilization of O/W and W/O emulsion

The effect of ferric and aluminum sulphates have been used as destabilizing agents for oil/water emulsion which was stabilized by non-ionic surfactant, the experiment results have been interpreted by studying the electrokinetic properties of the emulsions. The intensity and duration of mixing with slow and fast as target was studied before perform the final DAF experiment. The oil content analyzer was used to find out the changes in oil contents in water, it showed the oil contents reduced because of the electrolyte concentration and pH, then the factor to affect these quantities due to the colloidal stability of oil-in-water emulsions. The interaction force between droplets and particles cause the stability of colloidal dispersions. Finally both ferric sulphate and aluminum sulphate have been proved effective but the ferric is more effective in oil treatment than the aluminum sulphate (Al-Shamrani et al., 2002).

The synthetic solid microporous organosilicate material has been used as adsorbent to study the oil removal oil-in-water emulsion system. The results showed that the cationic surfactant has more adsorption than the neutral surfactant. The emulsions was prepared using neutral surfactant, but the most effective one was ethanol vapor in oil removal in oil-in-water emulsion systems, which have the highest activity (Twaiq et al., 2012).

The role of activated carbon on oil removal with one conventional Dissolved Air Flotation (DAF) system, and the recycle ratio have been studied as operating parameter. Additionally, flow rate, saturation pressure and the optimal concentration or dosage of chemicals was used are also studied. For the results analyze, the BOD and COD values was measured after collecting the samples with different flow rates: low and high flow rates give different efficiency, it lead to the less non-linear behavior with the higher flow rates at same residence time. Finally, adsorption of the activated carbon was proved effective in COD and BOD removals (Hami et al., 2007).

When the aluminum electrodes are used, the effects of under different parameters such as pH, oil content, electrical charge pass, operation mode and electrolyte have been studied. The bubbles (O_2 and H_2) was generated and treated in electrochemical method. The results found that if combine the technique of elctroflotation and elctrocoagulation will greatly enhance the efficiency of treatment process. The cell potential was decreased and electrolyte resistance was reduced as increase the strength of ions, pH and COD results were also affected. Experiment showed if the pH range between 5 to 9, and there is emulsion break and no COD values removal happened (Cañizares et al., 2007).

The W/O emulsion from petroleum sludge, the characteristics of this kind of emulsion need to be treated before discharge to environment. The method was used to measure the water droplets size distribution after the emulsion treated, the results are very important for optimizing and guiding emulsion treatment process. The samples from petroleum sludge were three different one and which were measured the DSC before the treatment. With the results after the emulsion treatment, many properties and behaviors of these petroleum sludge can be characterized by DSC. Water content reduced and water droplets size distribution can be identified even when the salt content exists (Huang et al., 2014).

The mechanism of the influences made by PAM on the characters of produced water/oil emulsion have been studied. The parameters of molecular weight and PAM concentration at oil in water emulsion interfacial tension, interface strength, and interface electric property of oil in water wastewater system was investigated. The analysis was conducted through Zeta potential measurement to show the functions of PAM concentration and different PAM molecular weight, the results show that the Zeta potential valves decreased as the PAM concentration increased, while Zeta potential will not change too much when it reach certain PAM concentration. From the study, it also showed there were no Zeta potential changes for different molecular weight. As I found in my experiments, the values of PAM zeta potential are negative. The study showed that the existence of PAM will greatly increase the electrical property of oil in water emulsion and membrane strength, while the interfacial tension decrease (LiYan et al., 1999).

The separation of oil in water emulsion which was produced by using amphoteric and cationic surfactants during EOR strategy of surfactant and polymer process have been studied. The anionic surfactant and formation brine and crude oil were used to prepare the stable water in oil emulsion. The formation brine was synthetic as field produced. Bottle tests in different conditions were conducted with different concentrations of cationic and amphoteric surfactant and the mixture of both surfactants. The results was analyzed using microscopy and preliminary experiments, the optimal concentration of addition of surfactant has been found, as well as proved that cationic surfactant has stronger influence on separation of water and oil emulsion (Hirasaki et al., 2011).

The treatment of the water in oil emulsion formed by natural surfactant like resins and asphaltenes have been investigated. As the reference that we can know most of emulsion in oil field is water in oil emulsion. It is necessary to use some chemical demulsifiers to break this kind of water oil emulsion formed with crude oil and natural surfactants. So the researcher here tried different demulsifiers such as alkylphenol-formaldehyde resins, copolymer, especially more than 10 kinds of the surface active ionic liquids had been applied as demulsifiers for the first time in this study. The analysis were performed by using FTIR spectrum, the volume of separated water has been recorded at different concentrations, optimal concentrations of demulsifiers have been proved at different time period (Guzmán-Lucero et al., 2010).

The properties of water in oil emulsion and several demulsifiers have been studied for commercial purpose to find out the best performance and rheological property among them for treatment of water in oil emulsion, which was prepared using real crude oil and formation brine. The performance of different molecular weight of demulsifiers range from

3900 to 79540 have been tested. Rheological property of emulsion, dynamic film tension, drop volume of interfacial tension, kinetic adsorption measurements have been conducted, to investigate the performance of demulsifiers at different of concentrations, the results showed that the demulsifiers with high molecular weight have stronger effect on separation of water oil emulsion (Kim et al., 1995).

The different demulsifiers with proper concentration to break the water in oil emulsion which was formed during Enhance Oil Recovery (EOR) process have been studied. A new formulation has been developed to find out the optimum concentration of demulsifiers, which was more effective and suitable for the emulsion was formed by heavy crude oil. First, the bottle test with one single demulsifier was used in water oil emulsion under fixed temperature and concentration to simulate the real water in oil emulsion. Once one of the best demulsifiers have been found out, the optimum concentration of demulsifiers with the pattern of concentration has been proceed. After the steps above, the different combination of these demulsifiers have also been investigated. The influence of the new formulation on the stability of water in oil emulsion, and the crude oil characterization have been considered for further analysis. The measurement on percentage of water separated after bottle test VS various concentrations of demulsifier, duration time, dynamic interfacial tension at different demulsifiers, without demulsifiers, and mixture of demulsifiers have been performed (Razi et al., 2011).

The rheological behaviour of polyacrylamide under different concentration from 400 ppm to 2000 ppm and temperature from 298 K to 328 K have been investigated, which was synthetic as real oil field data. Because as we increase the concentration of polyacrylamide, the viscosity of the liquid with polyacrylamide will also increase due to the property of

PAM itself. While as the increase the temperature of the low iconicity polyacrylamide will cause reducing viscosity. The effects of Polyacrylamide rheology, mainly based on the molecular weight and iconicity. As the results were found in the study indicated that most suitable polyacrylamides for EOR process are anionic with their low effect on temperature and viscosity (Soares et al., 2014).

The oil water emulsion generated from Alkaline and surfactant and polymer flooding using different polymer such as HPAM have been studied, to find the suitable dosage of HPAM used to decrease the stability of emulsion. The stability of emulsion was tested by using Zeta potential, high concentration of surfactant will leads to a high Zeta potential value and high stability. The crude oil in real field with surfactant and synthetic produced water to form the stable emulsion, and HPAM was used as flocculant to break this synthetic emulsion. Viscosity measurement and particles size distribute analysis, Zeta potential, interfacial tension between oil-water were conducted to find the optimum concentration of HPAM, the effects of different concentration of surfactant and NAOH were also investigated. The results proved that even the produced emulsion with high stability is difficult to be treated, but HPAM still are good option to be chose while the higher concentration of HPAM leads to higher viscosity as our experiment. Higher concentration of surfactant gives the higher stability of emulsion (Wang et al., 2011).

The methods of breaking the produced water in oil emulsion and oil in water emulsion for EOR chemical process, which was mainly considered and based on economic performance of EOR process have been studied. The paper was mainly focus on the strategy to treat the produce emulsion with polymer and surfactant on topside ground process. Results have been achieved by using laboratory methods, to find out the impact of surfactant and polymer chemical on produced water treatment and its efficiency, the bottle tests and dissolved air flotation have been introduced to this study. The analysis focus on the turbidity of separated water and the oil concentration in this separated water. The produced emulsion was synthetic with crude oil and water as 50 % v/v at room temperature. The interfacial tension between water and oil have been studied, morphology of prepared emulsion have been characterized, oil content in water phase have been measured (Argillier et al., 2014).

2.2 Destabilization of produced emulsion using DAF

The performance of Dissolved Air Flotation (DAF) have been studied for oil in water emulsion treatment which was formed from synthetic oils through adding chemicals such as the cationic surfactant CTAB (cetyltrimethylam-monium bromide), the coagulant PolyDADMAC (polydiallyldi methylammonium chloride) (also studied for oily wastewaters) or Epi–DMA (epichloro hydrin–dimethylamine copolymer) directly into the saturator (PosiDAF) in two different concentrations have been studied, so the optimal concentration to perform DAF by using coagulation-flocculation theory have been investigated. The total surface charge (TSC) and chemical oxygen demand (COD) was evaluated. Furthermore, by staining hydrophobic particles with Nile red he studied the usage of FCM for determining the hydrophobic particles in oil/water emulsions. The addition of surfactant increased the emulsification of oil by decreasing as the droplet sizes and significantly increasing the anionic nature of the O/W emulsions. The results showed that the PosiDAF by using the CTAB surfactant was not performing well, while it is better than traditional method coagulation-flocculation. This study of DAF with Poly DADMAC with O/W emulsion sample: oily wastewaters also contain other substances that cannot be removed with coagulants but increase COD value (Karhu et al., 2014).

The emulsified oil treated from water rapidly by flocculation, and which was followed in a customize jet cell by using flotation have been studied. The results of oil separated from oil in water emulsion in two different equipment was compared. The experiments showed the function of oil droplets and its oil concentration. DAF and induced air flotation (IAF) have been tried in this work extensively to study the oil removal from the stable oil in water emulsion. The results showed that the optimal concentration of oily water and the efficient oil droplets size with both experiment setups (Santander et al., 2011).

The different of chemical demulsifiers to treat the cutting oil emulsion have been studied. The separation kinetic movement of the oil emulsion was studied as well as the volume of separated water as function of certain time, the optimal concentration of demulsifiers have been found by Jar test experiments. By Using the varying concentration of emulsions, at the same time their turbidity was measured, experiments on investigate the physicochemical properties of the emulsions, dissolved air flotation (DAF) was followed to enhance the efficiency of separation process. Under DAF experiment, no matter what kinds of coagulants and dosages were used, and even the bursting speed, the separation was enhanced greatly but it will become constant after 20 minutes. A/S ratio have a significant improvement after this kind of treatment effectiveness (Bensadok et al., 2007).

The Micro flotation has been used to investigate the feasibility of bubbles generated by the coagulant. The analysis on the oil droplets size under different surfactant concentrations have been conducted. After oil in water emulsion was formed, the optimal concentration of the aluminum sulphate as coagulant and flocculation was studied. The size of bubbles and oil droplets were measured. When the surfactant concentration was increased while the oil droplets size decreased. Some surface-active agents could affect the oil droplets size at oil in water emulsion, as well as affect the efficiency of emulsion separation (Hanotu et al., 2013).

2.3 Characterization of formation brine

The comprehensive zeta potential experiments to characterize the dolomite rock particles and electrokinetics of limestone and in different synthetic brines that represent the Middle East reservoirs have been conducted. All experiments were carried out at 25°C and one elevated temperature, 50°C. For pH equal to 7, they found that the zeta potential for the limestone particle is positive in seawater (54,680 ppm TDS) which was due to the weak electrostatic repulsion caused by compression of the electric double layer. In aquifer water (5436ppm TDS) the zeta potential was always negative as a result of expanding the thickness of the electric double layers. Without Na+ and the other cations in the aquifer water increased the magnitude of the negative charges. The magnitude of the negative charges also increased as the aquifer water being diluted [**Figure 3**]. In aquifer water, the zeta potential had an ascending trend with pH. They found that increasing the temperature to 50°C results in more negative charges for the limestone particles immersed in aquifer water, and that was attributed to the increased solubility of calcium ions which will left the calcite lattice firstly, and thus, come out more negative charges. For the dolomite particles, the presence of Mg^{2+} in the particles lattice created different interactions. In general, the results showed that the trend of the zeta potential as function of the pH and the sign of zeta potential in the previously tested aqueous solution is relatively similar to the limestone particles, however, lack of SO_4^{2-} in the aquifer water had significantly increased the magnitude of zeta potential, while lack of Ca^{2+} had negligible effect. From this study, the concluded that low salinity water creates more negative charges by expanding the thickness of the electric double layer, and increasing the temperature will significantly decrease the zeta potential. Later, Alotaibi and Nas-El-Din studied the surface charges of crude oil and limestone particles at 50 ^{o}C and pH 8 in different aqueous solutions. Crude oil emulsions in seawater and low salinity aquifer water were prepared to study the surface charges at oil/water interface. In all measurements, zeta potential was negative, except for particles treated with the formation water. They found that the magnitude of zeta potential at the oil/water interface increased when the salinity decreased and when adding more sulphate or removing divalent cations from the water [**Figure 4**]. Oil-wet, intermediate-wet and water-wet limestone particles were prepared using special preparation procedures in order to assess the electrokinetics at different wettability conditions. Water wet limestone particles had positive charges due to excess of divalent cations in the formation water while the zeta potential was negative for oil-wet and intermediate-wet particles. The effect of the ionic strength was more significant than the others (Alotaibi and Nasr-El-Din, 2011).

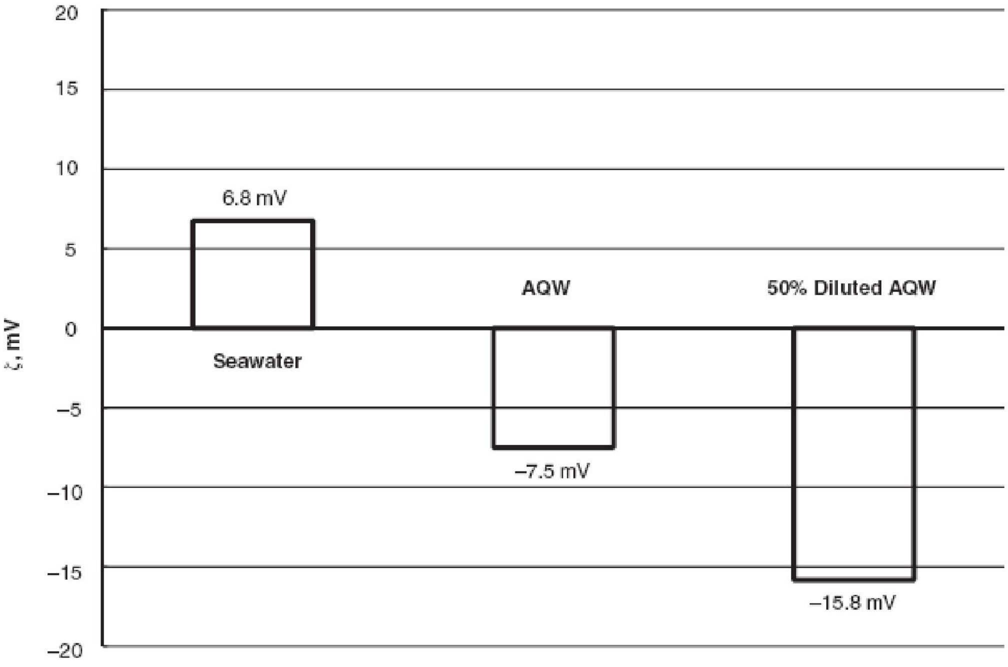


Figure 3: Effect of seawater zeta potential (Alotaibi and Nasr-El-Din, 2011)

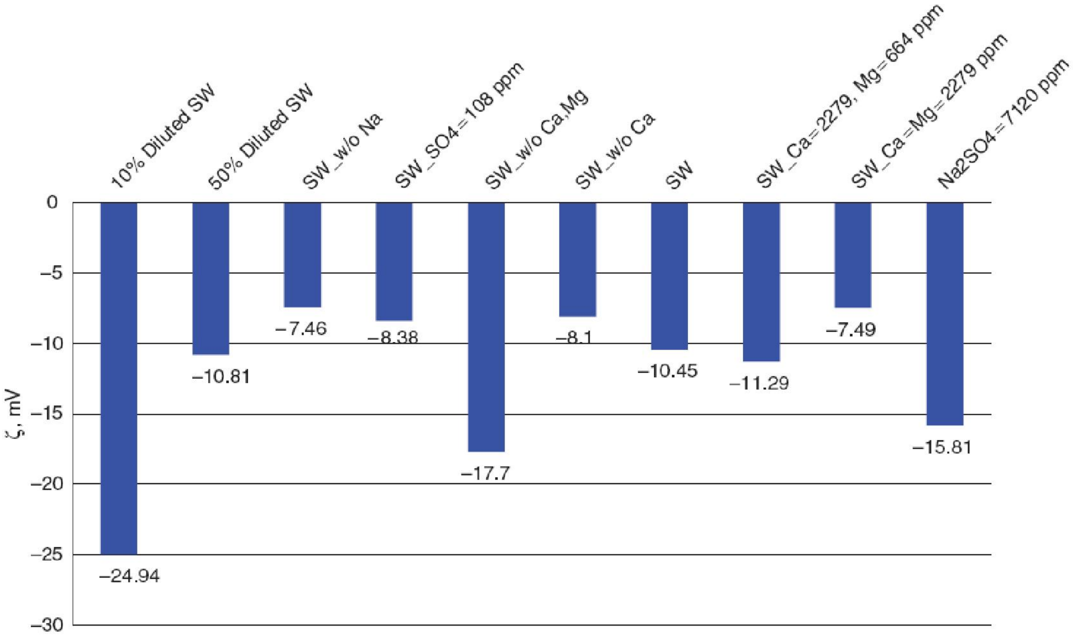


Figure 4: Zeta potential of crude oil droplets (Alotaibi and Nasr-El-Din, 2011)

The solubilities of the sulphates of barium, calcium, and strontium, and how their solubilities are affected by changes in salinity, temperature, and pressure have been studied. The primary objective of future testing is to demonstrate the effectiveness of chemical scale inhibitors in controlling scale deposition. The solubility of calcium sulphate is an order of magnitude greater than that of strontium sulphate, which in turn is about one and one-half order of magnitude greater than that of barium sulphate. We note that the barium concentration is comparatively low. The formation of barium sulphate scale has not been a concern except for any role it might play as a seeding agent in initiating the crystallization of strontium sulphate and calcium sulphate. Four key components are used in this program to determine the proportion of the source waters in the sample of unknown composition: calcium, sulphate, chloride, and TDS. On the basis of positive evidence of scaling encountered in one of the four field tests, it is concluded that a potential exists for precipitation and scale formation in the wellbore where seawater and Arab-D formation water can mix intimately under turbulent flow conditions (Lindlof and Stoffer, 1983).

The effect of potential determine ions in alternating the wetability of carbonate rock in presence of polar compounds using set of brines that represent Arabian Gulf sea water and different version of twice diluted seawater have been studied. The same brines will be used in the current study. These bines will be prepared in a way that enables studying the effect of potential determining ions individually by varying the concentration of a specific ion while keeping the rest of ions constant. High salinity formation water will be used for preparation of oil-wet particles (Jabbar et al., n.d.).

A method in wastewater treatment by using strong heavy metal chelating agents have been developed, which was based on the solubilization of Cu^{2+} of chelating agents at high pH of 10. The total levels of chelating agents and parameters such as properties of wastewater and natural water are compared. The chelating agents EDTA from solution concentration ranges from 0 – 0.0006 M have been investigated to find out the optimal and sensitive level that can help wastewater treatment (Kunkel and Manahan, 1973).

The new EOR methods by using chelating agents such as EDTA and HEDTA at high pH values. Interfacial tension and zeta potential of HEDTA and EDTA have been investigated to find out the optimal concentration of oil recover from initial oil in place at carbonate and sandstones cores. Most importantly, the IFT reduction mechanism was verified by using chelating agents at low IFT values, this mechanism help us to use chelating agent HEDTA as demulsifier on water in oil emulsion from EOR application. It was confirmed that chelating agent HEDTA can seize the cations in emulsion solutions so that the oil mobilization was increased, and IFT of emulsion was reduced by addition of chelating agent HEDTA only at high pH such as 12.2 (Mahmoud and Abdelgawad, 2015).

The using of chelating agents to wash the soils with metal pollution have been proved that EDTA is a very common and effective chelation agent to polluted soils treatment. In this paper, the new chelating agents such as EDDS, MGDA, and NTA as alternatives and compare them with the effectiveness of EDTA. The effect of reaction duration, pH, and the effectiveness at different metal such as Zn, Cu had been investigated. The results showed that when it was higher concentration of complex agents, the pH has less dependence as the heavy metal extraction increased (Tandy et al., 2004).

CHAPTER 3

MATERIALS AND MOTHODOLOGY

3.1 Materials

Produced water was prepared as emulsions of oil dispersed in formation brine. The water used in these experiments has different salinity of 200,000 ppm formation brine and 57,000 ppm seawater, and the commercial diesel used as synthetic oil. Armac HT Prills used as surfactant to form the stable water in oil emulsion. Produced water were prepared as emulsion of oil dispersed in formation brine. A concentrated W/O emulsion was prepared by mixing 60 (vol)% of formation brine or seawater with 40 (vol)% of diesel using IKA Ultra Turrax mixer at 2000 rpm for 10 minutes.

3.1.1 Brines

Synthetic aqueous brines were prepared using high purity salts (> 99.5% wt.) and ultra-pure deionized water. Listed salts in **Table 2** were supplied by Panreac Spain. Deionized water with a resistivity of 18.2 MΩ-cm at room temperature was produced by Barnstead Ultrapure Water System manufactured by Thermo Scientific.

Prepared brines were formulated in a way that enables studying the individual and relative effect of potential determining ions present in the Arabian Gulf Seawater (AGSW). Due to the salinity limits of the zeta potential analyzer used in the current study, all brines were prepared at constant ionic strength level equal to 50% diluted and this was achieved by manipulating the concentration of NaCl salt. Ionic composition of AGSW is shown in

Table 3 as reported by Lindlof and Stoffor (Lindlof and Stoffer, 1983). Zeta potential of the three rock samples in AGSW was measured only one time to make reference data points for comparison purposes.

Table 2: Salts used to prepare aqueous brines

Salt	Molecular Weight (grams/mole)
NaCl	58.44
$NaHCO_3$	84.01
Na_2SO_4	142.04
$CaCl_2.2H_2O$	147.02
$MgCl_2.6H_2O$	203.30

Table 3: Ionic composition of the Arabian Gulf Seawater

Ion	Concentration (ppm)
Na^+	18,043
Ca^{2+}	652
Mg^{2+}	2,159
Cl^-	31,808
SO_4^{2-}	4,450
HCO_3^-	173
TDS (ppm)	57,285
Ionic Strength	1.15

3.1.2 Surfactant

The surfactant for preparing the stable water oil emulsion was used in this study called Armac HT Prills, which is an acetate of hydrogenated tallow amine supplied by AkzoNobel Company. Armac HT Prills (**Table 4** and **Table 5**) is nonionic surfactant and it is an intermediates, emulsifier for oil components. Which have a water-soluble fragments, a hydrophilic portion of molecular like polyether instead of a charged head.

Table 4: Specifications of Armac HT Prills

Parameter	Limits	Method
Amine number, total	163-175 mg KOH/g	VV/2.013
Colour	max 8 Gardner	SC/2.001
Iodine value	max 5 gI/100 g	VV/1.002
Neutralisation	95-105%	VV/2.013
Water content	max 1.5%	VE/4.003

Table 5: Typical data of Armac HT Prills

Chemical and Physical Data	Typical Value
pH	6-9 (10% in 50/50 IPA/Water)
Particle size	1-3 mm (prills)
Density	550 kg/m³ (Bulk)
Density	880 kg/m³ at 60°C
Flash point	> 100°C
Melting point	60°C

3.1.3 Demulsifiers

Different types of electrolytes and polyelectrolytes as demulsifiers were used: Anionic Polyacrylamides (PAM) provided by SNF Floerger Company was used as chemical structure in **Figure 5**, three different change density of PAMs from low to very high, Aluminum sulphate and Ferrous sulphate was added in PAM also have been investigated, in the last chapter, the chelating agent contain different functional groups such as carboxyl, primary amine, ether and slphine that have the ability to seizing the multivalent cations (such as Ca^{2+}, Fe^{3+}, Mg^{2+}, and Al^{3+}). Hydroxyethyle-thylenediaminetriacetic acid (HEDTA) solution with 41 (wt)% provided by AkzoNobel company in **Figure 6** was used as demulsifier to investigate the efficiency of destabilization and treatment on W/O emulsion. All the PAMs used in this study are in powders which were dissolved in De-ionized water according to the recommended operating concentration, the best advantage of these powders is very pure with active matter of 100%.

The differences between coagulant and flocculant are described as below:

- The molecular weight of flocculant is much higher than coagulant: 3000000 to 20000000.
- The particles have already destabilized can be agglomerated by using this flocculant.
- The flocculant ionic will change on Cationicity (+) and anionicity (-) from 0 to 100%, which is based on the treated effluent.
- The flocculants have different physical forms: powder, liquid, emulsion, beads, dispersion.

There are two kinds of flocculants: Cationic and anionic, Cationic flocculant gives the positive charges, while anionic flocculant gives negative charges.

Flocculants are used to deal with the destabilized particles and which aggregates with the polymer chain. If the particles size presented in water phase was increased during the flocculation process results in forming the flocs. The sorts of bonds are mostly hydrogen bonds and ionic bonds locate between the flocculant and destabilized particles.

There are various reagents are used for flocculation process: flocculation additives, some minerals and organic coagulant such as electrolytes, cationic and anionic flocculants such as polymer as well as some pH change reagents like bases and acids.

This is the first time hydroxyethyle-thylenediaminetriacetic aid (HEDTA) chelating agent concentrations (10 wt%-30 wt%) used in destabilization of W/O emulsion were diluted with de-ionized water from an initial concentration of 41 wt%.

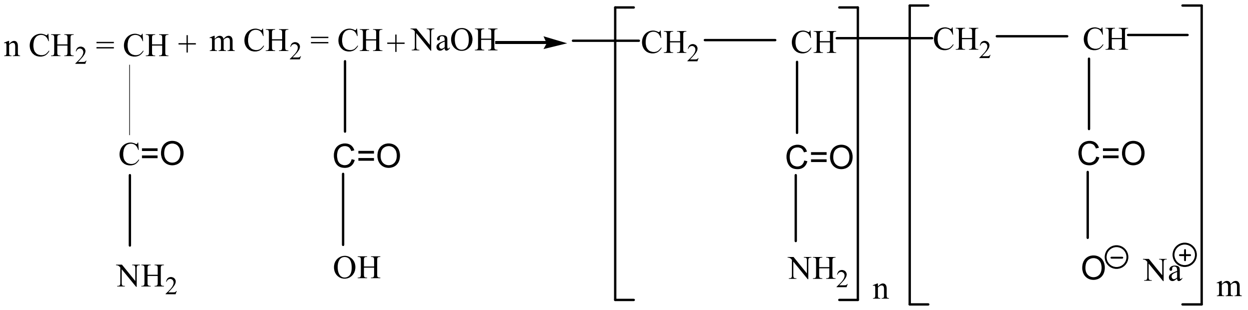


Figure 5: Chemical structure of anionic polyacrylamide

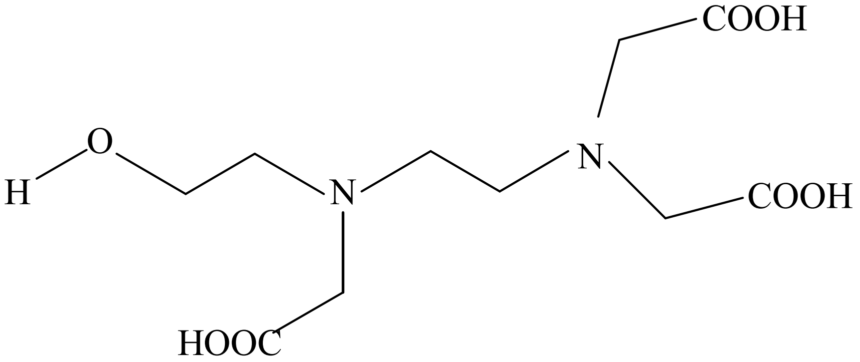


Figure 6: Chemical structure of chelating agent HEDTA

3.1.4 Preparation of Stable W/O Emulsion

Produced water was prepared as emulsions of oil dispersed in formation brine. The water used in these experiments has different salinity of 200,000 ppm formation brine and 57,000 ppm seawater, and the commercial diesel used as synthetic oil. A concentrated W-O emulsion was prepared by mixing formation brine or seawater 60% (vol) with 29.8% (vol) of oil and surfactant using IKA Ultra Turrax mixer at 2000 rpm for 10 minutes as **Figure 7**. When the formation brine was used as a water phase, a very stable water in oil emulsion can be formed which will stable for days and there is no any separation at emulsion phase apparently showed except only small amount of diesel at the top, while when the seawater was used as water phase, the W/O emulsion was also formed by the same method, but which only could stable for 2 hours then at the bottom small amount of water was separated from emulsion as well as the diesel at the top. This is due to low salinity have low stability when the emulsion was prepared (Al-Yaari et al., 2013).

3.2 Experimental Methodologies

3.2.1 Jar Test

Jar test is the most common equipment which used to physical-chemical process test. It has 6 stirrings which can be controlled with different speed for 6 beakers simultaneously so that we can compare the efficiency by adding different dosages or various products at the same time. Other equipment such as one stop watch, syringes and special modified beakers with valve at the bottom for collecting sample after separation are needed.

The purpose of the equipment here is to impose one laboratory testing procedure and to represent the real industrial conditions that we encountered, the follow procedures were

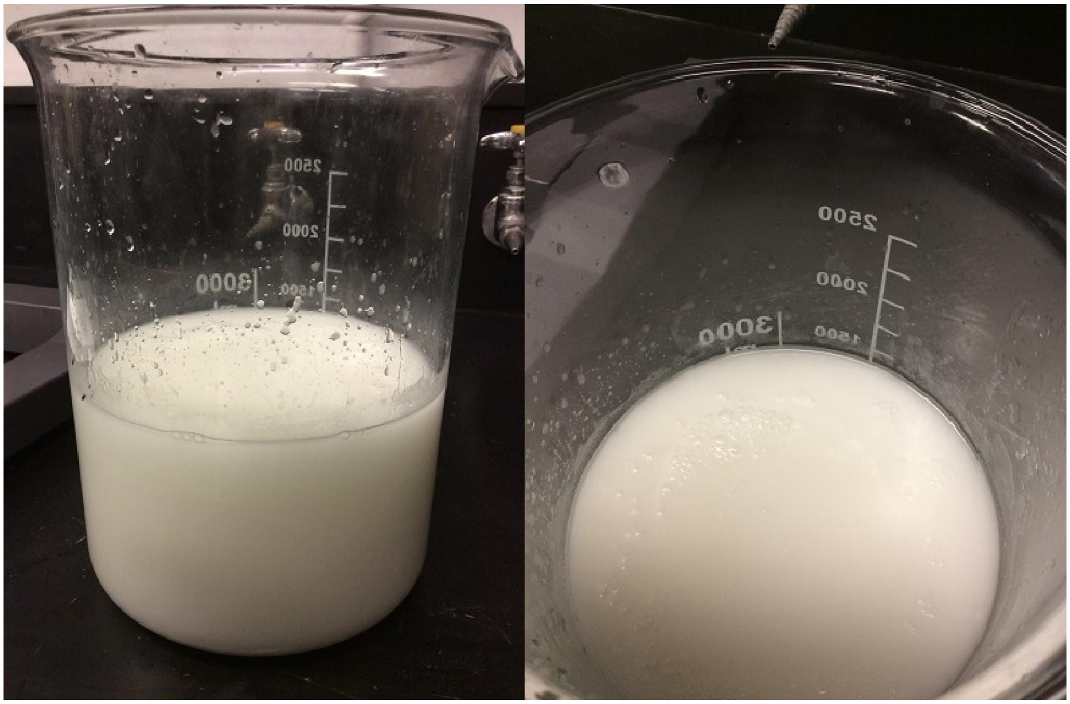


Figure 7: Stable water in oil emulsion

followed:

- After preparing the water in oil emulsion for comparison, the different concentrations of PAM and other coagulants should be injected simultaneously with predetermined dosages.
- After the flocculants injected, the mixing is required to distribute the reagents throughout the emulsion. And this mixing should be at particular speed and time as described: 250 rpm for 10 minutes then 30 rpm for 15 minutes for coagulant, and 250 rpm for 10 seconds and then 5 minutes at 30 rpm for flocculant.
- When the formation of flocs is finished, the samples should be settled down for certain period, for our case, duo to the high stability of our emulsion prepared with formation water, which was settled for 24 hours to collect the separated water, while it is only one hours to settled down for emulsion prepared with seawater because of its low stability.

3.2.2 Volume of Separated Water

Flocculator SW6 provided by STVART Company was used for jar test, modified jars with opening control valves at their bottoms where used to allow easy collection of separated water without mixing with emulsion and diesel at the top phases as in **Figure 8**.

After the jar test, for emulsion formed with the formation brine, the samples were kept for 24 hours to ensure stability of separated phases because there is no any separation observed from the jar without any demulsifier used as the reference after 24 hours settle down, after settle down for 24 hours there were three phases showed: diesel at the top, emulsion at the middle and water at the bottom could be clearly identified as in **Figure 9**. While for the emulsion formed with the seawater, the volume was measured immediately after jar test because the stability of emulsion with seawater much lower which could stable at least 1 hour after stable emulsion formed without adding any PAM. And then the water at the bottom of jars was collected and different measurements were conducted on the separated water to study the effectiveness of demulsifier in the process of emulsion separation. Those measurements are: volume of water separated (WS) in percentage, which is defined vol % as below:

$$\text{WS (vol \%)} = V / V^{\circ} \times 100 \tag{3.1}$$

where V° is the original volume of water contained and V is the volume of the water separated.

3.2.3 Turbidity Measurement

Turbidity is the measurement on water clarity, which is measured on how much materials are suspended in the water by passage of light throughout the water. There are various suspended materials contains clay and sand in soil particles, microbes, algae, plankton and other substances. The particle size range of these materials from 0.004 mm like clay and 1.0 mm like sand. The color of water also can affect the turbidity, but the turbidity is not color related, it depends more on the transparency loss in water because the effect colloid materials and suspended particles, sometime even both of them. So, a weak turbidity may cause the low pureness and clarity of water because the light could not pass the liquid because of the existence of different suspended particles and collides.

Figure 8: Flocculator for jar test

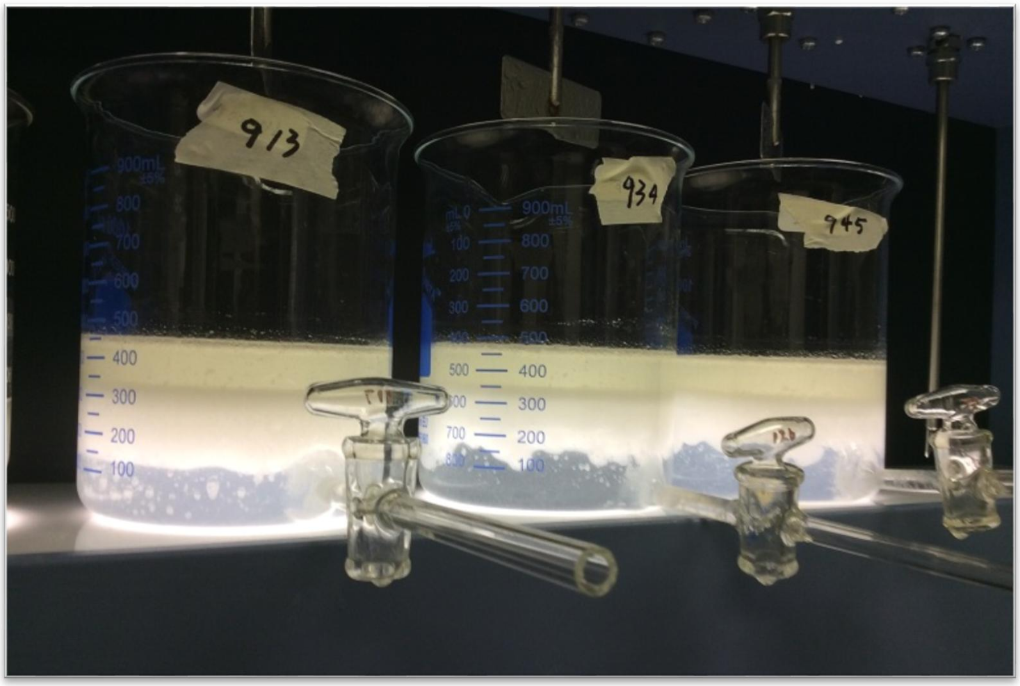


Figure 9: Volume of separated water after jar test

Turbidity meter [**Figure 10**] is made for measuring the turbidity, which is consisting of a light source that illuminates the water sample in specified transparent sample bottle, as well as a photoelectric cell that measures the intensity of light scattered at 90 angle by the particles in the sample. The units of turbidity are in NTUs or nephelometric turbidity units. Usually a turbidity meter can measure the range between 0 and 1000 NTUs. For example, the clear distilled water might have a turbidity of 0.1 NTU, while the turbidity of the liquid like milk more than 1000 NTUs, the turbidity values range from 0.1 NTU to 800 NTU are indicated as **Figure 11**, which is for calibrating samples.

HACH 2100N Turbidimeter was used to study the effectiveness of PAM in improving the pureness of the separated water through conducing turbidity test.

3.2.4 Density Measurement

Density of separated water was measured for viscosity calculation and further analyzing. The density meter we are using is supplied by Anton Paar Company [**Figure 12**], which is equipped most accurate density measurement in the world. The advantage of this density meter is that it could give you the results on your sample density in one cycle as well as under same sample condition.

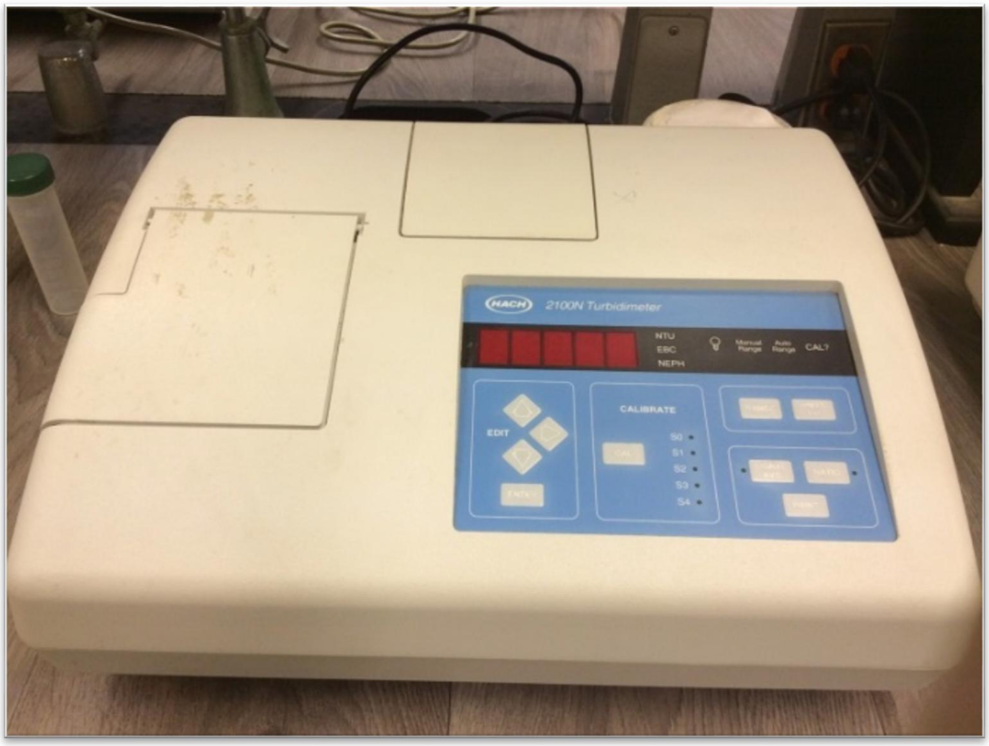


Figure 10: Turbidity meter

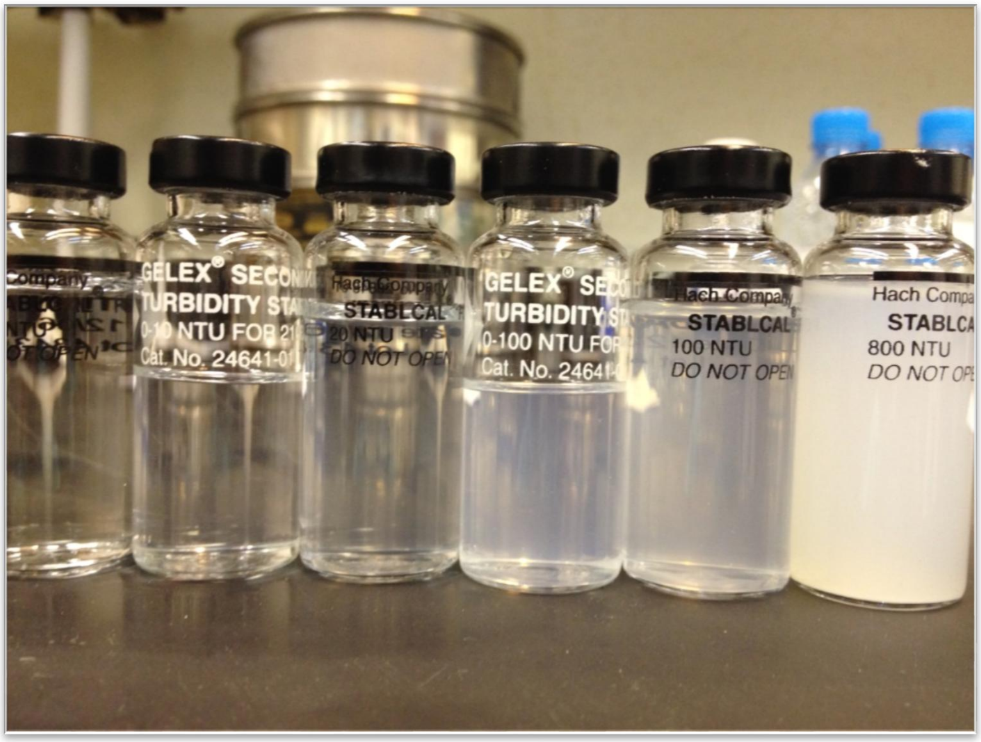


Figure 11: Turbidity values range from 0.1 NTU to 800 NTU

3.2.5 Viscosity Measurement

Viscosity of separated water was measured to compare it with usual water without PAM exists at the room temperature. The viscosity measurement was conducted by using Ostwald viscometer [**Figure 13**], which is device for measuring the liquid viscosity with density values measured from previous step. This method is measuring the time for certain volume of liquid sample at room temperature, record the time that this volume of liquid flow through the capillary tube from marked A to B due to the factor of gravity. Then use this recorded time, the constant valve of capillary tube size and know density to calculate the viscosity values as the formula below. Before running the measurement, it is recommended to calibrate the system with known viscosity materials such as pure distilled water.

$$\mu = (t_{ave} \times C) \times \rho \tag{3.2}$$

$\mu: viscosity; \quad t_{ave}: average\ time; \quad C = 0.008; \quad \rho: density$

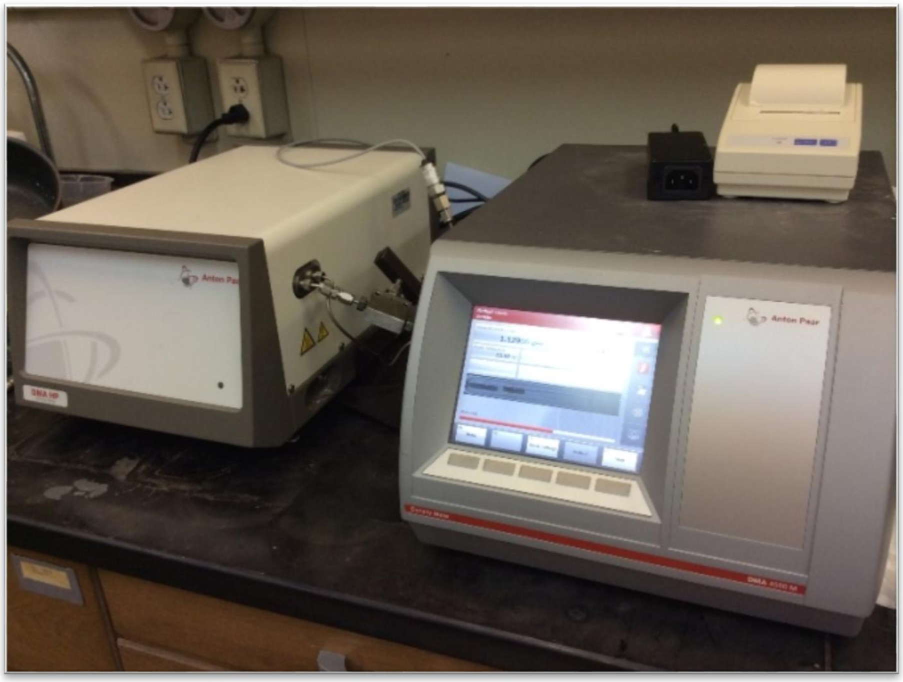


Figure 12: Density meter

Figure 13: capillary viscometer

3.2.6 Chemical Oxygen Demand (COD)

COD is the measurement of chemical pollutants in a water sample that can consume dissolved oxygen. It is significant factor since COD affects dissolved oxygen levels in rivers and lakeside or seawater, thus it affects the living organisms in the water environment.

Firstly started heating the COD reactor [**Figure 14**] at 150°C. To each sample batch, added two blanks, and two standards, of about 25 or 50 ppm COD. In each culture tube, we took 2.5 ml of sample (or smaller amount but diluted with distilled water to 2.5 ml). If sample salinity was very high, chloride may interfere with results, so it was necessary to added 0.8 g mercuric sulphate and mix thoroughly. Then continually added 2.5 ml dichromate reagent. Next ran 3.5 ml sulfuric acid reagent inside tube carefully so that an acid layer formed under the sample digestion solution layer. Last capped the tube tightly and inverted to mix the contents several times. All the tubes to be placed in pre-heated COD reactor for 120 minutes. We need observed and proceeded to the analysis when color of the solution was still yellow. If some samples have turned greenish, we had to repeat with smaller volume. For titration, 100 ml beaker was used with a magnetic stirrer, the contents of each tube were transferred into the beaker, and rinsed the tube into the beaker with distilled water until when there was 50– 60 ml solution in the beaker. Then 1-2 drops of ferrous indicator added. Titrated with 0.10M ferrous ammonium sulfate (FAS) solution when the orange color turned greenish. Again the color changed from greenish to blue, that indicated the end point was near. Slowly added FAS drop-wise, until color suddenly changed to orange/brown color. Analyzed blanks in the same manner. Titrated FAS against dichromate solution every day. The final calculation as the formula below:

$$\text{COD}\left(\text{mg}\ \frac{O_2}{L}\right) = (A - B)\ \times M\ \times \frac{8000}{sample\ vol.(ml)} \tag{3.3}$$

$A = \text{FAS of blank sample}$ $\quad$ $\text{B} = \text{FAS of samples}$ $\quad$ $\text{M} = \text{Molarity value of FAS}$

3.2.7 Fourier Transform Infrared (FTIR)

The quality of produced water was studied through FTIR [**Figure 15**] test to check if the separated water still contains any other hydrocarbon components such as surfactant or PAM. Fourier Transform Infrared spectroscopy has been used for materials analyze technique, the infrared spectrum can show the fingerprint of the certain sample due to the peaks absorption which represent the frequency of vibration among the bonds of atoms, which are basic element of material so that we can identify the samples by this kind of fingerprint. Because every different materials have their different fingerprints and which is unique combination of bonds or atoms, there are no two compounds have exactly same infrared spectrum. In this case and property, every materials have their own unique identification which can be found by infrared spectroscopy. When we have same peaks at same range, so the different size of these peaks in the spectrum will represent the different amount of certain material.

Figure 14: COD Measurements

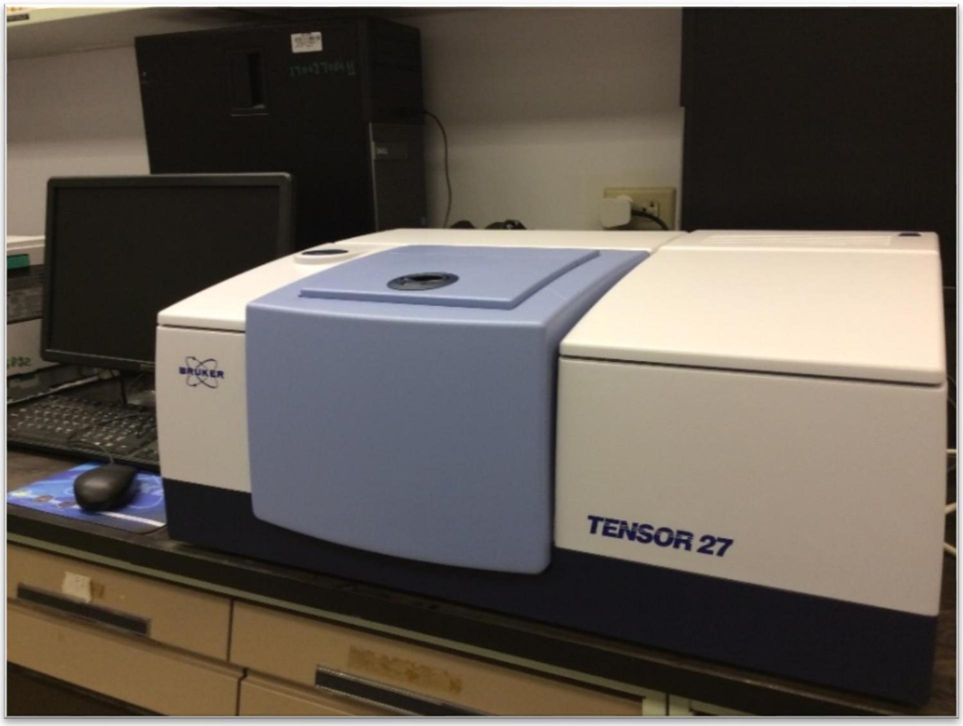


Figure 15: Fourier Transform Infrared (FTIR)

3.2.8 Zeta Potential

Brookhaven ZetaPALS instrument [**Figure 16**] was used to study the effect of double layer in the separation mechanism of surfactant phase from the emulsion as a result of adding PAM. Zeta potential (ζ) gives us the details on the stability of water in oil emulsion, which is controlled by some unknown strength colloids with electrical potential and the charged droplets velocity to be measured. When the zeta potential with large valves, no matter in positive or negative, it means the emulsion stability was increased and coalescence of droplets became more difficult, however the zeta potential values is dependent on the pH values, and there are some other factors also need to be considered for forecasting the coalescence of droplets.

The oil droplets in oil/water emulsion carry certain net charge at its surface. Usually the negative charge was carried based on the Helmholtz theory on the information of electrical double layers, and these negative charges in a straight line and near to the interface bound. The charges with negative ions will attract the positive ions from the emulsion and move to another zone with opposite charge, start forming the electrical double layers which may repel other ions of the oil droplets. Then these ions start keeping distance from the previous oil surface and going into another phase such as water phase, this is the reason of electrostatic potential decreases.

Oil/water emulsion are mainly stabilized through the electrostatic repulsion force among the oil droplets. If we consider the emulsion as a model, there is a distinction between the ions tightly bounded and the counter ions diffused in this solution, those ions are dependent on the droplets weakly. The inner layer is named Stern layer, and the amount of electrostatic potential that Stern layer carried named electrokinetic and zeta potential, the values of this zeta potential is greatly based on the emulsions stability.

The surfactants are main parameter to determine the high zeta potential, low interfacial tension and high interfacial shear viscosity. The repulsion forces electrically used to be neutralized when the polyvalent ions was added into the emulsion droplets with opposite charge, zeta potential begins to close zero and the coalescence will take place (Lissant et al., 1974).

Figure 16: **ZetaPALS**

CHAPTER 4

Destabilization and Treatment of Produced Water-Oil Emulsions using Anionic Polyacrylamide

Summary

Surfactant and polymer flooding technology can greatly enhance the oil recovery through the expansion of sweeping and displacing efficiency. The recovered oil from surfactant and polymer flooding emulsifies the residual chemical, which makes the separation of water from oil quite difficult, yet the impact of the enhanced oil recovery (EOR) chemicals on the produced water cycle is generally neglected in chemically-based EOR studies. This includes compatibility of EOR chemicals with the additives used to pre-treat the injected water or change reservoir wettability and result in producing oil/water emulsion after EOR breakthrough.

The produced water is believed to be the largest waste produced in oil and gas industries, as it contains different sort of organic and inorganic admixture. There are a number of treatment methods available for produced water. To separate water from oil in a much efficient manner and to reach the emission standard, a new class of water soluble polymer of polyacrylamides (PAMs) was used as destabilizing agents for water-oil emulsions, which have been stabilized by surfactant (Tallowamine Acetate).

The impact of the surface charge form, the density of polyacrylamides in turbidity reduction, zeta potential, COD, FTIR, viscosity and volume of separated water were

explored in this study. Different anionic polyacrylamide of different surface charge density were evaluated. Different anionic polyacrylamides were utilized, and at optimum dosage, anionic AN 934 PAM at its optimum concentration was proved as the best way to reduce the residual turbidity compared with other PAMs mentioned in this research. The effect of the different salinity (salt content: 200,000 ppm formation brine and 57,000 ppm seawater) of produced water will be evaluated using different PAM with different charge density as optimization. The results showed that the W/O emulsion stability related with its salinity, while the optimum concentration of demulsifier are same at both high and low salinity.

4.1 Introduction

The largest waste produced in oil and gas industries is believed to be the produced water, as it contains different sort of organic and inorganic admixture. The discharging of produced water contaminates not only the water, both surface and underground, but also the soil. There are a number of treatment methods available for produced water. To separate water from oil in a much efficient manner and to reach the discharge standard. Among common chemical EOR application by using surfactant (S) based on flooding technics due to the injection of surfactant to enhance the oil recovery through reduction of residual oil saturation, as well as by using polymer (P) flooding technics due to injection of predetermined amount of polymer into reservoir for enhancing oil recovery through a better sweep efficiency.

After the breakthrough because of the SP injected in EOR application or during production period, significant amount of SP chemicals will back to the surface in the formation of stable water in oil and oil in water emulsion (Di et al., 2001). Different studies have been conducted on the impact of EOR chemicals by using SP flooding on produced water treatment. Karhu in 2014 mentioned about the using of the polyelectrolytes and some electrolytes (Karhu et al., 2014); Al-Shamrani used the $Al_2(SO_4)_3$ and $Fe2(SO_4)_3$ as demulsifier which are most commonly used in wastewater treatment, the electrokinetic properties such as zeta potential and COD have been investigated (A. . Al-Shamrani et al., 2002). Wang studied the effect of HPAM as demulsifier in O/W emulsion from ASP flooding, the analysis were conducted on zeta potential, interfacial tension, and viscosity (Wang et al., 2011). Diego used certain copolymer to treat the W/O emulsion formed with crude oil and natural surfactant, the separated water have been studied through FTIR, volume only (Guzmán-Lucero et al., 2010). Argillier recently used the sulfonated polymer as demulsifier and O/W emulsion from SP flooding, interfacial tension and oil content have been analyzed (Argillier et al., 2014). However no literatures showed that different charge type and charge density of Polyacrylamides have been used in produced W/O emulsion treatment from SP flooding in EOR application.

In our work, to best of our knowledge, the PAM (Polyacrylamide) with different charge density as demulsifiers will be used which have never been studied before according literature, as well as there is no research in the literature showing the effect of the salinity (salt content) at 200,000 ppm and 57,000 ppm of produced water in emulsions destabilization. Three surface charger density of polyelectrolyte from low to medium and high will be used to investigate the effects of these different charge density in destabilization of emulsions will be evaluated. All previous studies have concluded that the mechanism of destabilization or separation is due to flocculation. While flocculation of fine particles in w/o emulsion may occurs because of charge neutralization, polymer bridging, depletion flocculation and some combination of these mechanisms have been investigated in our study through the combination of most common used analysis method such as: volume of separated water, turbidity, density, viscosity, FTIR, COD, and zeta potential.

4.2 Experimental Section

4.2.1 Stable Emulsion Preparation

In order to synthesis produced water, an emulsion of oil dispersed in formation brine was prepared. The water used in these preparations has different salinity content of 200,000 ppm formation brine and 57,000 ppm seawater as **Table 7**. A typical saturated hydrocarbon and common petroleum product diesel was used as oil phase. A concentrated W-O emulsion was prepared as in **Figure 17** by mixing the formation brine or seawater 60% (vol) with 40% (vol) of oil and surfactant (Armac HT Prills: Tallowamine Acetate) as **Table 6** using IKA Ultra Turrax mixer at 2000 rpm for 10 minutes. When the formation brine was used as a water phase, a very stable water in oil emulsion was formed. The stability was measured and the mixture remained stable for many days and there was no any phase separation except only small amount of diesel was formed at the top of the mixture. When the seawater was used as water phase, the W/O emulsion was also formed by the same method, however, the mixture remain stable only for 2 hours and then at the bottom of the vessel, small amount of water was separated from emulsion as well as some diesel was formed at the top. The emulsion is the low stability is due to the low salinity of the sea water compare to formation water (Al-Yaari et al., 2013).

Table 6: Tallowamine Acetate, Chemical and Physical properties

Characteristics	Value
Appearance, 20°C	Solid prills
Bulk density	550 kg/m^3
Density, 60°C	880 kg/m^3
Flash point	>100°C
Melting range	60 - 80°C
Particle size, prills	1-3 mm

Table 7: Chemical analysis of water used in w/o emulsion preparation

Ion	Water type concentration, mg/L (ppm)	
	Formation brine	Seawater
Na	59,000	18,300
Ca	23,400	650
Mg	1,510	2082.729
SO_4	110	4,290
Cl	137,000	32,200
HCO_3	353	120
Total dissolved Solid*	221,673	57642.729

* Sum of all the concentration of ions

Figure 17: Stable w/o emulsion

The above synthetic produced water is used in the de-emulsification tests. In this study, three potential types of anionic based PAM was defined as potential de-emulsifiers by using SNF FLOERGER, INC, France provided us with some polyacrylamides (PAM) based polyelectrolytes to be used for the preliminary test. Three methods were used to study the emulsion breakdown including jar test, turbidity and COD measurements. **Table 8** summarizes the properties of polyacrylamides used in this study.

To investigate the effect of different charge density of polyacrylamides as the demulsifies, anionic polyacrylamides with three different percentage charge density were investigated starting from low charge density AN 913, medium charge density AN 934, and high charge density AN 945.

Table 8: Types of properties of PAM used

PAM Types & Properties	**AN 913**	**AN 934**	**AN945**
Charge density	Low	Medium	High
Molecular weight	Standard*	Standard*	Standard*
Mesh size	2 maxi	2 maxi	2 maxi
Bulk density	0.80	0.80	0.80
Brookfield viscosity (cp)	1000	1650	1600

*Standard = 8 – 12 x 10^6 Dalton

4.2.2 Jar Test

The jar test was performed using Stuart Flocculator SW6. And the stable water in oil emulsion was prepared as the procedure described above and which were distributed into 6 different modified beakers which has one valve at the bottom for collecting the separated water from bottom directly. The experiments were conducted using a 400 ml of emulsion in six jars, and then a predetermined amount of PAM as demulsifier was transferred into the jars with 5 different concentrations of 600mg/L, 700mg/L, 800mg/L, 900mg/L, and 1000mg/L with allowing one jar without demulsifier to be considered as reference for comparing the enhancement of emulsion separation without demulsifier. The Jar test was performed at 250 rpm for 10 minutes to promote the coagulation process before it continued at 30 rpm for another 15 minutes to promote the flocculation and destabilization process. After the jar test, for emulsion formed with the formation brine (without PAM), the samples were kept for 24 hours to ensure stability of the emulsion. For this sample, no any phase separation was observed in the first 8 hours, however, the other 5 jars with demulsifier after 24 hours there were three phases showed: diesel at the top, emulsion at the middle and water separated at the bottom could be clearly identified. While the emulsion formed with the seawater, the volume was measured immediately after jar test because the stability of emulsion with seawater much lower which could stable at least 2 hour after stable emulsion formed without adding any PAM. And then the water separated at the bottom of jars were collected and different measurements were conducted on the separated water to study the effectiveness of demulsifier in the process of emulsion separation. The volume of water separated (WS) in percentage, was defined as vol % using the following equation:

$$WS\ (\text{vol}\ \%) = V/\ V° \times 100 \tag{4.1}$$

where V is the volume of the water separated and V° is the original volume of water contained. HACH 2100N Turbidimeter was used to measure the turbidity of the supernatant and to study the effectiveness of PAM in improving the pureness of the separated water. Density of the separated water was measured for viscosity calculation using density meter (Anton Paar, US). Chemical oxygen demand (COD) was measured after the separated water samples heated at 150°C for 2 hours using HACH COD reactor. Fourier transform infrared spectroscopy (FTIR) was used to check the presence of any chemical such as the PAM and or surfactant or demulsifier (Bruker Tensor27, UK). And Brookhaven ZetaPALS instrument was used to study the effect of double layer in the separation mechanism of surfactant phase from the emulsion as a result of adding demulsifier.

4.3 Results and Discussion

Volume of separated water. Figure 18 shows the effect of demulsifier concentration on the volume of water separated. As we can see in that increasing the concentration of PAM from 600 mg/L to 800 mg/L results in dramatically increase in the volume of water separated from 48.21% to 73.21% in case of brine and from 53.57% to 77.14% in case of seawater. While increasing the PAM concentration higher than 800 ppm did not show any increase in the separated water for both cases of brine and seawater which indicates that optimal PAM concentration is 800 mg/L. Some small flocs were formed when the concentration of polyacrylamide was less than 800mg/L but which in a state of suspension and not easy to separate. With an increase of polyacrylamide concentration, the effect of flocculating improved clearly, which was duo to the bridging occur between particles with polyacrylamide chains, while here the anionic polyacrylamide we used gives anionic character provided by the copolymerizing acrylamide. The main reason that the bridging occur here when polyacrylamide added as flocculant because of the action of its high molecular weight, two or three particles can form flocs because this bridge from function of high molecular weight, then by bridging help particles gather some random structure. Oil droplets start coalescence constantly, so when the concentration of polyacrylamide at both salinity of aqueous phase was higher than 800mg/L, no more oil droplets coalescence cause no more separation increase observably, this is due to the optimum concentration of flocculation required was achieved, further addition of polyacrylamide concentration will not increase volume of separated water efficiently. The optimum concentration of anionic polyacrylamide for flocculation is directly responsible for the amount of particles absorption. Thus, polyacrylamide bridging plays a main mechanism here, where these anionic polyacrylamide gather the particles to coalescence.

When, using formation brine as water phase instead of sea water, it was found that the formed emulsion was more stable, this may be due to higher salinity which is agree with what has been reported in the literature (Al-Yaari et al., 2013), which have been reported that as salinity increase the viscosity of the emulsion increases and this due to the large and strong oil drops created and hence become more stable. This means that treating emulsion produced from saline environment is more challenging, in term of both cost and handling.

In **Figure 20** each Jar test was prepared 400ml of emulsion, the amount of different charge density Anionic PAM were used. When Jar test is completed, we can see the emulsion break and clear liquid in the sample flocculated using AN 913 to AN 945. From the observation, the amount of oil at the top for all jars was around 100 ml after for 24 hours of settling.

Figure 19 compares the volume of separated water for the three different charge density anionic PAMs used in both formation brine and seawater. This figure clearly shows that mixing of those PAMs with seawater result in higher amount of separated water compare to formation brine, and we can see also that increasing the charge density of PAM will result in increasing the volume of separated water for both brines. As an increase of charge density on polyacrylamide cause an increase of zeta potential values in **Table 13**, the oil droplets became difficult to aggregate together because high electrostatic repulsion exist in high charge density, so the emulsion relatively more stable than the lower change density, that is the reason the volume of separated water decreased to 68.5 % in the case of formation brine and 65.7 % in the case of seawater used as aqueous phase.

Turbidity test. The effect of polyacrylamide as flocculant on turbidity of separated water after jar test is demonstrated in **Figure 21**. The concentration of PAM 800mg/L shows the lowest turbidity among the five concentrations examined. This test also shows that the existence of some specific interaction to be balanced in weighing of electrostatic repulsion among the negative charged particles in aqueous phase and anionic polyacrylamide. The optimal demulsifier concentration is 800 mg/L for both cases of formation water and seawater, increasing the PAM concentration from 600 mg/L to 800 mg/L did not show significant effect on separated water turbidity but when the concentrations of higher than 800 ppm were used the turbidity unit increase suddenly from 14 NTU to 15.6 NTU in case of brine and from 10.9 NTU to 12.3 NTU in case of

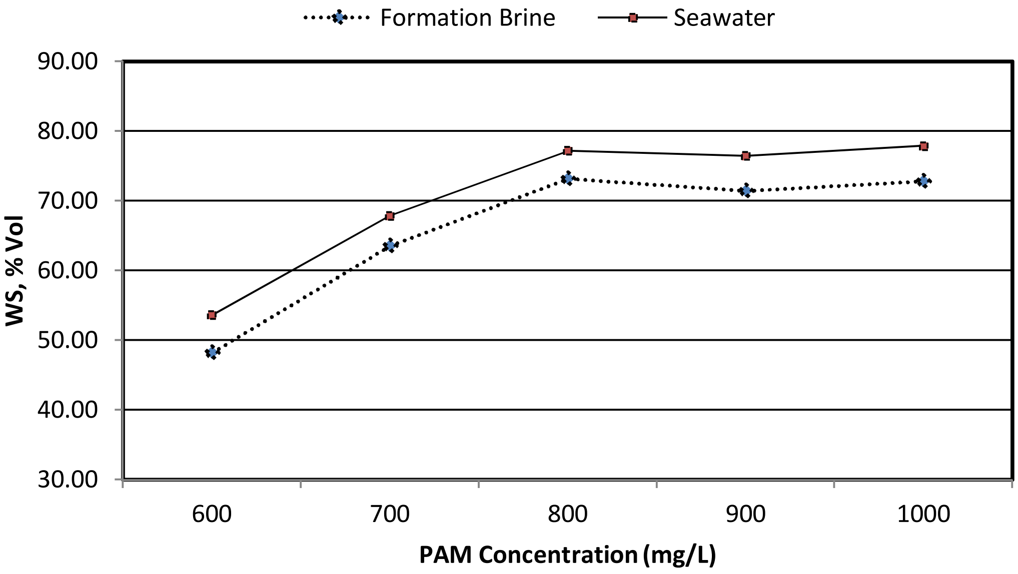


Figure 18: Demulsifying efficiency as a function of its concentration

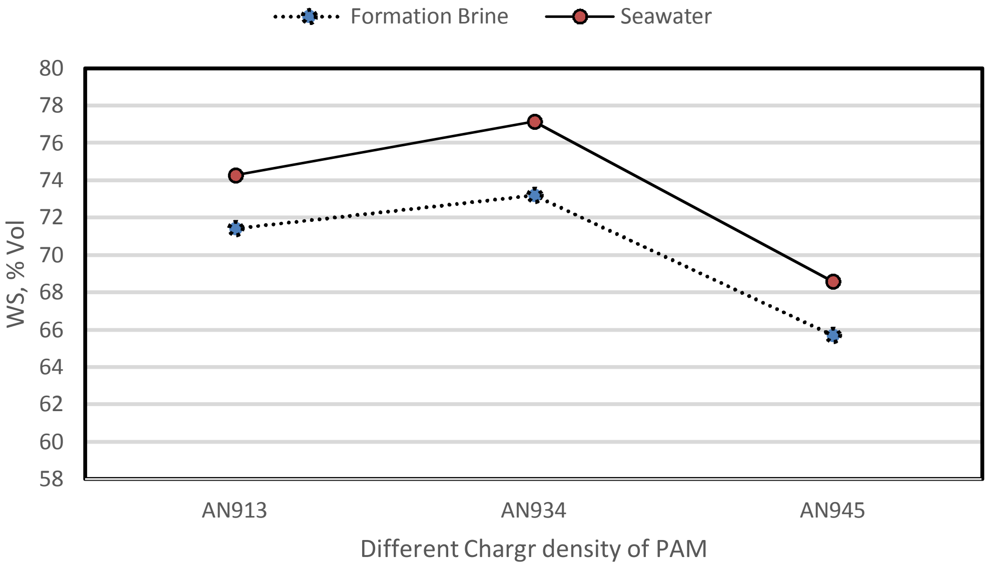


Figure 19: Demulsifying efficiency as a function of different charge density of PAM

Figure 20: Separation after Jar test at different charge density

seawater when PAM concentration increased to 900 mg/L due to the interaction overweighting the electrostatic repulsion among the charged particles in original aqueous phase and anionic polyacrylamide.

Figure 22 clearly show that medium charge density PAM AN 934 exhibits the lower turbidity for both formation brine and seawater. This is expected as the percentage charge density increases to certain level the adsorption of the amide group to the surface of the droplet is increases and hence promote the destabilization process. However, increasing the percentage surface charge to every high limit could create flocculation depletion and increase the overall repulsive force. That is why the turgidity increase by changing the charge density from high (PAM AN934) to very high (PAM AN945).

Density measurement. As we can see in **Figure 23** shows mixing of formation brine and seawater with PAM result in decreasing density of those brines as a result of removing some cations and anions initially present on those brines. The density of formation brine was decreased to 1.13 when 600mg/L of PAM was mixed with formation brine after jar test. Then increasing the concentration of PAM was resulting in decrease in formation brine density from 1.130 to 1.096. The same effect was noticed when PAM is mixed with seawater but due to lower concentration of salt in seawater compared to formation brine the rate of decrease in density is lower this time, as we can see in **Figure 23** the density of seawater decreased from 1.031 to 1.026 when PAM concentration increased from 600mg/L to 1000mg/L. The density of separated water shows slight decrease at both aqueous phase due to the mixing with an increase volume of polyacrylamide, because the decreased density for both case here is directly related to density of polyacrylamide itself,

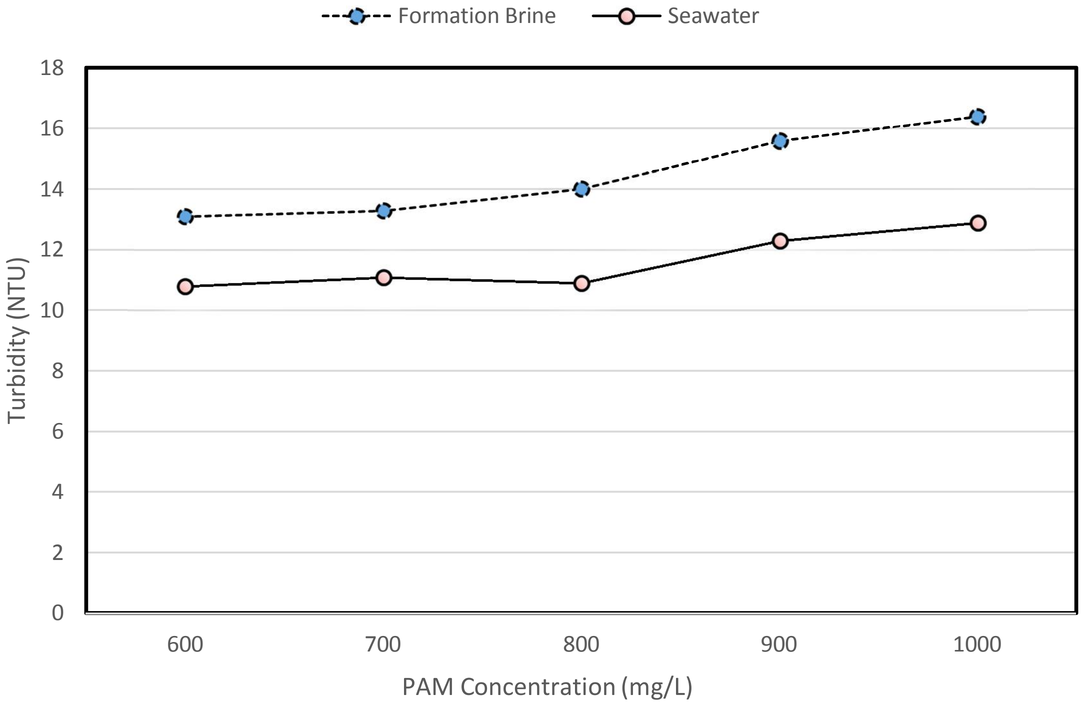


Figure 21: Turbidity test results

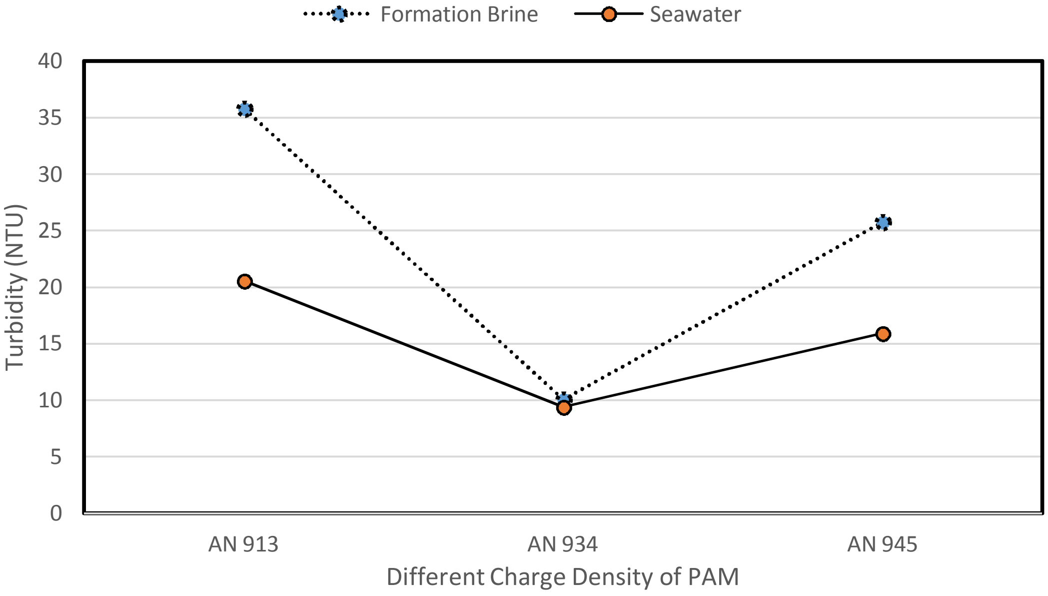


Figure 22: Turbidity test results

the original density of polyacrylamide is around 0.8 in **Table 8**, so as an increase of polyacrylamide concentration means more volume of polyacrylamide have been added, then density of separated water at formation brine decreased more obviously due to the gap between 0.8 and 1.15 is greater than between 0.8 and 1.03 at seawater case.

Figure 24 compares the density values of the three different charge density of anionic PAMs mixed with both formation brine and seawater. This figure also shows that increasing charge density of PAM results in very slight decrease in density of separated water from both brines. This slight difference on density values for the 3 different charge density of PAM was due to the use of the same volume of PAM since the density values of separated water is mainly affected by the added volume of PAM. The density of separated water shows slight decrease at both aqueous phase due to the mixing with an increase volume of polyacrylamide, because the decreased density for both case here is directly related to density of polyacrylamide itself, the original density of polyacrylamide is around 0.8 in **Table 8**, so as an increase of polyacrylamide concentration means more volume of polyacrylamide have been added, then density of separated water at formation brine decreased more obviously due to the gap between 0.8 and 1.15 is greater than between 0.8 and 1.03 at seawater case.

Viscosity measurement. Figure 25 shows the results of viscosity studies for both formation brine and seawater after treatment with different PAM concentration. Compare to both original viscosity of formation brine and seawater, it is obviously showing the viscosity increase sharply at both salinity aqueous phase because the viscosity of polyacrylamide itself is extremely high, which is observed during preparing the polyacrylamide solution and when transfer it to jar test. So, with an increase of polyacrylamide concentration or volume added into emulsion. After interaction of particles between oil droplets and aqueous phase, the oil droplets coalescence and separation from aqueous phase by the interphase of emulsion could not be absorbed with polyacrylamide. The separated aqueous phase mixed with polyacrylamide solution after interaction between oil droplets and aqueous phase, the viscosity of separated water at both case increased as concentration of polyacrylamide increased, this is because the original viscosity of polyacrylamide used here is huge, from **Table 8** we can know the viscosity of polyacrylamide is around 1650 cp. So it is acceptable when the concentration of polyacrylamide was increased, the viscosity of separated water after jar test also increased, the polyacrylamide itself make separated water from both cases of formation brine and seawater with an increase of viscosity results as **Figure 25**.

Figure 26 summarizes the viscosity values of separated water when the three different charge density of anionic PAM were mixed with formation brine and seawater, the viscosity values were rapidly decreased with increasing the charge density of PAM, the formation brine viscosity was decreased from 3.577 cp to 2.728 cp while seawater viscosity decreased from 2.894 cp to 2.504 cp.

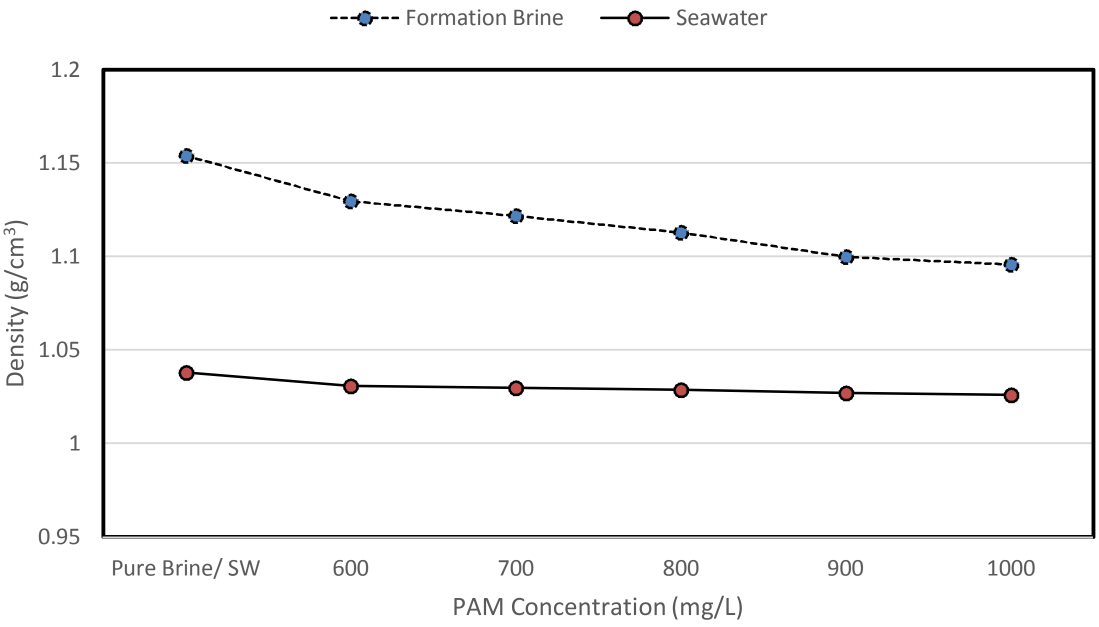


Figure 23: Density of separated water

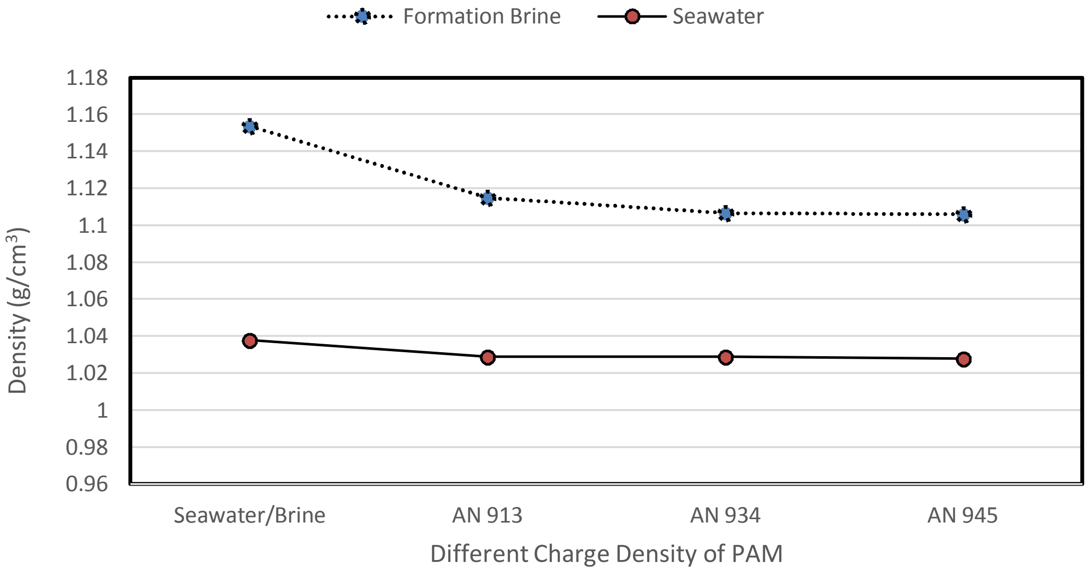


Figure 24: Density of separated water at different salinity

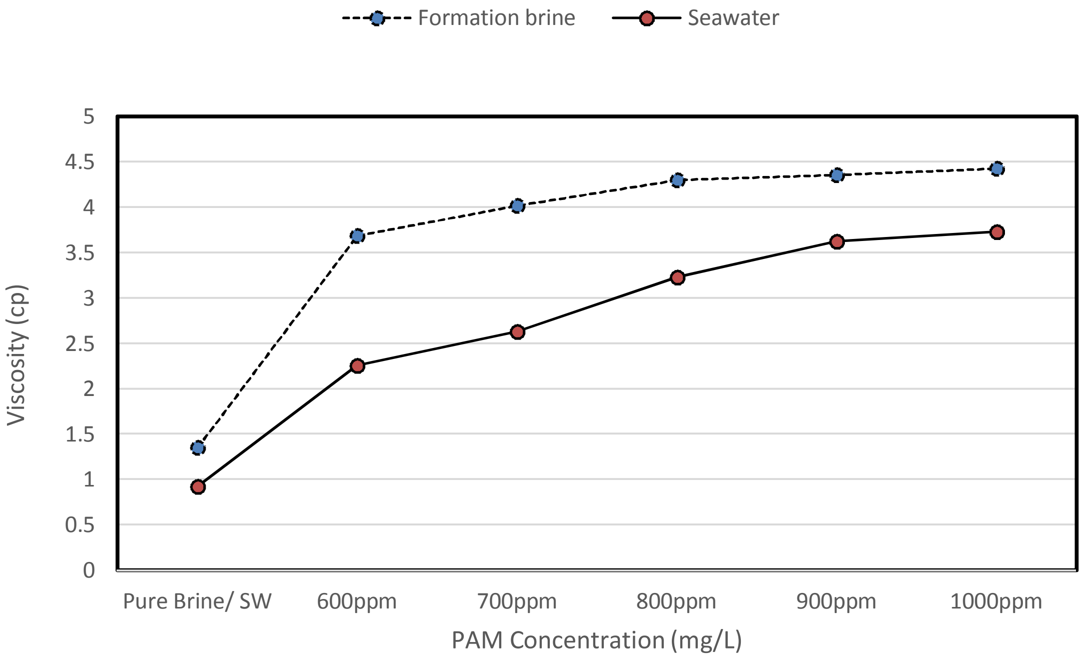


Figure 25: Viscosity vs PAM concentrations

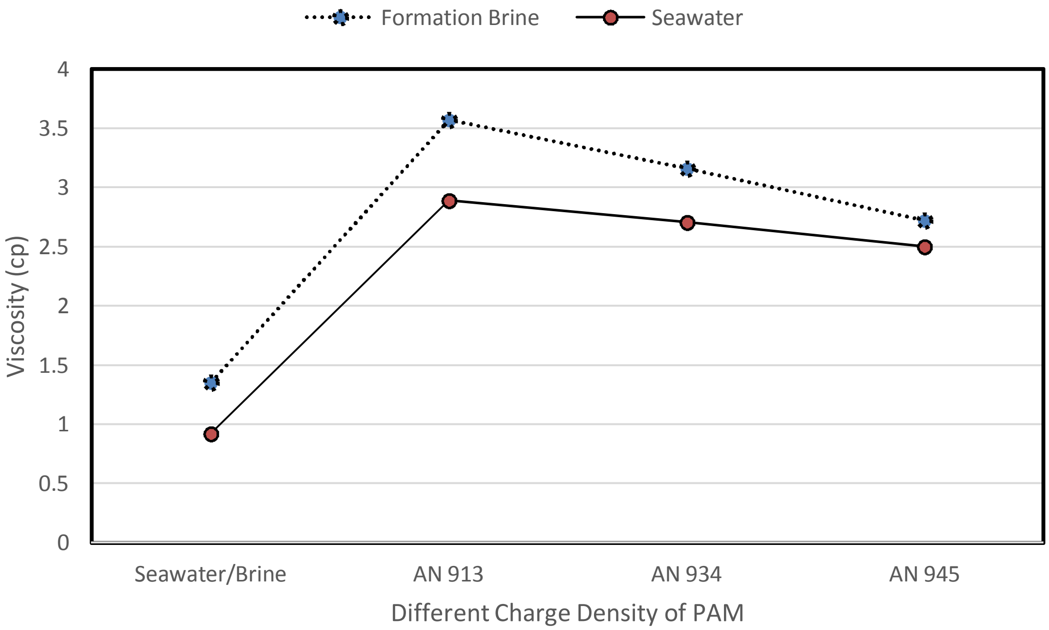


Figure 26: Viscosity at different charge density

Chemical Oxygen Demand (COD). The COD of original synthetic emulsion in formation brine was measured and found to be 63258.63 ppm, while the COD of emulsion in seawater was found to be 48660.48 ppm. **Table 9** summarizes the results of COD reduction test and it is clear that emulsion destabilized using 600 mg/L of PAM gives the lowest COD reduction rates of 98.75% and 98.83% for formation brine and seawater respectively. Increasing the PAM concentration will gradually increase the COD reduction, 97.96% and 98.37% of COD reduction efficiency could be achieved at 800 mg/L of PAM. By adding PAM in different concentration from 600mg/L to 1000mg/L, after jar test and coagulation treatment, COD reduction efficiency in formation brine and seawater reached 97.56% and 97.22%, respectively.

Table 9: COD reduction rates

PAM Concentrations	COD in Brine (ppm)	COD Reduction Rates	COD in Seawater (ppm)	COD Reduction Rates
600mg/L	792.1	98.75%	570.3	98.83%
700mg/L	1415.0	97.76%	865.9	98.22%
800mg/L	1288.3	97.96%	794.1	98.37%
900mg/L	1541.8	97.03%	1288.3	97.35%
1000mg/L	1879.7	97.56%	1351.7	97.22%
Emulsion	93258.6		48660.5	

The COD of original synthetic emulsion in formation brine and seawater was measured. The values of COD were found to 63258.63 ppm for formation brine, 48660.48 ppm for sea water. **Table 10** summarizes the results of COD reduction test, low charge density of PAM gives the lowest COD reduction rate of 98.59 % and 98.73% for formation brine and seawater respectively. Increasing the PAM charge density gradually decreases the COD reduction, medium charge density AN 934 gives COD reduction of 97.96% and 98.37% for formation brine and seawater. Use of the higher charge density of PAM AN 945 results in 97.49% and 97.68% COD reduction for both brines. It is worthy to mention that reaching 98% of COD reduction showed that Anionic PAM is an efficient demulsifier and can effectively remove the dissolved hydrocarbon under high salinity.

Table 10: COD reduction Rates at different charge density of PAM

PAM Types	COD in Brine (ppm)	COD Reduction Rates	COD in Seawater (ppm)	COD Reduction Rates
AN 913	892	98.59%	620	98.73%
AN 934	1288	97.96%	794	98.37%
AN 945	1585	97.49%	1128	97.68%
Emulsion	63258		48660	

Fourier transform infrared spectroscopy (FTIR). FTIR measurement was performed to verify whether the separated water after jar test still contains any other components such as surfactant or polyacrylamide, the measurement was conducted with the spectra of pure seawater compare to the other five samples collected from separated water after jar test at 5 different concentrations of polyacrylamide [**Figure 27**], and to examine the existence of surfactant in separated water after jar test as **Figure 28**, and the seawater used as background for all of the measurements. The separated water after Jar test at 5 different concentrations match with Claudia's study (Simonescu, 2012), the concentration of component can be detected based on intensity of the absorption, in **Figure 27** as an increase of concentration of polyacrylamide, the intensity of absorptions are also increased. The comparison between spectra of polyacrylamide and spectra of surfactant, results is shown in **Figure 28** and **Table 11** below:

Table 11: FTIR Spectra Chart

Peak Position (cm^{-1})	**Peak Assignment**
3600 – 3200	*N-H stretching for -NH_2 emanating from PAM*
2950 – 2200	*C-H stretching for CH_2*
1460	*C-H deformation for CH_2*
1300	*C-H deformation for CH*
1190	*N-H wagging for –NH_2*

The **Table 11** shows the chemical functional groups present in the FTIR spectra of sea water and PAM in very high concentration, as well as the separated water PAM in different concentrations. Especially, PAM solution FTIR spectrum reveals the chemical functional groups listed in **Table 2**. The evidence of traces of PAM solution in seawater and emulsion samples can be justified by the similitude of the peaks of these functional groups (as seen in their spectra) when compared to that of PAM solution revealing high peaks. This existence is due to the PAM overdose, while there is no evidence of surfactant spectra in separated water sample. So we can concluded that overdosed polyacrylamide still exists in separated water after jar test but there is no any residual surfactant after destabilization of emulsion.

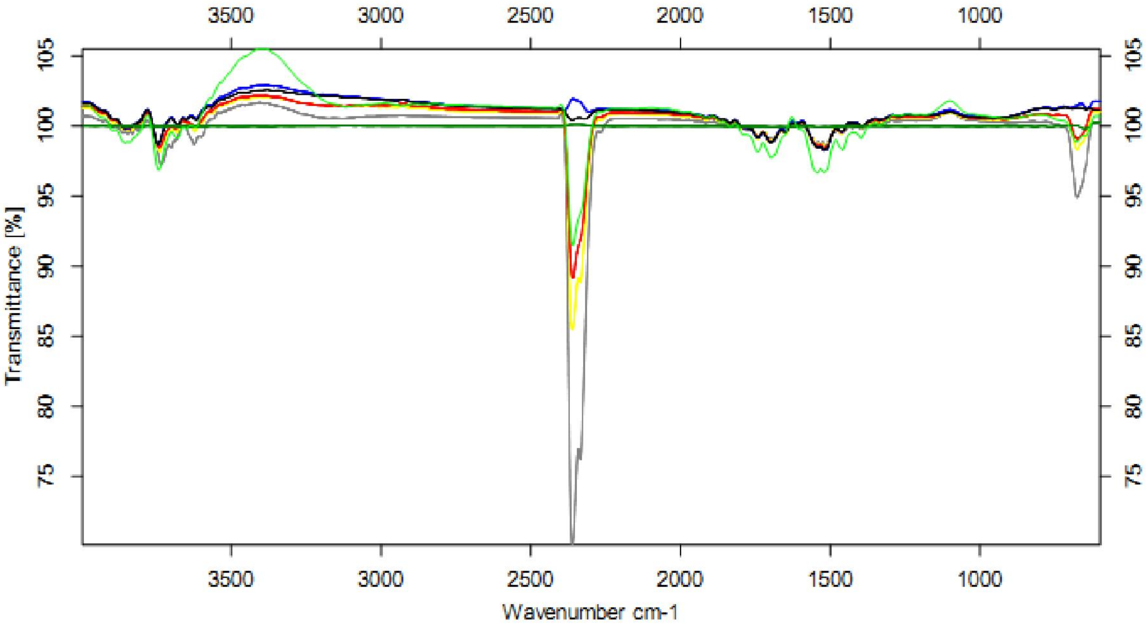


Figure 27: FTIR spectra of PAM vs separated seawater

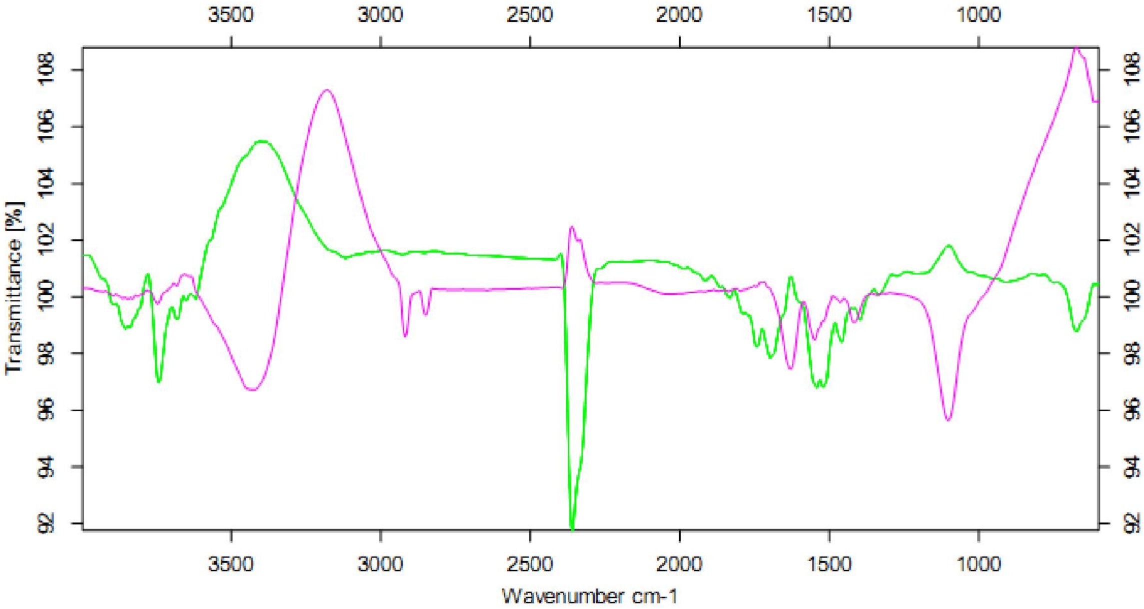


Figure 28: FTIR spectra of PAM vs surfactant

Zeta potential. To investigate the effect of different concentration of demulsifiers such as PAM, a W/O emulsion was prepared to mimic the produce emulsion from the oilfields, using sea water as water phase and diesel as oil phase, a suitable emulsifier (ARMAC HT PRILLS) was used to form the emulsion. Emulsifiers, due to their amphiphilic nature, adsorb at the interface between oil and water, then form an interfacial film, which reduce interfacial tension. The reduction of interfacial tension through addition of emulsifiers allows emulsion formation. For an electro-statically stabilized emulsions, it was found that the higher the absolute value of zeta potential, the more stable the dispersion is likely to be, in another words emulsion will be stable, thus coalescence of droplets will be more difficult (Zhou et al., 2009). The prepared emulsion was distributed into 6 beakers as shown in **Figure 8**, different concentrations of the PAM were added to each jars, then the effect of demulsifier concentration was examined using the jar test, it was observed that the emulsions were separated into oil and water phases after the jar test was completed, with some parts remained in the emulsified form, a samples were collected from the each beaker, afterward a value of the zeta potential was measured as illustrated in **Figure 29**. The higher zeta potential value (-30 mV) was observed, when no PAM added to the emulsion. While the addition of 600 mg/L of the PAM resulted in slight reduction in the zeta potential value to -26.9 mV (10.3% reduction), when the concentration increased from 700 mg/L to 900 mg/L, the zeta potential reading result increased from -25.5 mV to -16.39 mV (35.7% reduction), further increase in the concentration (1000 mg/L) did not result in a significant reduction (7.3% decrease). Conclusively, with increasing the demulsifier concentration (PAM) reduction in the absolute value of the zeta potential was noticed, this could be related to adsorption of the PAM molecules on the surface of the oil droplets of the dispersed phase (seawater), which promote the aggregation, by the formation of inter particle bridging between dispersed phase droplets. More specifically, since the positive charge from aqueous phase will be very small, so it seems like the polyacrylamide molecules just attached in the end not along the length of the bond chain, so the electrostatic interaction is from this type of bonding, there is a beginning of zeta potential when some absorption become more difficult even impossible, while this kind of bonding still have repulsion force between emulsion particles, and this repulsion force can help the particles to bridge, although individual bond strength of polyacrylamide is low, but the molecular weight of polyacrylamide is very high more than one million, it can form great amount of these bonds, then the bonding force become high overall. The absorbed charged polyacrylamide molecular cause the reduction of zeta potential as **Table 12**, which allow the particles gather together by Van der Waals attraction. So the polyacrylamide bond ends attaches two particles, then more absorption occur cause the particles to coalescence (Moss and Dymond, 1978).

Table 12: Zeta Potential Measurement Results

PAM concentrations (mg/L)	Ave. Zeta Potential (mv)
0	-30
600	-26.90
700	-25.50
800	-22.50
900	-16.39
1000	-15.20

Table 13 shows the study of effect of PAM charge density on the double layer, this figure indicate clearly that the interface between emulsion and separated seawater is negatively charge for all the PAMs with different charge density used in this study. And increasing charge density of PAM resulted in increasing the negative magnitude of the zeta potential at separated water/emulsion interface.

Table 13: Zeta potential results at different charge density

Measurement	**AN 913**	**AN 934**	**AN 945**
1	-20.39	-23.37	-25.46
2	-22.02	-28.2	-34.62
3	-21.18	-25.67	-37.72
Average	-21.18	-25.67	-32.60

It has long been accepted that zeta potential is a very good indication of the magnitude of the electrical repulsion and interaction forces between colloidal particles. Measurements of zeta potential are commonly used to evaluate the stability of colloidal and particles and oil droplets. If all the colloidal particles or oil droplets in suspension have a large negative or positive zeta potential, then the system will remain in a stable status and there will be no tendency for the particles or emulsion to come together. However, if the particles or oil droplets have low zeta potential values, then there will be tendency for the particles coming together and flocculating. In general, colloidal particles or oil droplets in suspensions with zeta potentials more positive than +30 mV or more negative than −30 mV are normally considered stable (Duman and Tunç, 2009). **Figure 30** shows the relation between the zeta potential of oil droplets at different PAM types. The results show that the emulsion can destabilize since the zeta potential values of at least two of the PAMs less than -30 mV.

4.4 Conclusions

The effects of different concentration and charge density of polyacrylamide on destabilization of water in oil emulsion under different salinity have been investigated and the following conclusions were drawn:

- Generally, the polyacrylamides were successfully used as demulsifier of produced W/O emulsion prepared with Tallowamine acetate as surfactant and different salinity of water as water phase, diesel as oil phase because polyacrylamide bridging to reduce the zeta potential of colloidal system thus stability of emulsion was also decreased.
- Different types and charge density of polyacrylamides were found very critical on destabilization of W/O emulsion. Higher charge density of polyacrylamide cause higher Zeta potential results, which indicated that the emulsion will remain stable state and not easy to break.
- Low concentration of Anionic polyacrylamide was found more efficient on destabilization of W/O emulsion compare to Cationic and Amphoteric polyacrylamides.

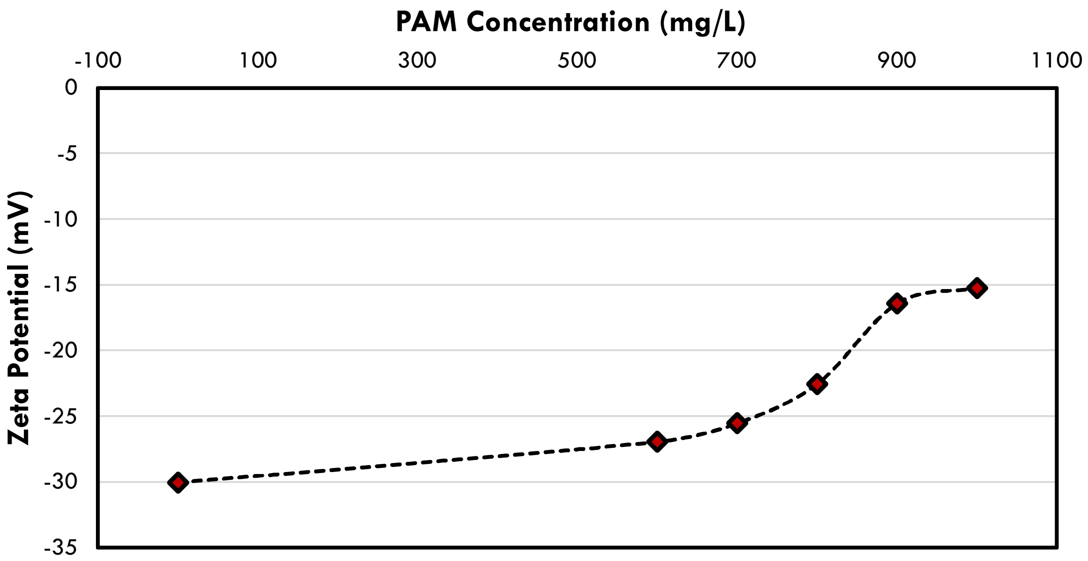


Figure 29: Zeta Potential Measurement Results at pH 7.5, room temperature

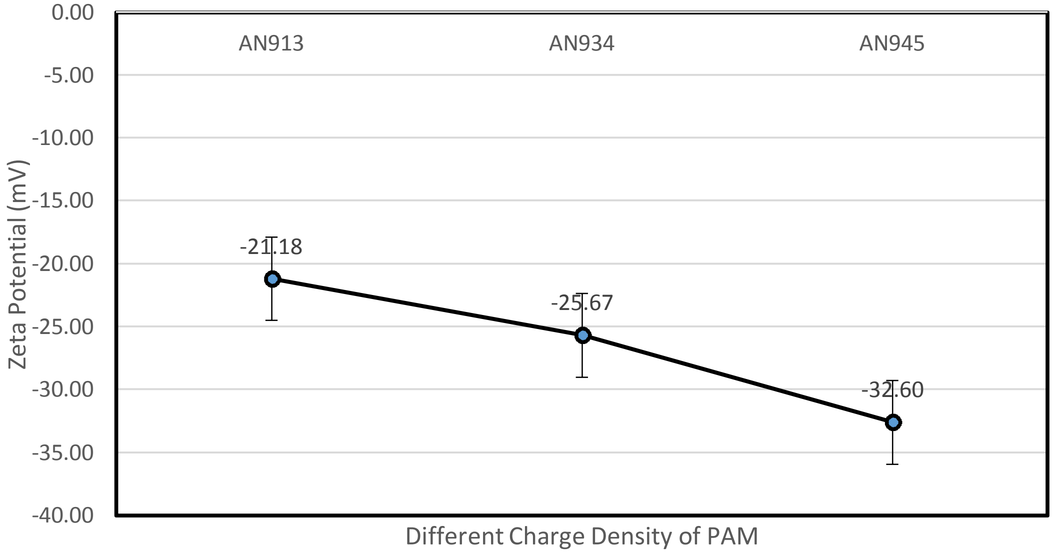


Figure 30: Zeta potential results at different charge density

CHAPTER 5

Destabilization and Treatment of Produced Water-Oil Emulsions using Anionic Polymer with Existence of Electrolytes

Summary

Surfactant and polymer flooding technology can greatly enhance the oil recovery through the expansion of sweeping and displacing efficiency. The recovered oil from surfactant and polymer flooding emulsifies the residual chemical, which makes the separation of water from oil quite difficult, yet the impact of the enhanced oil recovery (EOR) chemicals on the produced water cycle is generally neglected in chemically-based EOR studies. This includes compatibility of EOR chemicals with the additives used to pre-treat the injected water or change reservoir wettability and result in producing oil/water emulsion after EOR breakthrough.

The largest waste produced in oil and gas industries is believed to be the produced water, as it contains different sort of organic and inorganic admixture. There are a number of treatment methods available for produced water. To separate water from oil in a much efficient manner and to reach the emission standard, a new class of water soluble polymer of polyacrylamides (PAMs) with the addition of aluminum and ferrous sulphate were used

as destabilizing agents for water/oil emulsions, which have been stabilized by surfactant (Tallowamine Acetate).

The impact of polyacrylamides with the addition of sulphates in turbidity reduction, COD, viscosity of volume separated water, and zeta potential were explored in this study. The effects of electrolytes such as aluminum sulphates and ferrous sulphate on produced water degree of flocculation in the existence of anionic polyacrylamide were investigated in terms of turbidity reduction and volume of separated water after jar test. Different concentrations of both sulphates added into optimum concentration polyacrylamide selected from jar test were utilized, and at optimum dosage, anionic AN 934 PAM with aluminum sulphate at its optimum concentration was proved as the best way to reduce the residual turbidity compared with other additives mentioned in this research. The results showed that the volume of separated water increased more than 25% compared when only PAMs were used, and the turbidity, viscosity, and COD reduction of separated water improved significantly. Addition of electrolytes such as aluminum sulphate and ferrous sulphate into polyacrylamide are both enhance the destabilization of water in oil emulsion in general compare to when only polyacrylamide used.

5.1 Introduction

Water is most precious commodity needed in all human activities and for all in general. The large quantities of produced water have been generated in oil and gas industry. There are eight barrel of associated water for producing a barrel of oil. Produced water rates are increasing as the more sensitive production and exploration expands, while the discharge limits are being tightened for all environmental concerns.

In last over 30 to 40 years, there are various technologies of produced water treatment have been introduced, this paper focus on the new class of produced water treatment using Polyacrylamide (PAM) with the addition of most common demulsifier such as aluminum sulphate and ferrous sulphate (Bratskaya et al., 2006).

From the literature review, Twaiq used synthetic solid microporous organosilicate material to be used as adsorbent to study the oil removal oil-in-water emulsion system. His results showed that the cationic surfactant has more adsorption than the neutral surfactant (Twaiq et al., 2012), while in our studies, the very effective neutral surfactant which could form extremely stable emulsion have been used. Pablo studied when the aluminum electrodes are used, the effects of under different parameters such as pH, oil content, electrical charge pass, operation mode and electrolyte (Cañizares et al., 2007). Bensadok used different chemical demulsifiers to treat the cutting oil emulsion. The separation kinetic movement of the oil emulsion was studied as well as the volume of separated water as function of certain time, the optimal concentration of demulsifiers have been found by Jar test experiments (Bensadok et al., 2007). Huang studied the W/O emulsion from petroleum sludge, the characteristics of this kind of emulsion need to be treated before discharge to environment (Huang et al., 2014). Some previous research also have studied the mechanism of the influences made by PAM on the characters of produced water/oil emulsion through interfacial tension, interface strength, and interface electric property of oil in water wastewater system, but only single PAM has been used. However, the optimal concentration among different charge type and charge density of PAM will selected with addition of aluminium and ferrous sulphate as mixture of demulsifier have never been studied, the optimal concentration of sulphates should be used to achieve most efficient separation will be investigated in our study.

In our work, PAM (Polyacrylamide) with addition of electrolytes such as aluminum sulphate and ferrous sulphate as demulsifiers will be used which have never studied before according literature in emulsions destabilization. Different concentrations of electrolytes with the optimum concentration of polyacrylamide was proved as the best way to reduce the residual turbidity compared with other additives mentioned in this research. The mechanism of the flocculation of fine particles in W/O emulsion may occurs because of charge neutralization because of the cations from addition of Al^{3+} and Fe^{2+}, polymer bridging because of the high molecular weight of PAM, depletion flocculation and some combination of these mechanisms have been investigated in our study through the combination of most common used analysis method such as: volume of separated water, turbidity, density, viscosity, FTIR, COD, and zeta potential.

5.2 Experimental Section

5.2.1 Materials

In order to preparing an emulsion of oil dispersed in formation brine. The water used in these preparations has salinity content of 200,000 ppm formation brine. A typical saturated hydrocarbon and common petroleum product diesel was used as oil phase. A concentrated W-O emulsion was prepared by mixing the formation brine or seawater 60% (vol) with 40% (vol) of oil and surfactant (Armac HT Prills: Tallowamine Acetate) using IKA Ultra Turrax mixer at 2000 rpm for 10 minutes. When the formation brine was used as a water phase, a very stable water in oil emulsion was formed. The stability was measured and the mixture remained stable for many days and there was no any phase separation except only small amount of diesel was formed at the top of the mixture.

Table 14: Tallowamine Acetate, Chemical and Physical properties

Characteristics	**Value**
Appearance, 20°C	Solid prills
Bulk density	550 kg/m^3
Density, 60°C	880 kg/m^3
Flash point	>100°C
Melting range	60 - 80°C
Particle size, prills	1-3 mm

Table 15: Chemical analysis of water used in w/o emulsion preparation

Ion	**Water type concentration, mg/L (ppm)**
	Formation brine
Na	59,000
Ca	23,400
Mg	1,510
SO_4	110
Cl	137,000
HCO_3	353
Total dissolved Solid*	221,673

* Sum of all the concentration of ions

The above synthetic PW is used in the de-emulsification tests. SNF FLOERGER, INC, France provided us with some polyacrylamide (PAM) based polyelectrolytes to be used for the preliminary test.

In these set of experiments, the PAM was prepared for Jar test using the previously determined optimal concentration at 800mg/L. The electrolytes such as aluminum and ferrous sulphate were added at the same time with PAM.

Table 16: Types of properties of PAM AN 934 used

PAM Types & Properties	AN 934
Charge density	Medium
Molecular weight	Standard*
Mesh size	2 maxi
Bulk density	0.80
Brookfield viscosity (cp)	1650

*Standard = 8 – 12 x 10^6 Dalton

5.2.2 Jar Test

The jar test was performed using Stuart Flocculator SW6. And the stable water in oil emulsion was prepared as the procedure described above and which were distributed into

6 different modified beakers which has one valve at the bottom for collecting the separated water from bottom directly. The experiments were conducted using a 400 ml of emulsion in six jars, and then a predetermined amount of PAM with optimal concentration of 800 mg/L as demulsifier, The aluminum and ferrous sulphate were added at the same time with PAM was transferred into the jars with 6 different concentrations of 50mg, 250mg, 500mg, 1000mg, 1500mg and 2000mg. The Jar test was performed at 250 rpm for 10 minutes to promote the coagulation process before it continued at 30 rpm for another 15 minutes to promote the flocculation and destabilization process. After the jar test, for emulsion formed with the formation brine (without PMA), the samples were kept for 24 hours to ensure stability of the emulsion. For this sample, no any phase separation was observed in the first 8 hours, however, the other 6 jars with demulsifier after 24 hours there were three phases showed: diesel at the top, emulsion at the middle and water separated at the bottom could be clearly identified. And then the water separated at the bottom of jars were collected and different measurements were conducted on the separated water to study the effectiveness of demulsifier in the process of emulsion separation. The volume of water separated (WS) in percentage, was defined as vol % using the following equation:

$$\text{WS (vol \%)} = V/ V^{\circ} \times 100 \tag{5.1}$$

where V is the volume of the water separated and V° is the original volume of water contained. HACH 2100N Turbidimeter was used to measure the turbidity of the supernatant and to study the effectiveness of PAM in improving the pureness of the separated water. Density of the separated water was measured for viscosity calculation using density meter (Anton Paar, US). Chemical oxygen demand (COD) was measured after the separated water samples heated at 150°C for 2 hours using HACH COD reactor.

5.3 Results and Discussions

5.3.1 Volume of Separated Water

The volume of emulsion for Jar test was prepared 400 ml for each sample, the same volume of Anionic PAM was used for each emulsion sample, and six different dosage of Aluminum sulphates of 50 mg, 250 mg, 500 mg, 1000 mg, 1500 mg and 2000 mg have been investigated. After Jar test completed, the see the emulsion breakdown was very obvious and the clearance of the separated water increase as the dosage of Aluminum sulphate increased. Consequently, the amount of oil at the top for all jars was found to be around 80 ml to 100 ml after settle down for 24 hours.

The color of the separated water change for the sample that coagulated using ferrous sulphate in **Figure 32**, because of the property of ferrous sulphate itself. **Figure 33** shows the volume of separated water when aluminum sulphate and ferrous sulphate were added to PAM. The results indicates that increasing the concentration of sulphates up to 500mg have no effect on the volume of separated water, while increasing the concentration higher than 500mg gradually increased the volume of separated water and adding same amount of aluminum sulphate result in higher increase in volume of separated water than ferrous sulphate. The volume of separated water increased up to 22% when 2000 mg aluminum sulphate existed with PAM.

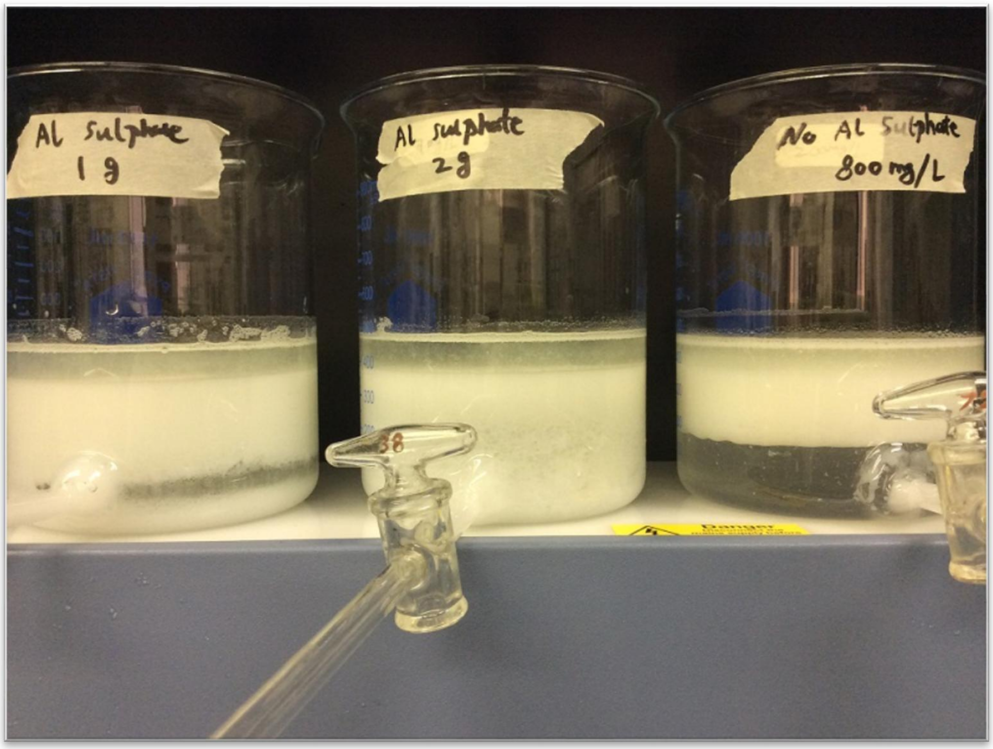


Figure 31: Separation after Jar test when aluminum sulphate added

Figure 32: Separation after Jar test when ferrous sulphate added

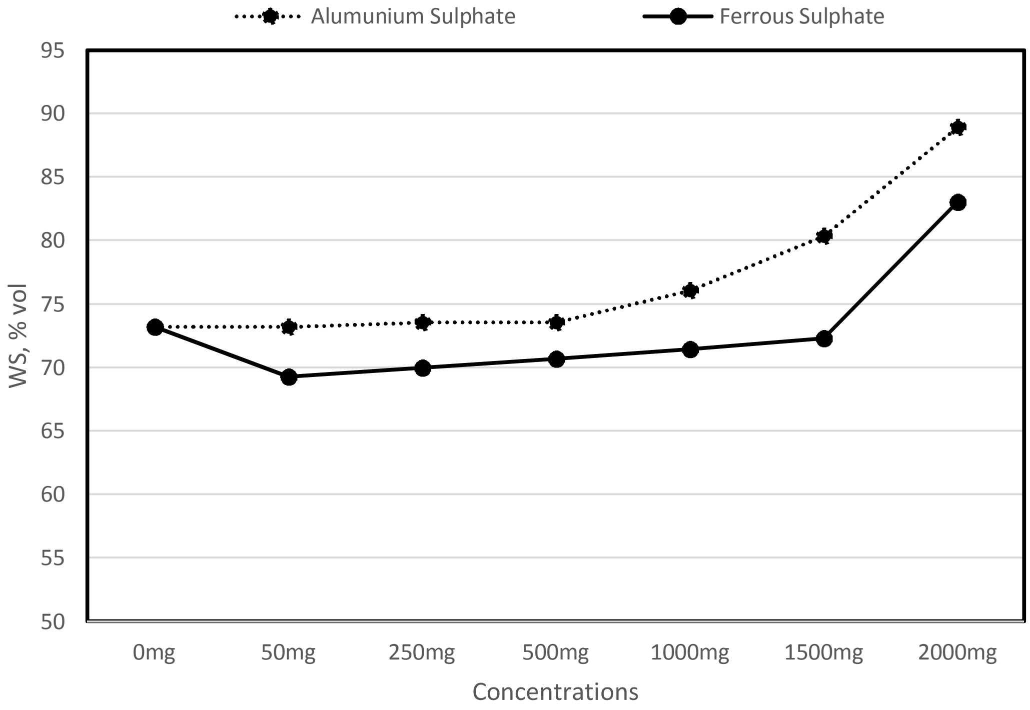


Figure 33: Volume of separated water when existence of sulphates

5.3.2 Turbidity Test

Figure 34 shows that addition of ferrous sulphate significantly increased the turbidity value of separated water from 10.1 NTU to 18.8 NTU due to the nature of ferrous. It is noticed that the turbidity value at 0 mg was 10.1 NTU, which is the turbidity value of separated water at optimal concentration of 800 mg/L as the experiment previously. The turbidity value of pure W/O emulsion is more than 1000 NTUs name matter in the case of formation brine or seawater. On the other hand addition of 500 mg of aluminum sulphate lead to significant decrease in turbidity of separated water from 10.1 NTU to 0.655 NTU, more increase of aluminum sulphate concentration showed slight decrease in turbidity value. This result shows that only small amount of aluminum sulphate was enough to further remove the suspended remaining oil droplets. Hence one can conclude that adding coagulant in addition to PAM will improve the quality of the separated water.

5.3.3 Density Measurement

Table 17 compares the density values when aluminum sulphate and ferrous sulphate were added with 800mg/L PAM, this table shows that increasing concentration of both aluminum sulphate and ferrous sulphate results in very slight decrease in density of separated water. The reduction is due to the removal of suspended oil droplet by Aluminum sulphate or ferrous sulphate and this in good agreement with turbidity results above.

Table 17: Density when aluminum sulphate and ferrous sulphate exists

Concentrations	50mg	250mg	500mg	1000mg	1500mg	2000mg
Aluminum Sulphate	1.117	1.117	1.117	1.116	1.116	1.115
Ferrous Sulphate	1.117	1.116	1.116	1.116	1.115	1.115

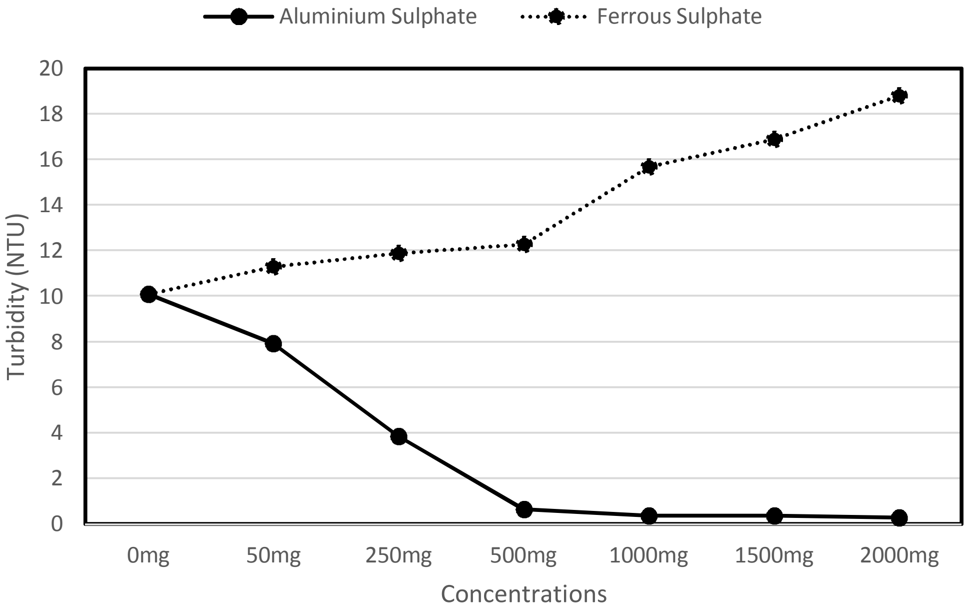


Figure 34: Turbidity results when Aluminum sulphate and ferrous sulphate used

5.3.4 Viscosity Measurement

Figure 35 shows the use of both aluminum sulphate and ferrous sulphate will result in decrease the viscosity of separated water, the viscosity value of 0 mg in the figure is the viscosity of separated water at optimal concentration of 800 mg/L. As we can notice that the addition of 500 mg of any of sulphate will significantly reduce the viscosity of separated water from 3.162 cp to 1.385 cp while adding more sulphates showed slight decrease on viscosity values from 1.385 cp to 1.36 cp and 1.262 cp for ferrous sulphate and aluminum sulphate respectively. This result again support that adding ferrous sulphate and aluminum sulphate will further remove the suspended remaining oil droplets.

5.3.5 Chemical Oxygen Demand (COD)

The effect of ferrous sulphate and aluminum sulphate with PAM in COD reduction is investigated. At first, there were 0.5ml, 1.0ml, samples from each concentration had been directly used for COD test, but it became green after mixing with reagents for COD test because the concentration was too high, so we diluted 5ml each sample into 50 ml distilled water and then take 0.5ml and 1.0 ml from each samples.

Table 18: COD reduction rates

Concentrations	Aluminum Sulphate (ppm)	COD Reduction Rates	Ferrous Sulphate (ppm)	COD Reduction Rates
50mg	134.4	99.78%	168.9	99.73%
250mg	86.016	99.86%	134.8	99.78%
500mg	6.336	99.99%	101.376	99.84%
1000mg	22.176	99.96%	95.04	99.85%
1500mg	3.168	99.99%	25.344	99.96%
2000mg	3.168	99.99%	12.672	99.98%
Emulsion	63258.63		63258.63	

Table 18 showed that adding aluminum sulphate and ferrous sulphate to 800 mg/L of PAM result in increasing efficiency of COD reduction, and increasing the concentration of any of those sulphates will result in increasing COD reduction rate.

In overall coagulant such as aluminum sulphate has great impact on destabilization process and this not only the volume of separated water increased when aluminum sulphates was used but also the degree of flocculation jar tests, as well as the viscosity, turbidity and COD were significantly improved.

5.3.6 Zeta potential

Emulsifiers, due to their amphiphilic nature, adsorb at the interface between oil and water, then form an interfacial film, which reduce interfacial tension. The reduction of interfacial tension through addition of emulsifiers allows emulsion formation. For an electro-statically stabilized emulsions, it was found that the higher the absolute value of zeta potential, the more stable the dispersion is likely to be, in another words emulsion will be stable, and thus coalescence of droplets will be more difficult. The higher zeta potential value (-30 mV) was observed, when no PAM added to the emulsion which indicated that the w/o emulsion here is very stable, as we increase the concentration of aluminum sulphate with addition of PAM solution at fixed 800 mg/L. The zeta potential result decreased to -20 mV when only 0.125g/L of aluminum sulphate was added, the zeta potential valve was around -23 mV when only PAM was used at optimal concentration of 800 mg/L. As we continually increased the concentrations of aluminum sulphate to 1.25g/L, the zeta potential nearly dropped to 0 mV, which means that when the concentration of 1.25g/L of aluminum sulphate with 800 mg/L gives the best effectiveness of separation and turbidity reduction. The addition of aluminum sulphate to w/o emulsion have two effects: Firstly the great amount of cations addition such as Al^{3+} can depress the effectiveness width of the double layer around oil droplets as well as to reduce the surface charge on the oil droplets. This is the main reason of reduction of the zeta potential, and droplets aggregates start to form as in **Figure 36**. The absorbed charged polyacrylamide molecular cause the reduction of zeta potential when only PAM was added, while charge neutralization mechanism also have enhanced all the process of w/o emulsion destabilization and oil droplets coalescence.

5.4 Conclusions

The effects of addition of electrolytes into polyacrylamide on destabilization of water in oil emulsion have been investigated and the following conclusions were drawn:

- Addition of electrolytes such as aluminum sulphate and ferrous sulphate into polyacrylamide are both enhance the destabilization of water in oil emulsion in general compare to when only polyacrylamide used.
- Aluminum sulphate is more efficient on enhance the volume of separated water, turbidity, COD reduction compare to ferrous sulphate.

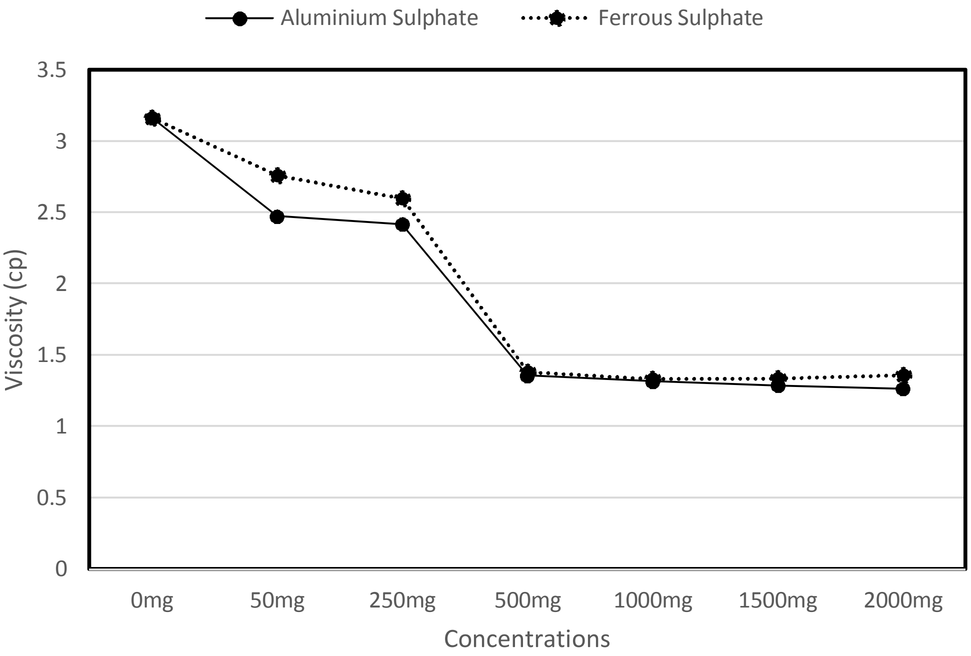


Figure 35: Viscosity results when aluminum and ferrous sulphate exist

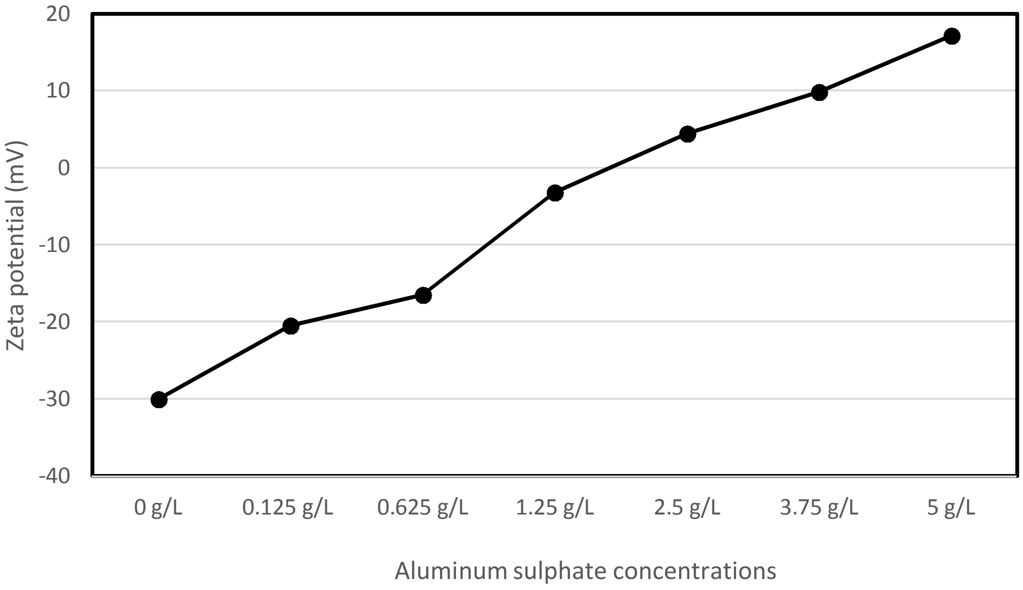


Figure 36: Zeta potential when Aluminum sulphate used

CHAPTER 6

Destabilization and Treatment of Produced Water-Oil Emulsions using Chelating Agent

Summary

Surfactant and polymer flooding technology can greatly enhance the oil recovery through the expansion of sweeping and displacing efficiency. The recovered oil from surfactant and polymer flooding emulsifies the residual chemical, which makes the separation of water from oil quite difficult, yet the impact of the enhanced oil recovery (EOR) chemicals on the produced water cycle is generally neglected in chemically-based EOR studies. This includes compatibility of EOR chemicals with the additives used to pre-treat the injected water or change reservoir wettability and result in producing oil/water emulsion after EOR breakthrough.

The chelating agent HEDTA have been studied for the first time in produced water treatment from EOR application after ASP flooding. The impact of different concentration of chelating agent without dilution, optimum diluted concentration in weight percentage, and the effect of different pH on destabilization of produced water in oil emulsion have been investigated through conducting the measurement on turbidity reduction, COD reduction rates, viscosity and volume of separated water were explored in this study. The results showed that chelating agent HEDTA as demulsifier can break water in oil emulsion easily only at high pH values due to the existence of carboxyl groups in HEDTA decrease

the interfacial tension between oil and aqueous phase of emulsion. Chelating agent HEDTA at 10% (wt) is most efficient and economical for destabilization of produced water in oil emulsion.

6.1 Introduction

Oil refining, the petrochemical industry, as well as mining, metallurgical and chemical industries generate many types of oily wastewaters. During crude oil exploration and production large volumes of petroleum hydrocarbon bearing effluents, the so-called produced waters, are concurrently recovered. Oils in these produced waters must be removed before the water can be reused in a closed-loop process or discharged into the sewer system or to surface waters. The treatment of oily produced waters poses a huge challenge because of their heterogeneous composition and the large volumes generated by various industries.

These oily waters are mainly in the form of oil-in-water (O/W) emulsions that pose a great problem in facilities attempting to stay in compliance with discharge limits. Emulsion breaking and oil removal require a basic understanding of the physical properties and chemical composition of O/W emulsions. In produced water treatment process, the addition of coagulants (salts of high volume cations: $AlCl_3$, $CaCl_2$, $FeCl_3$, $FeSO_4$) have been widely used because these cations could depress the effectiveness of oil droplets which leads to the reduction of zeta potential so that the coalescence occurs. As well as certain polymers such as HPAM, and copolymer are also used to w/o destabilization because of its high molecular weight cause polymer bridging mechanism.

From the literature review, Kunkel developed a method in wastewater treatment by using strong heavy metal chelating agents, which was based on the solubilization of Cu^{2+} of chelating agents at high pH of 10 (Kunkel and Manahan, 1973). And Tandy studied the using of chelating agents to wash the soils with metal pollution. It is already proved that EDTA is a very common and effective chelation agent to polluted soils treatment (Tandy et al., 2004). Robert and Michael used EDTA, HEDTA to improved water quality of overboard waters discharged from off-shore oil producing rigs in his patent No. US 5128046 A in 1990, he claimed that handling the oily produced water fraction, which holds dissolved iron salts with an effective hydrocarbon coagulating and coalescing sum of a combination including: an iron chelating agent, and polymeric coagulant coalescing agents. In 1990 a process and apparatus in which continuously separating for water, oil and solid particles from emulsions was proposed (Ernest, 1990). The practice, involving heating the mixture to at least 115° C, then rapid cooling applied below 100° C, the technique promote adding a flocculant preceding to cooling stage. Result in separating the solids from the liquids and the water from the oil. Recently, a method of an emulsion breaking was suggested through transferring metal from a hydrocarbon to water phase (Tran et al., 2013). This process achieved via adding a specific mixture to crude oil, the composition contains at least one demulsifier (of an oxyalkylated alkyl resin or a cross-linked polypropylene glycol) and mixtures, no less than one surfactant, chelating agent (diketone) and solvent.

It is clear from what have been reported in the literature the use of the chelating agent (HEDTA) for produced emulsions destabilization from SP flooding in EOR application, have never been investigated. Therefore, the main objective of this work is to utilize

(HEDTA) as demulsifier. Furthermore, the effects of chelating agent with different concentrations and pH will be studied in this research.

6.2 Experimental Section

6.2.1 Preparation of Stable Emulsion

In order to synthesis produced water, an emulsion of oil dispersed in formation brine was prepared. The water used in these experiments has different salinity content of 200,000 ppm formation brine [**Table 20**]. A typical saturated hydrocarbon and common petroleum product diesel was used as oil phase. A concentrated W/O emulsion was prepared by mixing the formation brine or seawater 60% (vol) with 40% (vol) of oil and surfactant (ARMAC HT as in **Table 19**) using using IKA Ultra Turrax mixer at 2000 rpm for 10 minutes. When the formation brine was used as a water phase, a very stable water in oil emulsion was formed. The stability was measured and the mixture remained stable for many days and there was no any phase separation at emulsion phase apparently showed except only small amount of diesel was formed at the top, while when the seawater was used as water phase, the W/O emulsion was also formed by the same method.

Table 19: Tallowamine Acetate, Chemical and Physical properties

Characteristics	Values
Appearance, 20^0C	Solid prills
Bulk density	550 kg/m^3
Density, 60^0C	880 kg/m^3
Melting range	60 - 80^0C
Particle size, prills	1-3 mm

Table 20: Chemical analysis of water used in w/o emulsion preparation

Ion	**Water type concentration, mg/L (ppm)**
	Formation brine
Na	59,000
Ca	23,400
Mg	1,510
SO_4	110
Cl	137,000
HCO_3	353
Total dissolved Solid*	221,673

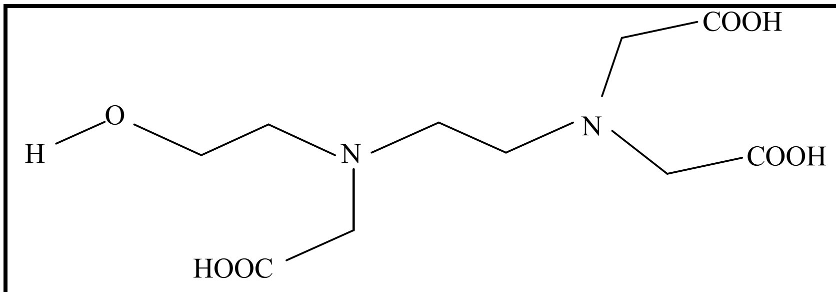
* Sum of all the concentration of ions

6.2.2 Demulsification Tests

This is the first time hydroxyethyle-thylenediaminetriacetic aid (HEDTA) with original 41 wt% concentration in weight was evaluated as demulsifier for destabilization of w/o emulsion [**Table 21**].

Chelating agent concentrations (10% (wt) 20% (wt), and 30% (wt)) used in destabilization of W/O emulsion were diluted with de-ionized water from an initial concentration of 41% (wt). Chelating agent HEDTA with 41 wt% concentration were diluted into another 3 different concentrations: 10% (wt) 20% (wt), and 30% (wt) and its original concentration of 41% (wt) in weight corresponding to 2.71g/L, 10.92g/L, 24.75 g/L and 46.67g/L as the demulsifier according to procedures was followed.

Table 21: Chelating agent HEDTA structure



Hydroxyethyle-thylenediaminetriacetic aid (HEDTA)

6.2.3 Jar Test

The jar test was performed using Stuart Flocculator SW6. And the stable water in oil emulsion was prepared as the procedure described above and which were distributed into 6 different modified beakers which has one valve at the bottom for collecting the separated water from bottom directly. The experiments were conducted using a 250 ml of emulsion in six jars, and then a predetermined amount of HEDTA as demulsifier, which was transferred into the jars with 5 different concentrations of 29.08g/L, 46.67g/L, 62.29g/L, 77.14g/L, and 90.87g/L. The Jar test was performed at 250 rpm for 10 minutes to promote the coagulation process before it continued at 30 rpm for another 15 minutes to promote the flocculation and destabilization process. After the jar test, for emulsion formed with the formation brine (without HEDTA), the samples were kept for 24 hours to ensure stability of the emulsion. For this sample, no any phase separation was observed in the first 8 hours, however, the other 5 jars with demulsifier after 24 hours there were three phases showed: diesel at the top, emulsion at the middle and water separated at the bottom could be clearly identified. And then the water separated at the bottom of jars were collected and different measurements were conducted on the separated water to study the effectiveness of demulsifier in the process of emulsion separation. The volume of water separated (WS) in percentage, was defined as vol % using the following equation:

$$\text{WS (vol \%)} = V / V^{\circ} \times 100 \tag{6.1}$$

where V is the volume of the water separated and V° is the original volume of water contained. HACH 2100N Turbidimeter was used to measure the turbidity of the supernatant and to study the effectiveness of PAM in improving the pureness of the separated water. Density of the separated water was measured for viscosity calculation using density meter (Anton Paar, US). Chemical oxygen demand (COD) was measured after the separated water samples heated at 150°C for 2 hours using HACH COD reactor.

6.3 Results and Discussion

6.3.1 Effect of original HEDTA concentration without dilution

Volume of separated water. Figure 37 shows the effect of HEDTA demulsifier concentration on the volume of water separated. The results indicate that increasing the concentration of HEDTA from 29.08g/L to 77.14g/L results in significantly increase in the volume of water separated from 81.1% to 86.3%. While increasing the HEDTA concentration higher than 46.67g/L did not show any increase in the separated water which indicates that optimal HEDTA concentration is 46.67g/L.

Turbidity test. Figure 38 show the results of turbidity test and the results indicate that the optimal demulsifier concentration is 29.08g/L, but 46.67g/L is also comparably good than the concentrations high than 46.67g/L. As indicated in **Figure 38** with an increasing of the HEDTA concentration from 29.08g/L to 62.29g/L did not show significant effect on separated water turbidity but when the concentrations of higher than 62.29g/L were used the turbidity unit increase suddenly from 1.38 NTU to 1.89 NTU when HEDTA concentration increase to 62.29g/L.

Density measurement. As we can see **Figure 39** mixing of formation brine with HEDTA result in decreasing density of those brines as a result of removing remaining oil emulsion and some cations and anions initially present on those brines. As we can see in **Figure 39** the density of formation brine was decreased to 1.151 when 46.67g/L of HEDTA was mixed with formation brine after jar test. Then increasing the concentration of HEDTA was resulting in sharp increase in formation brine density from 1.152 to 1.180.

Viscosity measurement. Figure 40 shows the results of viscosity studies for formation brine after treatment with HEDTA, the result shows clearly that 46.67g/L of HEDTA give the lowest value of viscosity. The figure also indicates the viscosity is increasing significantly from 1.404 to 1.992 when the HEDTA concentration increased from 46.67g/L to 90.87g/L. This is means that the 46.67g/L concentration of HEDTA is the optimum concentration and above this concentration the HEDTA will remain in the water as result of overdose.

Chemical oxygen demand (COD). The COD of original synthetic emulsion in formation brine was measured and found to be 63258.63 ppm. **Table 22** summarizes the results of COD reduction test, 15ml and 25ml of HEDTA gives the highest COD reduction rates of 62.34% and 69.55%. Increasing the HEDTA concentration will greatly decrease COD reduction rate, it means increasing the concentrations of HEDTA also increase the chemical oxygen demand valve and which can made strong pollution to the environment, because as we can see in the table below only 7.85% of COD reduction efficiency could be achieved at 90.87g/L of HEDTA. However, comparably the COD reduction rate of the optimal concentration of HEDTA which is 46.67g/L give us acceptable range. However, the anionic PAM is much stronger than HEDTA in the breaking and separating of such stable emulsion.

Table 22: COD Reduction Rates

HEDTA Concentration (g/L)	COD Values	COD Reduction Rates
29.08	23823	62.34%
46.67	19261	69.55%
62.29	43845	30.69%
77.14	55503	12.26%
90.87	58291	7.85%
W/O Emulsion	63258	

Interfacial-Tension (IFT) measurements. IFT was measured between brine and oil by using IFT tensionmeter at atmospheric pressure and room temperature. An IFT experiment conducted with rising drop method, while the density of drop fluid is smaller than the density of bulk-fluid. Firstly, one drop of oil phase was created from specified capillary into water phase in an experiment cell at room conditions. Then, a camera with computer connection records the shapes of the oil drop with the rising-drop method, and

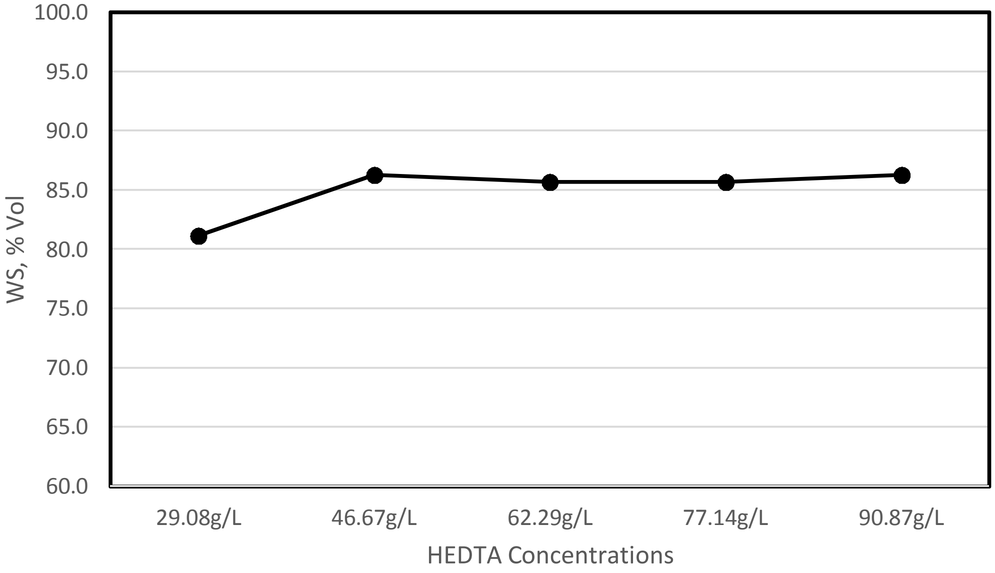


Figure 37: Demulsifying efficiency as a function of HEDTA concentration

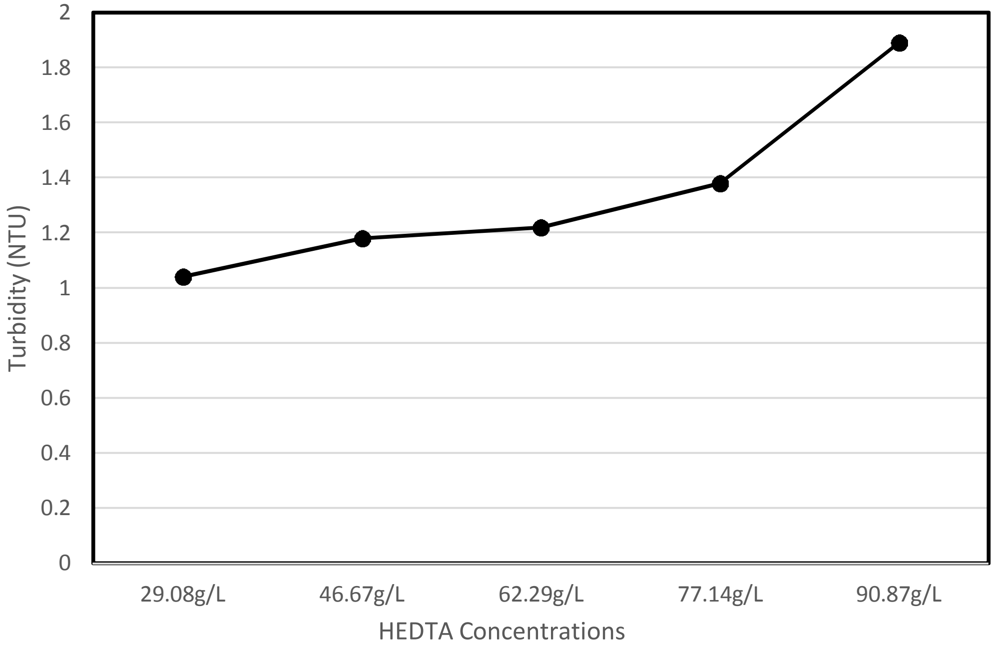


Figure 38: Turbidity Test Results at different HEDTA concentrations

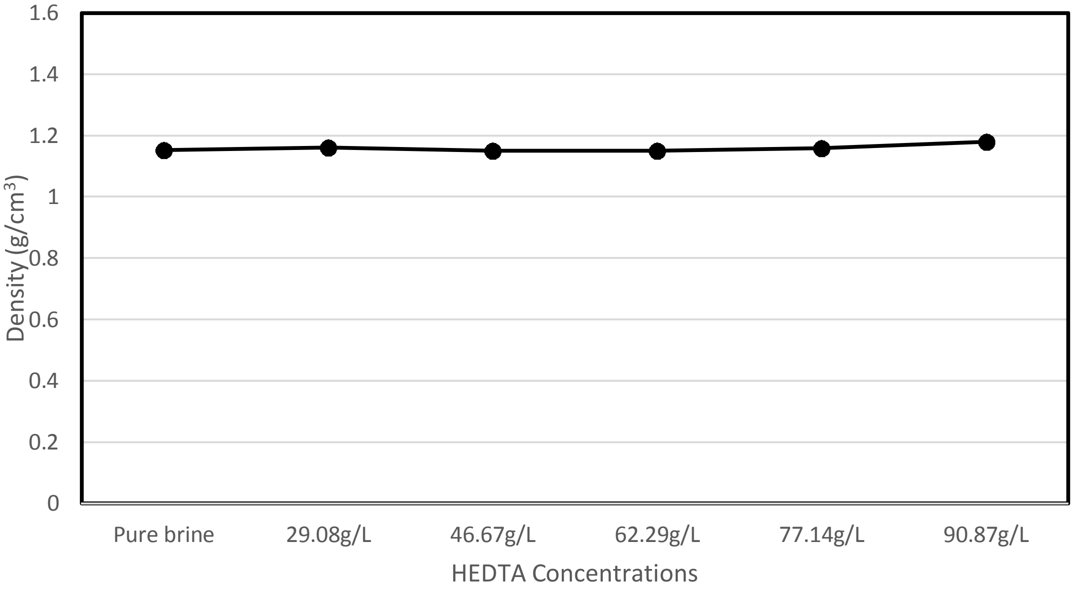


Figure 39: Density of separated water at different HEDTA concentrations

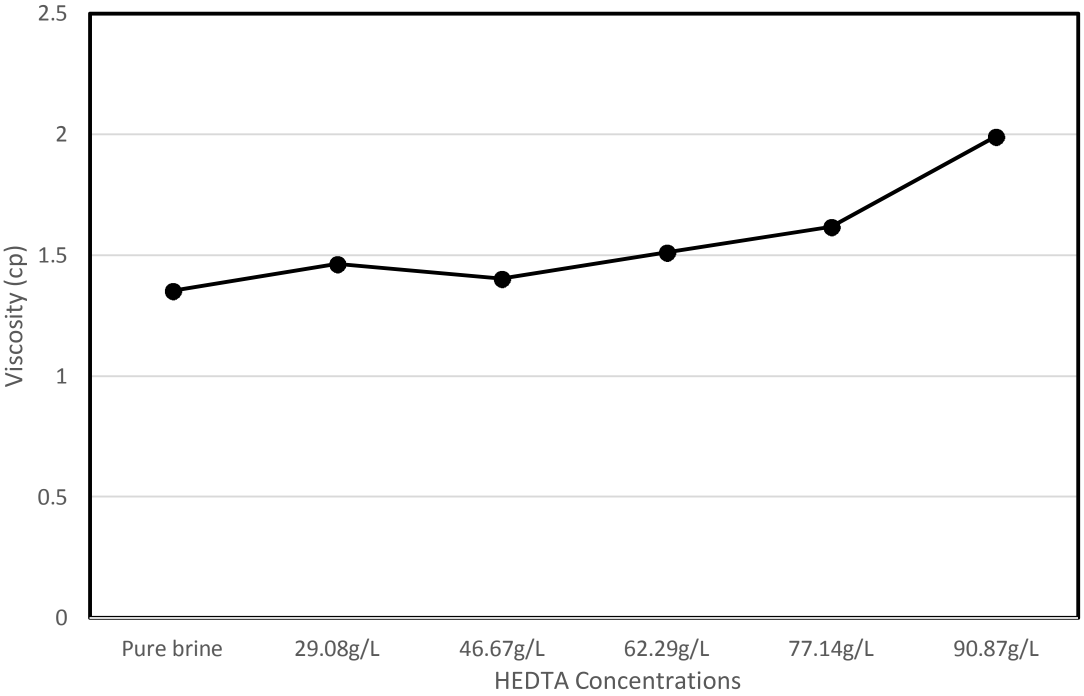


Figure 40: Viscosity of separated water at different HEDTA concentrations

IFT valves were provided by solving Laplace equation. As an increase of HEDTA concentration, from **Figure 41** it is easily observed that there was a slight increase of IFT when the concentration of HEDTA was 46.67 g/L, while the reduction of IFT was found obviously as we increase the concentration of HEDTA from 46.67g/L to 90.87g/L, which can be attributed to increase of the carboxyl group concentration as addition of HEDTA. Chelating agent HEDTA contain carboxyl group which have the ability to seize multivalent cations such as Ca^{2+}, Mg^{2+}, Fe^{3+} and Al^{3+}, as well as the carboxyl groups will increase the oil solubilization, and act like surfactant or polyacrylamide that we used to reduce the interfacial tension between oil and aqueous phase in W/O emulsion destabilization.

6.3.2 Effect of Diluted Chelating Agent HEDTA

Volume of separated water. Figure 42 shows the effect of diluted HEDTA as demulsifier concentration on the volume of water separated as we can see in **Figure 43** increasing the concentration of HEDTA from 2.71g/L to 10.92g/L of diluted HEDTA results in dramatically increase in the volume of water separated from 85.7% to 88.6%. While increasing the concentration of diluted HEDTA concentration higher than 24.75g/L did not show any increase in the separated water which indicates that optimal HEDTA concentration is 24.75g/L of diluted HEDTA, but 2.71g/L of HEDTA is also acceptable from economically consideration.

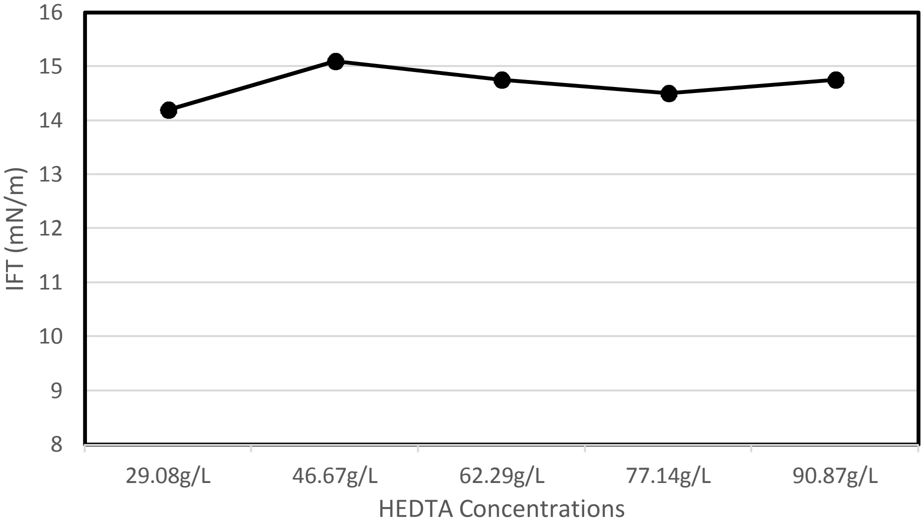


Figure 41: IFT results when HEDTA without dilution

Turbidity test. Figure 44 shows the results of turbidity test and this figure also indicate that the optimal demulsifier concentration is 20% of diluted HEDTA, while 10% of diluted HEDTA is also comparably better than others.

As indicated in **Figure 44** increasing the HEDTA concentration from 10.92g/L to 46.67g/L of diluted HEDTA showed significant effect on separated water turbidity, which was increased from 0.48 NTU to 1.18 NTU.

Density measurement. As we can see **Figure 45** mixing of formation brine with diluted HEDTA result in increasing density of those brines. As we can see in **Figure 45** the density of formation brine was increased to 1.157 when 24.75g/L of HEDTA was mixed with formation brine after jar test. Then increasing the concentration of HEDTA was resulting in sharp decrease in formation brine density from 1.157 to 1.151.

Viscosity measurement. Figure 46 below shows the results of viscosity studies for formation brine after treatment with HEDTA, this figure shows clearly that 2.71g/L of

HEDTA give us the lowest value of viscosity. The figure also indicates the viscosity is increasing gradually from 1.345 to 1.657 when the diluted HEDTA concentration increased from 2.71g/L to 46.67g/L.

Chemical oxygen demand (COD). When the COD of original synthetic emulsion in formation brine was measured which reached 63258.63 ppm. **Table 23** below summarizes the results of COD reduction test, 2.71g/L and 10.92g/L of diluted HEDTA gives the highest COD reduction rates of 92.87% and 89.98%. Increasing the HEDTA concentration will greatly decrease COD reduction rate, it means increasing the concentrations of

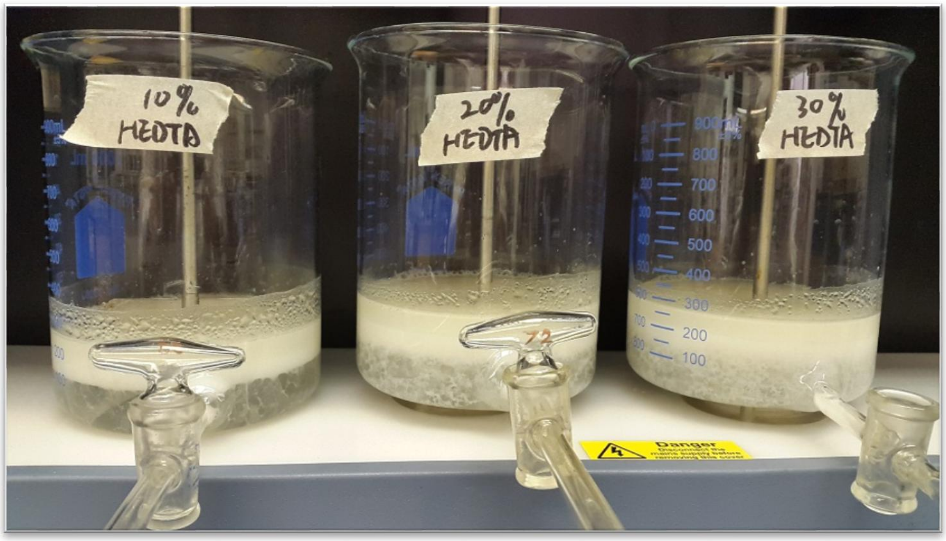


Figure 42: Separated water after Jar test at diluted concentration of HEDTA

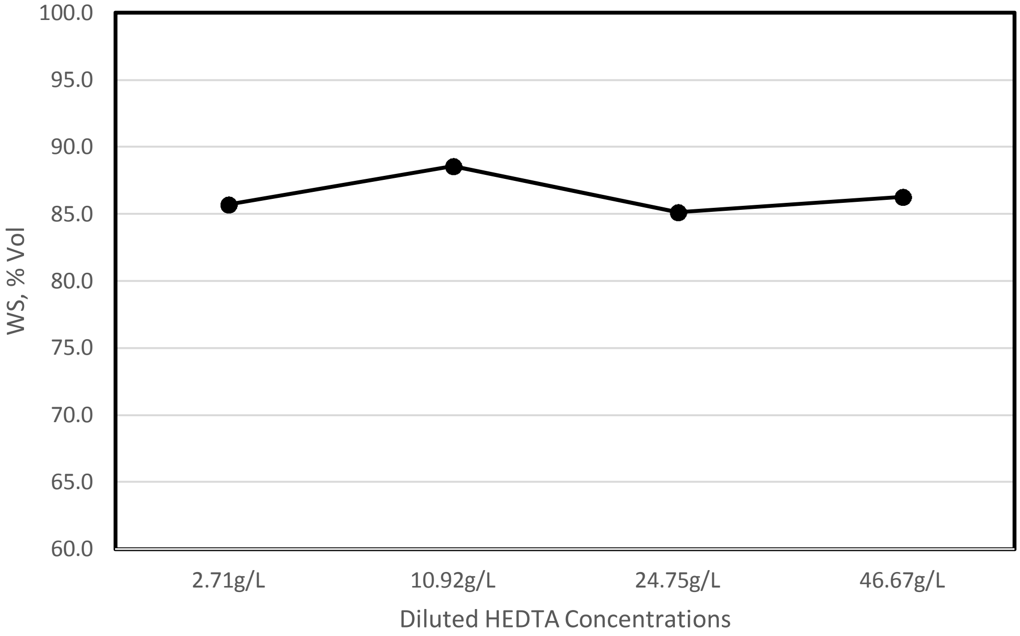


Figure 43: Demulsifying efficiency as a function of diluted HEDTA concentrations

Table 23: COD reduction rates

HEDTA Concentrations (g/L)	COD Values	COD Reduction Rates
2.71	4511	92.87%
10.92	6336	89.98%
24.75	15967	74.76%
46.67	19261	69.55%

HEDTA also increase the chemical oxygen demand valve and which can made stronger pollution to the environment.

Interfacial-Tension (IFT) measurements. From **Figure 47** we can see as an increase of HEDTA concentration, there was a slight decrease of IFT values when the concentration of HEDTA was increased from 10% (wt) to 41% (wt), the reduction of IFT was found obviously, which can be attributed to increase of the carboxyl group concentration as addition of HEDTA. Even the concentrations of diluted HEDTA solution at pH 12.2 was only around 2.71 g/L, but it has almost same effect of 10.92 g/L from IFT values. That is the reason that we can have very similar results in volume of separated water and turbidity reduction. Chelating agent HEDTA contain carboxyl group which have the ability to seize multivalent cations such as Ca^{2+}, Mg^{2+}, Fe^{3+} and Al^{3+}, as well as the carboxyl groups will increase the oil solubilization, and act like surfactant or polyacrylamide that we used to reduce the interfacial tension between oil and aqueous phase in W/O emulsion destabilization.

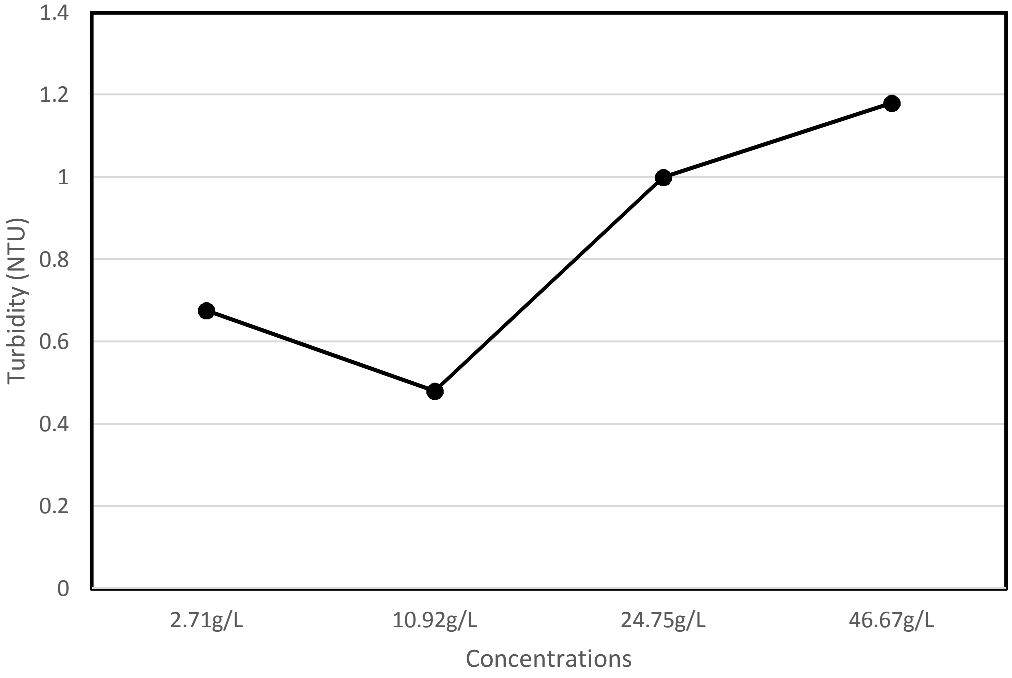


Figure 44: Turbidity test results at different concentration of diluted HEDTA

6.3.3 Effect of different pH of Chelating Agent HEDTA

After the optimum concentration of diluted chelating agent HEDTA have been found, to understand the mechanism of chelating agent HEDTA break the water in oil emulsion, the effect of different pH of chelating agent also need to be investigated. The original pH of chelating agent HEDTA was 12.2, another two pH values were set as: 4.2 and 8.2.

While there was no any separation when the pH values was decreased to 8.2 and 4.2 as **Figure 48**. Chelating agent HEDTA contain carboxyl group which have the ability to seize multivalent cations such as Ca^{2+}, Mg^{2+}, Fe^{3+} and Al^{3+}, as well as the carboxyl groups will increase the oil solubilization, and act like surfactant or polyacrylamide that we used to reduce the interfacial tension between oil and aqueous phase in W/O emulsion destabilization. So only the chelating agent at high pH values such as 12.2 can reduce the interfacial tension between oil and aqueous phase, as long as we increased the concentration of HEDTA will reduce more interfacial tension, while when we decrease the pH of HEDTA to 4.2 and 8.2, interfacial tension between oil and aqueous phase will not decrease as at high pH value 12.2 so there is no any separation at low pH values (Mahmoud and Abdelgawad, 2015).

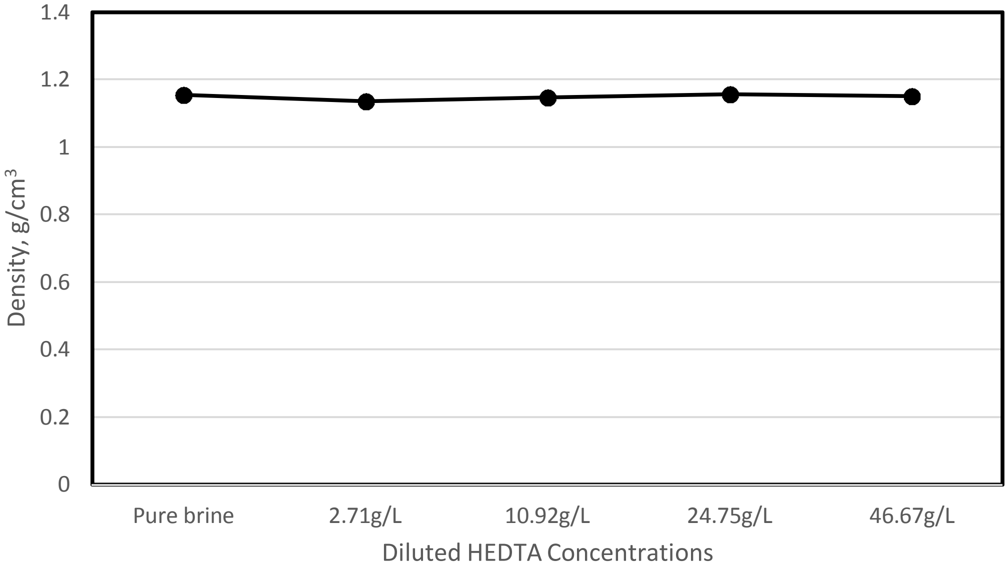


Figure 45: Density test results at different concentration of diluted HEDTA

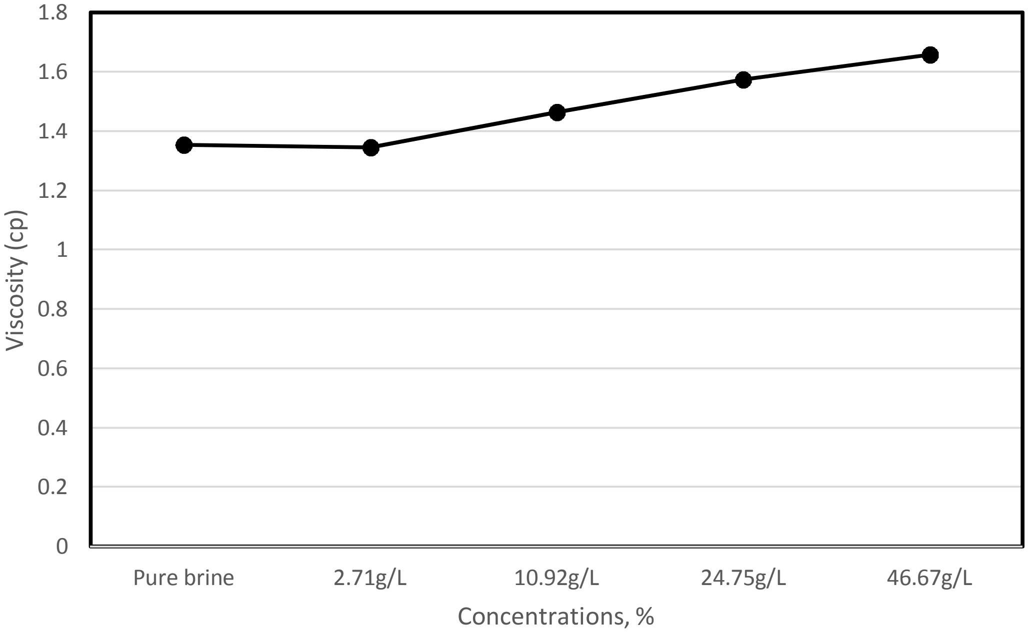


Figure 46: Viscosity results at different concentration of diluted HEDTA

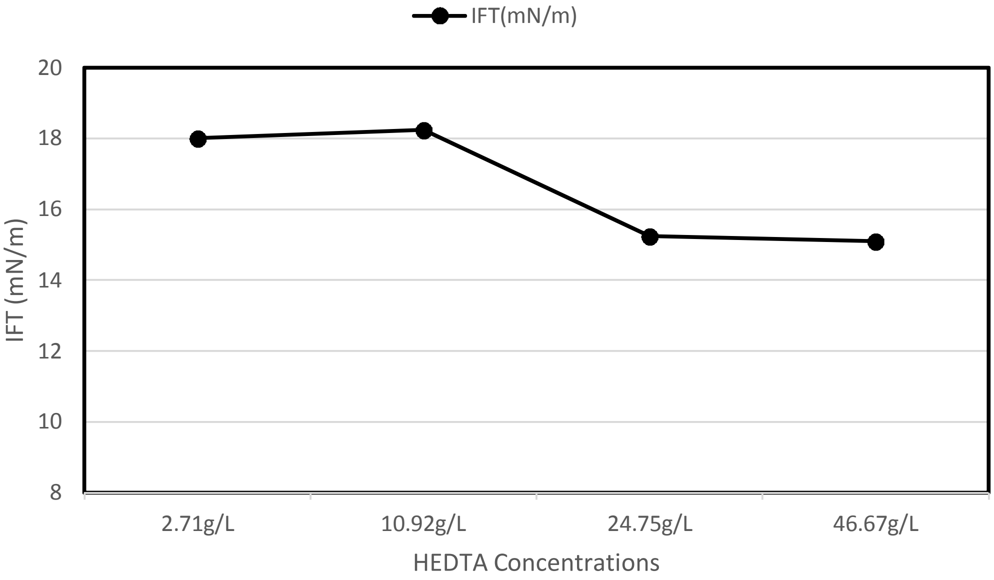


Figure 47: IFT results of diluted HEDTA

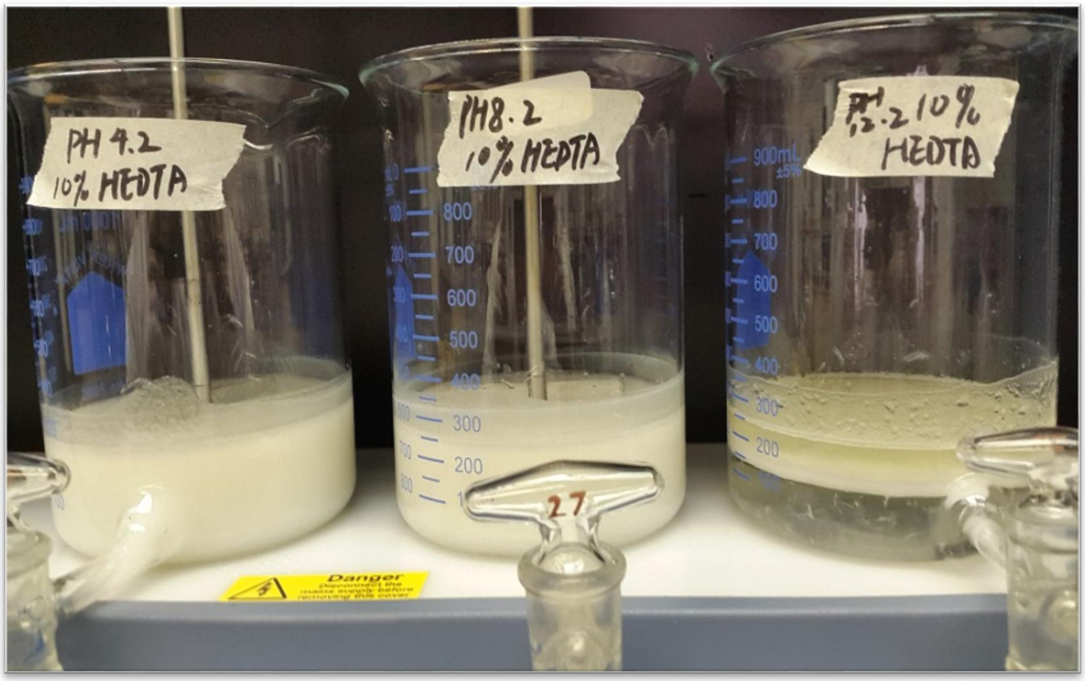


Figure 48: effect of different pH of chelating agent HEDTA

6.4 Conclusions

The effects of chelating agent HEDTA as demulsifier on destabilization of water in oil emulsion have been investigated and the following conclusions were drawn:

- Chelating agent HEDTA as demulsifier can break water in oil emulsion easily only at high pH values due to the existence of carboxyl groups in HEDTA decrease the interfacial tension between oil and aqueous phase of emulsion.
- Chelating agent HEDTA at 10 wt% is most efficient and economical for destabilization of produced water in oil emulsion.

6.5 Recommendations

Above all, based on the observation and conclusions of this research, the following recommendations are suggested for the future work in this area.

1. The water in oil emulsion at fix pH have been studied in this research, the effect of pH on emulsion stability should be considered and investigated.
2. Repeat the experiments using crude/waste oil from field and formation brine to match real field conditions
3. A pilot test of optimum Polyacrylamide concentration and the optimum condition of Polyacrylamide with existence of aluminum sulphate and ferrous sulphate on flotation system.
4. A pilot test on the real field emulsion from SP flooding in EOR application should be conducted.
5. Further study should be conducted on chelating agent HEDTA as demulsifier.

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