

**DEVELOPMENT OF EMULSIFIED GELS FOR WATER  
CONTROL IN OIL AND GAS WELLS**

BY

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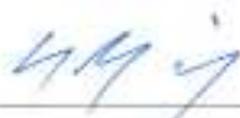
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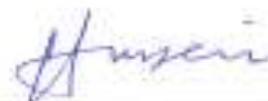
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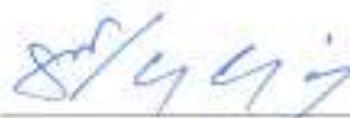
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## **Dedication**

The fruit of this humble effort is devoted to my beloved perpetually, my parent, faithful wife, brothers and sisters for their unconditional and continuous support. To you all words fall short to express my gratitude, however may” Allah” continues blessing you abundantly.

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## ABSTRACT

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Thesis Title : DEVELOPMENT OF EMULSIFIED GELS FOR WATER  
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Water production is a serious issue in oil and gas producing wells. Emulsified gels have been proposed as means of selectively reducing the water effective permeability without significantly affecting the hydrocarbon phase. In this study, emulsified polyacrylamide (PAM) polyethylenimine (PEI) system was developed for high temperature high salinity applications. A scientific approach based on the hydrophilic lipophilic balance (HLB) of the surfactant, was developed for screening surfactants for water in oil (W/O) emulsions. Additionally, Organoclay (OC) was proposed as a substitute for classical surfactants used in such application. The thermal stability of the emulsified PAM/PEI gels was extensively studied. A relationship between the emulsified system droplet size and its thermal stability was developed. Dynamic rheology was used to study gel strength and gelation time. Emulsification was found to slow down cross-linking rate and reduce elastic modulus (~54%). No significant impact was observed on the elastic modulus, when different types of emulsifiers were used. The gel strength of the emulsified PAM/PEI increased by about 32% when the temperature was increased from 120°C to 150°C. Generally, gel strength was established to decrease in the presence of salts. The proposed emulsified PAM/PEI system was found to yield adequate gel strength at high temperature using field mixing water (1,122 ppm).

## ملخص الرسالة

الاسم الكامل: عبدالحليم ابراهيم عبدالحليم محمد

عنوان الرسالة: : تطوير مستحلب مادة هلامية للتحكم بإنتاج المياه من ابار النفط والغاز

التخصص: هندسة البترول

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ان انتاج المياه يعتبر من المشاكل الكبرى في الابار المنتجة للنفط و الغاز. مستحلبات الهلام البولمري تم اقتراحها كوسيلة لخفض النفاذية الفعالة للمياه من دون التأثير على نفاذية المواد الهيدروكربونية بشكل ملحوظ. في هذا البحث تم تطوير مستحلب البولي اكريل اميد و البولي ايثيلين امين لاستخدامه في التطبيقات ذات درجات الحرارة والملوحة العالية. مقارنة علمية مبنية على درجة الفة المياه و الفة الزيت للمؤثر السطحي تم اقتراحها لاختيار المؤثر السطحي المناسب لتكوين مستحلبات الماء في الزيت.بالاضافة لذلك تم اقتراح ارجانوكلي كبديل للمؤثرات السطحية التقليدية المستخدمة في مثل هذه التطبيقات. تم دراسة الاستقرارية الحرارية لمستحلبات البولي اكريل اميد و البولي ايثيلين امين حيث تم ربط حجم قطرات هذه المشتحلبات باستقراريتها الحرارية. تم دراسة وقت تكون و صلاحية الهلام البوليمري عبر تحليل الخواص الحركية للمستحلب حركياً بدراسة عدة من العوامل المؤثرة في هذه العملية. حيث وجد ان الاستحلاب يثبط معدل التفاعل و يقلل قوة الجل (54%~). وانه لا يوجد تأثير ملحوظ علي قوة الجل عندما تم استخدام مؤثرات سطحية مختلفة. لوحظ ان قوة الجل المتكون تزداد بمعدل 32% عندما تزيد درجة الحرارة من 120 الي 150 درجة مئوية.عموماً وجد ان قوة الجل المتكون تقل في وجود الاملاح. ان مستحلب البولي اكريل اميد و البولي ايثيلين المقترح اثبت قوة معتبره عند درجات الحرارة العالية باستخدام مياه الحقول المالحة.

# CHAPTER 1

## INTRODUCTION

### 1.1 Water Production

Oil and gas wells in mature fields suffer from high water production during hydrocarbon recovery. A process needed to reduce water production, when it exceeds economic limits of a given oil or gas field. Roughly, \$40 billion is spent annually to handle the unwanted water produced from hydrocarbon reservoirs (Bailey et al., 2000; Seright et al., 2003), this number has increased to \$45 billion in the year 2002 (Mercado et al., 2009; Boye et al., 2011), more recent cost data is not reported. Information on the amount of produced water is available; 210 million barrels per day (BD) worldwide in the year 1999 (Veil et al., 2004), for the year 2000 same figure was reported (Bailey et al., 2000). In 2005 this number increased to 249 million BD (Khatib, 2007). Additionally, if the produced water contains mercury, arsenic, and other salts the disposal of this water will seriously affects the environment (Hibbeler and Rae, 2005).

Most of the corrosion and scale problems in the oilfield are consequence of water production (Donham, 1991; Nasr-El-Din, 2003; Merdhah and Yassin, 2009; Al-Tolaihy and Bukhari, 2010). Excessive water production could be handled with mechanical and/or chemical methods. The mechanical methods include the application of particular completion tools, casing replacement or separation of produced water by use of hydro-cyclones (Vega et al., 2012). Chemical methods include silicate (Grattoni et al., 2001; Nasr-El-Din and Taylor, 2005; Elewaut et al., 2006; Al-Dhafeeri et al., 2008; Boye et al.,

2011), resins (Seright et al., 2003), cements and polymer gels (Seright et al., 2003; Sydansk 2007; Lightford et al., 2008; Al-Muntasheri et al., 2010). In-situ polymerization has been used to shut off water produced through perforations (Saltel et al., 1999). Polymer gels, applied in the oilfield due to their low cost compared to other methods, the ease of pumping, and the penetration into the rock matrix. Polymer gels are prepared by cross-linking a polymer with a cross-linker such as PAtBA with PEI. Recent research revealed that some low cost polymers can be used such as polyacrylamide (PAM) instead of the existing one (PAtBA) (Al-Muntasheri et al., 2009).

It is clear from the data presented that large financial resources are devoted to handling/managing the excess water. With the growing demand on energy, there is a need for reducing the water production rates. That will avoid extra costs for the production of oil, in addition to improving the oil recovery.

### **1.1.1 Disproportionate Permeability Reduction**

Polymer and polymer gels are well suited for reducing water production during oil and gas production, but there exist a risk that they reduce oil flow appreciably, together with water. The risk is smaller when water is reduced by disproportionate permeability reduction (DPR), but may be sufficient to instil caution about using the chemicals. This explains largely the frequent use of mechanical means to isolate oil layers and ensure that polymer enters only in the water layers where it is needed. The use of mechanical isolation or, alternatively, dual fluid injection, is impracticable in most wells. This is particularly true for deviated, horizontal, and multilateral wells, which are being increasingly used in different parts of the world. In those wells there is a need of

polymers and gel treatments that can be injected without the mechanical isolation of the oil layers (treatments that can be bullheaded).

The polymer is reported to reduce the permeability to water much more than the permeability to oil, particularly in wells where water and oil are produced from the same zone so that the water-bearing zones cannot easily be isolated. This phenomenon of selective or disproportionate permeability reduction is known as Relative Permeability Modification, which results in permeability reduction of porous media. The lack of non-mechanical methods to selectively place a sealing system or a plugging type barrier and the high costs involved in placement operations necessitated developing selective systems. These selective barriers mainly block the water flow by selectively reducing effective water permeability, causing little or no restriction to oil flow. These systems are generally formed by water-soluble copolymers that adsorb on the rock surface, forming a hydrophilic film that reduce water mobility and require no special placement technique (Vinson, 1986; Zaitoun et al., 1991; Liang et al. 1995; Seright 1995; Zaitoun et al. 1998; Al-Sharji et al. 1999; Willhite et al. 2002). This disproportionate permeability reduction (or relative-permeability modification) is essential if polymers or gels are placed in production wells without protecting hydrocarbon-productive zones (Liang et al. 1993). With existing polymers gels and technology, disproportionate permeability reduction may have its greatest value when treating production wells that intersect a fracture or fracture-like features (Seright et al. 1999, 1993; Marin et al. 2002). Nonetheless, many people are very interested in exploiting this property to reduce excess water production from unfractured wells (i.e., radial flow into porous rock or sand) in many cases, direct injection of polymers or gels in production wells has proven to be an efficient method to

prevent excessive water production (Mofitt, 1993; Zaitoun et al., 1999). The idealistic goal of this technology is to develop a material that can be injected into any production well (without zone isolation) and that will substantially reduce the water-productivity index without significantly impairing the hydrocarbon productivity.

### **1.1.2 Emulsification in Oilfields**

Perhaps the first introduction of emulsification technique in oil industry started by invention of emulsified acid (1933). Emulsified acids were invented to address corrosion problems rather than improve the stimulation job (De Groote, 1933). As a result, many researchers comprehensively studied this technique for further understanding of advantages and disadvantages of emulsified acids (Dill et al., 1961; Knox and Lasater 1964; Davis et al., 1965; Knox et al., 1965; Crenshaw and Flippen 1968; Nierode and Kruk 1973; Navarrete et al., 1998; Al-Anazi et al., 1998; Nasr-El-Din et al., 2000). Moreover, extensive studies on the effect of droplet size, emulsifier concentration, and acid volume fraction on the rheological properties and stability of emulsified acids were reported (Al-Mutairi et al., 2008; Sayed et al., 2011). Recently, the emulsification technique gained momentum in the oil and gas industry. Emulsification has been employed for well stimulation applications (Fatah and Nasr-El-Din, 2010; Sayed et al., 2013). Recently, Stavland et al., 2006 proposed a new method for water control by the use of bullhead injection. Normally it is described as disproportionate permeability reduction. (Stavland and Nilsson 2001) suggested a general mechanism for DPR, where DPR is governed by segregated or preferred flow of oil and water at the pore level.

In a patent, Arne and Nilsson suggested injection of the gelant as an emulsion for field application (Arne and Nilsson 1999). In Arne et al., 2006 work, a water based gelant is emulsified in oil and injected into the formation. The emulsion is designed to separate into a water phase and an oil phase at static conditions in the formation. Upon reaction in the formation the water phase gels up while the oil phase remains mobile. It has been found that the controlling parameter for disproportionate permeability reduction (DPR) is to control the fraction of gel occupying the porous media. The water fraction in the emulsion controls the reduction in relative oil and water permeabilities.

Their work did not include enough information about how the emulsified system has been created, the emulsifier selection criteria, the effect of designing parameter such droplet size and how it can be correlated to stability of the emulsion. Moreover, no extensive investigations of the emulsified gel rheological measurements have been reported.

## **1.2 Thesis Summary**

This section gives general outline of this manuscript-based thesis.

## **CHAPTER TWO**

In this section, different commercial surfactants were evaluated for use as emulsifiers for water in oil (W/O) polymeric gel solution. A scientific approach has been developed for screening surfactants for W/O emulsions. The technique is based on the hydrophilic lipophilic balance (HLB) of the surfactant. Emulsifier concentration was used to control the stability of produce emulsion. Thermally stable emulsified water in oil systems that can withstand high temperature up to 120°C and high salinity (221,673 ppm)

environments employing HLB method was successful identified. Furthermore, new insights on structure-surfactant stability relationship, beyond the HLB approach, were presented for surfactant selection.

### **CHAPTER THREE**

Currently, many nanomaterials have been developed for several applications in various fields of endeavors, due to their high surface area of the dispersed nano-sized particle, availability, low-priced and more importantly environmentally friendly. This chapter discuss the possibility of employing organoclay as a substitute for classical surfactants used for water in oil polymeric gel formulations, that utilized in water shut-off applications. In this work, two emulsifier systems were evaluated, organoclay as standalone emulsifier and coupled with another surfactant. The proposed emulsifier produced stable emulsion systems, which can tolerate wellbores having high pressure and high temperature (120°C) with high salinity (221,673 ppm) much better than current surfactants used in oil industry.

### **CHAPTER FOUR**

In this chapter, the stability of emulsified polyacrylamide /polyethylenimine gels was extensively investigated at high temperature high salinity conditions. The influence of different parameters, such as water and oil phase fractions, salinity, intensity of mixing, surfactant concentration and temperature, on the droplet size and the thermal stability of the emulsion was studied. The emulsion stability has improved with the increase in surfactant concentration, mixing intensity water/oil ratio. Increase in temperature was

found significantly reduce the stability. Emulsion droplet size has been correlated to thermal stability. Emulsions with smaller droplet size were found to be more stable.

## **CHAPTER FIVE**

The gel strength and gelation time of the organically cross-linked polyacrylamide (PAM) crosslinked with polyethylenimine (PEI) emulsified into diesel was extensively studied exploiting dynamic rheology. Several parameters were investigated. These included: emulsifier type, separation time, temperature, polymer concentration, retarders and the effect of mixing water. Emulsification (separation time) was found to slow down cross-linking rate. The effect of the emulsification is more pronounced when stable emulsified PAM/PEI was used instead of emulsified PAM/PEI with complete separation within one hour where the elastic modulus decreased from 746 Pa to 343.6 Pa. The elastic modulus of the emulsified PAM/PEI increased by about 32% when the temperature was increased from 120°C (248°F) to 150°C (266°F). Generally, elastic modulus was established to decrease in the presence of salts.

## **CHAPTER SIX**

Brief conclusions as well as recommended future work for emulsified gels is presented in this chapter

## CHAPTER 2

### **Screening of Surfactants used in Emulsified Polymeric Gel Formulations in High Temperature High Salinity Conditions**

#### **Abstract**

Polymer gels are commonly used for water control in oil and gas reservoirs. Emulsified polymeric gels have the advantage of selectively reducing the water production without substantially damaging the hydrocarbon phase. To form water in oil (W/O) emulsion, surfactants are commonly utilized to emulsify the water soluble material. The selection of a specific surfactant for such jobs is critical and it is certainly very expensive exercise. There has been no practical methodology in the oil industry to optimally select the right emulsifier. Therefore, a scientific approach for screening surfactants for W/O emulsions was developed. The method is based on the surfactant hydrophilic lipophilic balance (HLB). In this paper, different commercial surfactants were evaluated for use as emulsifiers for W/O polymeric gel solution. The proposed surfactants have formed thermally stable W/O emulsions at 120°C in saline water. The stability of the emulsion is controlled by controlling the emulsifier concentration. The proposed surfactants are suitable for wellbores having high temperature up to 120°C with high salinity field water (221,673 ppm). This work was successful in identifying stable emulsified water in oil systems that can tolerate high temperature high salinity environments using HLB approach. New insights on structure-surfactant stability relationship, beyond the HLB approach, were provided for surfactant selection.

## **2.1 Introduction**

Emulsions are widely used in various fields such as pharmaceutical (Nielloud and Marti, 2000), hydraulic fluids (Greaves et al., 2009), polymerization (Anderson and Daniels, 2003), paints (Osemeahon, 2011) and food industries (McClements, 2009 and Friberg, 2003). Furthermore, emulsification technology has been extensively applied in the oil industry in applications such as drilling fluid formulations (Lawhon et al., 1967; Patel, 1999; Ebeltoft et al., 2001), well stimulation treatment (Fatah and Nasr-El-Din 2010; Sayed et al., 2013), drag reduction in multiphase flow (Al-Yaari et al., 2014) and quite recently for the application of excessive water production treatment (Stavland et al., 2006). However, there is no systemic procedure in the oilfield for selecting a suitable emulsifying agent. The industry mainly relies on the experience and service providers' recommendations.

An emulsion is mixture of two or more partially or completely immiscible fluids (Tadros et al., 1983), where a dispersed phase exists suspended in an external (continuous) phase in the form of droplets. The emulsion system is innately thermodynamically unstable, because the surface of each droplet is an interface between hydrophilic and lipophilic molecules (Weiss, 2002). When two immiscible fluids are mixed an emulsion is created, during the stirring progression both liquids have a tendency to develop phases (Rieger, 1976; Tamilvanan, 2010). If a surfactant is added to a 2-phase system, it has a propensity to form and stabilize a dispersed and a continuous phase, since it delays the breaking of emulsion such as flocculation, creaming and coalescences (Becher, 1983). The emulsion stability depends on different parameters including existence of satiric barriers on the droplets, interfacial film physical nature, droplets size, continuous phase viscosity, water oil ratio (volume fraction), temperature and mixing

time (Joshi et al., 2012). Stability of the emulsion is also correlated to the amount of adsorbed surfactant at the interface. With the adsorption of more surfactant, the interfacial tension is reduced and the emulsifier molecules function as a film slowing down the droplets coalescence (Becher 1983; Joshi et al., 2012; Rai and Pandey, 2013).

### **2.1.1 Emulsification in the Oilfields**

Emulsification techniques were introduced in the oil industry through the use of emulsified acids in 1933. Emulsified acids were invented to address corrosion problems rather than improve the stimulation job (De Groote, 1933). As a result, many researchers comprehensively studied this technique for further understanding of advantages and disadvantages of emulsified acids (Dill et al., 1961; Knox and Lasater 1964; Davis et al., 1965; Knox et al., 1965; Crenshaw and Flippen 1968; Nierode and Kruk 1973; Navarrete et al., 1998; Al-Anazi et al., 1998; Nasr-El-Din et al., 2000). Moreover, stability and rheological properties of emulsified acids were extensively investigated through studying the impact of different parameters such as: the dispersed phase droplet size, surfactant concentration and acid volume fraction (Al-Mutairi et al., 2008; Sayed et al., 2011). Recently, the emulsification technique gained momentum in the oilfields. Emulsification has been employed for well stimulation applications (Fatah and Nasr-El-Din, 2010; Sayed et al., 2013). In addition to the well stimulation applications, a new application of emulsification technique in the oilfield is proposed recently as a method for water control with bullhead injection. In this case disproportionate permeability reduction (DPR) or relative permeability modification (RPM) takes place. Multilayered reservoirs with no crossflow with regions producing only oil or in dealing with coning problems, DPR fluids will be efficient (Liang and Seright 1993; Stavland et al., 1998; Botermans and Van

Batenburg, 2001). The DPR fluids are extensively used in oil and gas fields (Schneider 1982; Sparlin 1976; Zaitoun 1999; Liang and Seright 1992, Kalfayan and Dawson 2004). In a patent, Stavland and Nilsson suggested emulsified gels for RPM field application (Stavland and Nilsson 1999). In Stavland et al., work (2006), the emulsified system formulated to break up into a oil and an water phases. Then, the water phase, which contains the water soluble polymers transform to gels that obstruct formation water flow, whereas the oil phase remains mobile providing open passageway for the hydrocarbon flow. Controlling the gel fraction occupying the porous media (saturation of the gel in the pore space) has been found a designing parameter for DPR. The water fraction in the emulsified system constitutes the decrease in the relative permeability (Stavland et al., 2006).

Undoubtedly, the type of emulsion is critical for those applications, therefore the emulsifier which will be employed to accomplish the emulsification must be cautiously selected to meet the requirements of those applications, so a fair rate of success could be seized. The objective of this paper is to introduce, for the first time, a screening process based on HLB using different commercial surfactants. Furthermore, the effects of temperature, surfactant concentration and water salinity on the emulsion stability are investigated.

## **2.2 Experimental**

In this section, details about materials, equipment, experimental procedures, emulsion preparation and characterization are discussed.

### 2.2.1 Materials

The surfactants used in this study were supplied by Sigma-Aldrich®, AkzoNobel and Capstone® as presented in **Table 2.1** Sea water and formation brine were used as water phase, **Table 2.2** shows their chemical analysis. Diesel from local gas stations is used for the oil phase. Diesel is representative of the oil used in the field by local industry for preparing emulsified acids. Salts used in this study were American Chemical Society (ACS) grade.

### 2.2.2 Equipment

The emulsions were prepared in a high performance dispersing instrument (Ultra-Turrax T 50 Basic) provided by VWR International. The homogenizer is equipped with a variable speed drive with different 6 speeds in the range 500 – 10,000 rpm. All emulsions were prepared at room temperature at 2000 rpm mixing speed for 5 minutes. The mixing speed and time were selected following a separate investigation. A Conductivity meter provided by HACH (CDC401 model) with a range of 0.01  $\mu\text{S}/\text{cm}$  to 200,000  $\mu\text{S}/\text{cm}$ . The device can handle total dissolved solids (TDS) in the range 0 to 50 mg/L as NaCl, operation temperature 10 – 110°C (14 to 230°F), minimum sample depth 45 mm [1.77 in]. The meter was used to classify the emulsion type. GL-18 high temperature disposable test tubes, soda-lime-glass (18 x 180 mm) of approximate volume of 32 ml and operation temperature of 180°C were used. The high temperature tubes were sealed with a screw-cap and a rubber seal case to prevent evaporation. The fact that no evaporation is taking place was assured by comparing the initial and final volumes of the sample at the end of the experiment. HAAKE FISONS hot oil bath Model N3, Temperature range: ambient to

300°C. employed to study the emulsion separation: separated volume fraction of the phases versus time.

### **2.2.3 Emulsion Preparation**

The screening procedure for various surfactants is shown in **Figure 2.1**. Several emulsion systems with varying surfactant concentrations were prepared in a systemic way to ensure the reproducibility of the results. Two methods have been used based on the HLB of the surfactant utilized to prepare the emulsion: surfactants with HLB value < 10: Lipid soluble (water insoluble), the emulsifier (at a specific concentration) was added to the diesel in the homogenizer. All emulsions were prepared at room temperature at 2000 rpm mixing speed for 5 minutes.

The emulsifier was given enough time to mix thoroughly in the diesel. Then, the desired volume of the water phase was slowly added to the hydrocarbon phase (diesel and emulsifier solution). It is important to add the water phase droplets slowly and uniformly throughout the mixing. The same routine was followed for surfactants that have HLB value > 10 that are water soluble (lipid insoluble). However, in this case the emulsifier was added to the water phase and then the desired volume of the diesel was added droplet wise. These two methods have been used simultaneously in some experiment to observe how the preparation routine may affect the outcome as Bancroft's rule states that the phase in which an emulsifier is more soluble constitutes the continuous phase (Langmuir, 1996). It is important to note that the rate of the addition of the dispersed phase to the continuous phase and the intensity of mixing are critical to the produced emulsion. The coarsest emulsion will be produced when all the dispersed phase is added at once to the continuous phase and then shaken by hand. Conversely, the finest emulsion will be

produced when the dispersed phase is atomized with a spray bottle to the continuous phase in a blender at very high mixing speed (Al-Mutairi 2008).

### **2.3 Emulsion Characterization**

Surfactant selection is an expensive practice. To investigate the HLB capability of providing some guide lines for optimized choice, different surfactants with wide range of HLB values were selected. Conductivity and dilution tests were used simultaneously to identify the type of emulsions.

#### **Hydrophilic-lipophilic balance Determination**

HLB of a surfactant is a measure of the degree to which it is hydrophilic or lipophilic. HLB offers an efficient way of picking the suitable surfactant for a specific application as suggested notably by Griffin (1949, 1954). A scale of 0 to 20 is suggested. An HLB value of 0 corresponds to a completely lipophilic/hydrophobic molecule and a value of 20 corresponds to a completely hydrophilic/lip-phobic molecule. The HLB values for W/O emulsifiers are in the range 3.5- 6.

**Table 2.1:** Description of the surfactants used in this study

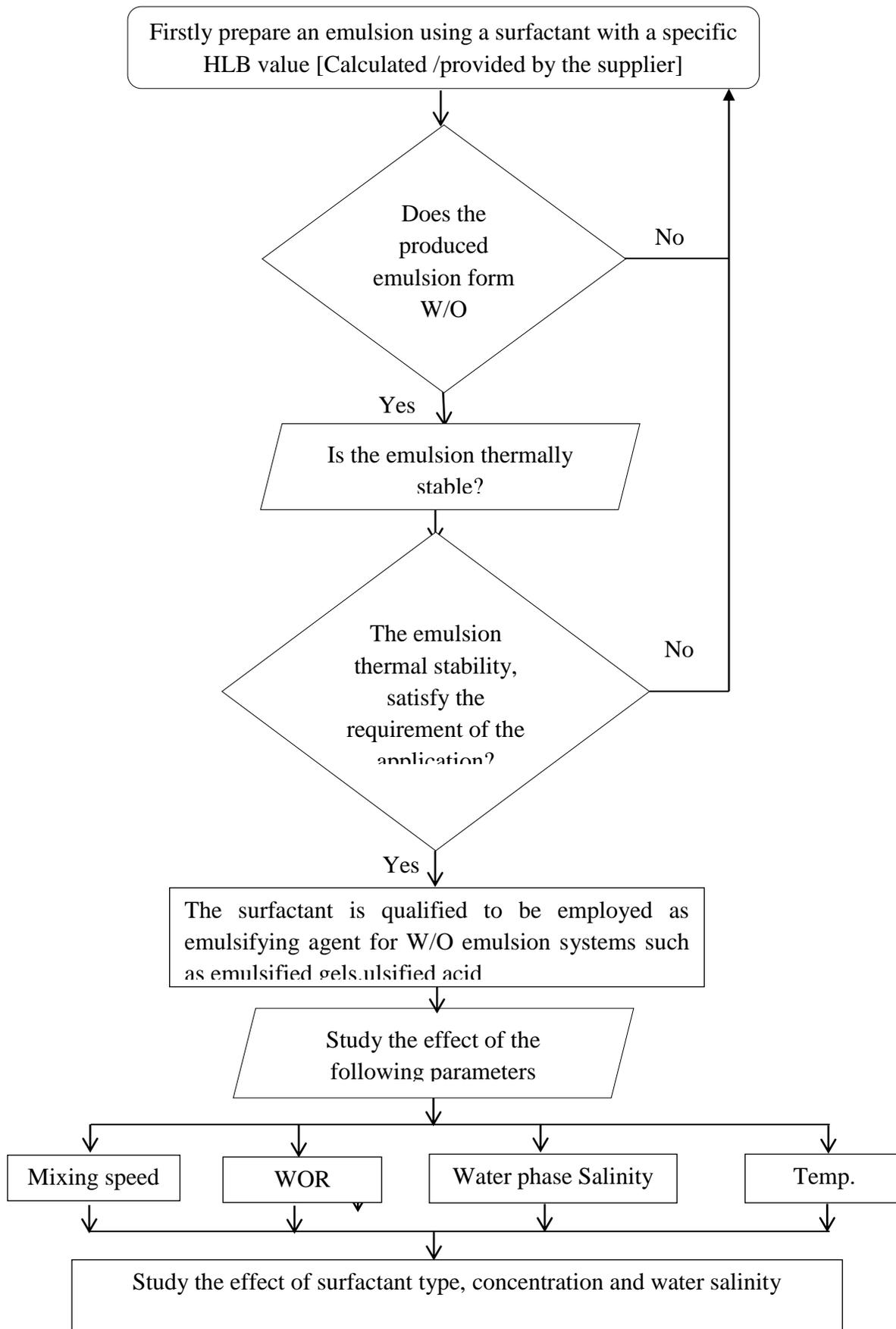
Surfactant	Type	Mw (g/mol)	HLB (wt. ratio)
Glycolic Acid Ethoxylate-1Ether (C <sub>14</sub> H <sub>24</sub> O <sub>6</sub> )	AIS*	288.34	12 (61.1%)
Glycolic Acid Ethoxylate-2 Ether (CH <sub>3</sub> (CH <sub>2</sub> ) <sub>11-13</sub> (OCH <sub>2</sub> CH <sub>2</sub> ) <sub>n</sub> OCH <sub>2</sub> CO <sub>2</sub> H (n=6))	AIS*	739.20	7.14 (35.7%)
Glycolic Acid Ethoxylate-3 Ether (C <sub>55</sub> H <sub>112</sub> O <sub>8</sub> )	AIS*	901.47	2 (9.76%)
Polyethylene Glycol-1 Ether (C <sub>58</sub> H <sub>109</sub> KO <sub>24</sub> S)	AIS*	1260.09	14 (69.8%)
Ethylenediamine – Tetro (C <sub>3</sub> H <sub>6</sub> OC <sub>2</sub> H <sub>8</sub> N <sub>2</sub> C <sub>2</sub> H <sub>4</sub> O) <sub>x</sub>	N/A	3,600	1-7
Fluorosurfactant -1	N/A	N/A	N/A
Fluorosurfactant -2	N/A	N/A	N/A
Polyethylene Glycol-2 Ether (C <sub>18</sub> H <sub>35</sub> (OCH <sub>2</sub> CH <sub>2</sub> ) <sub>n</sub> OH,n~2 )	NIS**	356.58	4
Polyethylene Glycol-3 Ether (C <sub>16</sub> H <sub>33</sub> (OCH <sub>2</sub> CH <sub>2</sub> ) <sub>n</sub> OH,n~2 )	NIS**	330	5
Polyethylene Glycol-4 (C <sub>4</sub> H <sub>10</sub> O <sub>2</sub> )	NIS**	90,12	N/A
Amine Acetates-1	IS***	N/A	6.8
Amine Acetates-2	IS***	200	21
Amine Acetates-3	IS***	263	6.8
Ethoxylated Amides -1 ( Ethomid-1)	N/A	N/A	9.7
Ethoxylated Amides -2 ( Ethomid-2)	N/A	340-360	10.1

\*AIS=Anionic surfactant; \*\*NIS=Nonionic surfactant; \*\*\*IS=Ionic surfactant;

**Table 2. 2** Chemical analysis of the waters used in the experiments

<b>Ion , ppm</b>	<b>Water type Concentration, mg/L</b>	
	<b>Formation brine</b>	<b>Sea water</b>
Na	59,300	18,300
Ca	23,400	650
Mg	1,510	2,082.729
SO <sub>4</sub>	110	4,290
Cl	137,000	32,200
HCO <sub>3</sub>	353	120
Total Dissolved Solids*	221,673	57,642

\* TDS were determined by addition.



**Figure 2.1** Surfactant screening flow chart

while that of O/W are in the range 8-18. Wetting agents have HLB values in the range 7-9. One of the first empirical rules developed to describe the type of emulsion that could be stabilized by a given emulsifier was proposed by Bancroft (Langmuir, 1996). Bancroft's rule states that the phase in which an emulsifier is more soluble constitutes the continuous phase. Hence, a water soluble emulsifier forms O/W emulsions, whereas an oil soluble emulsifier stabilizes W/O emulsions (Langmuir, 1996; Min et al., 2008). Emulsion type depends more on the nature of the emulsifying agent than on the relative proportions of oil or water present or the methodology of preparing the emulsion.

### **Dilution Test**

The dilution test was used to identify the emulsion's continuous (external) phase. In this test, few droplets of the formed emulsion were dispersed in water and diesel to see if they spread or sink. If the placed droplet disperses then the external phase is the same as the fluid used for the test (Al-Yaari et al., 2013).

### **Emulsion Stability Test**

To investigate the thermal stability of the formed emulsion a high temperature test tube was used to conduct stability tests. The separated volume fraction of oil and water phases was monitored at constant temperature. Such a test can give an indication about emulsion quality.

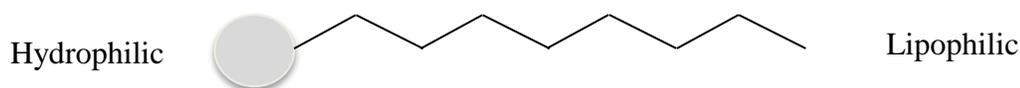
## **2.4 Results and Discussion**

Emulsions were prepared using each surfactant. In this study, 2 vol% surfactant concentration was added to 28 vol% diesel, then mixed for a minute at 500 rpm at room temperature. Afterward, the mixing speed was raised to 4000 rpm, and sea water was

added to the solution of the hydrocarbon (surfactant and diesel) at a specific rate. Then the emulsions are characterized to identify the external and dispersed (internal) phases. The emulsions are either W/O emulsions where the oil is the continuous phase and water is the dispersed phase or oil in water emulsions which are the opposite.

#### 2.4.1 Hydrophilic-lipophilic balance Determination

HLB of a surfactant is a measure of the degree to which it is hydrophilic or lipophilic. It is determined by calculating the contributions of different constituents of the molecular structure (see **Figure 2.2**) as described by Griffin (1949, 1954). Another method was suggested in 1957 by Davies. It is based on the chemical groups of the molecule. The advantage of this method is that it takes into account the effect of stronger and weaker hydrophilic groups. However, it requires more information such as numbers of hydrophilic and lipophilic groups in the molecule and values of hydrophilic and lipophilic groups. Consequently, the value of HLB for a particular surfactant has been either provided by the supplier or calculated for a number of surfactants employing Griffin's method and the weight ratio of hydrophilic part to hydrophobic as well as shown in **Table 2.1** Exact HLB value qualifies the surfactant for specific application as seen in Table 9. This will be cross checked against results of the conductivity and the droplet tests.



**Figure 2.2** Surfactant Structure

## 2.4.2 Conductivity and Dilution (Emulsion Drop) Test

The type of emulsion has been determined by exploiting the conductivity. This is a qualitative method based on the electrical properties of the water phase, which is highly conductive, whereas oil phase is nonconductive. It should be noted that the emulsion's conductivity is dominated by the external phase. Thus oil in water emulsion is conductive, whereas water in oil emulsion is nonconductive. Furthermore, dilution test was employed to confirm those finding as demonstrated in **Table 2.3**.

**Table 2. 3** Surfactant characterization based on conductivity and dilution tests

Surfactant	Conductivity Test	Dilution Test	Observations
Fluorosurfactant -1	4.5 [ $\mu\text{S}/\text{cm}$ ]	O/W	Separation started in < 3 minutes. The surfactant generates foam consequently the conductivity probe reading and drop test not reliable.
Fluorosurfactant -2	N/A	N/A	The surfactant not oil soluble.
Glycolic Acid Ethoxylate-2 Ether	1034 ( $\mu\text{S}/\text{cm}$ )	O/W	formed stable O/W.
Glycolic Acid Ethoxylate-3 Ether	20.5 ( $\text{mS}/\text{cm}$ )	O/W	Separation started in < 3 minutes.
Glycolic Acid Ethoxylate-1 Ether	N/A	N/A	The surfactant is not oil soluble, separation started immediately at the end of the mixing process.
Ethylenediamine - Tetrol	1072 ( $\mu\text{S}/\text{cm}$ )	O/W	Separation started in < 5 minutes after mixing.
Polyethylene Glycol-1 Ether	N/A	N/A	The surfactant did not dissolve in oil phase.
Glycolic Acid Ethoxylate-1 Ether	N/A	N/A	separation started immediately after the mixing process finished
Glycolic Acid Ethoxylate-3 Ether	23.5 ( $\text{mS}/\text{cm}$ )	O/W	Separation started < 4 minutes at the end of the mixing.
Ethylenediamine - Tetrol	7.82 ( $\text{mS}/\text{cm}$ )	N/A	Separation started in < 5 minutes after mixing.
Polyethylene Glycol-1 Ether	1078 ( $\mu\text{S}/\text{cm}$ )	N/A	Mixing time was extended to 10 minutes, however separation started in < 2 minutes.

Most of these surfactants formed oil in water emulsion, but Glycolic Acid Ethoxylate-2 Ether is the only surfactant that produced stable O/W emulsion under the conditions of the study. The application of emulsified gel or acid, water in oil emulsion, is critical to the success of the job. Therefore, additional surfactants that can do the job were examined as shown in **Table 4**. They have been selected based on their HLB value.

**Table 2.4** New selected surfactant based on the HLB

Surfactant	HLB	Application based on the HLB	Conductivity Test	Dilution Test
Polyethylene Glycol-2 Ether	4	W/O Emulsifier	0.02 $\mu\text{S}/\text{cm}$ [ 18.3 °C ]	W/O
Amine Acetates-2	21*	O/W Emulsifier	3.5 ms/cm - 20 ms/cm	N/A
Amine Acetates-3	6.8	W/O Emulsifier	0.01 $\mu\text{S}/\text{cm}$ [23.9 °C ]	N/A
Ethoxylated Amides -1	9.7 *	W/O Emulsifier	0.02 $\mu\text{S}/\text{cm}$ [21.1 °C ]	W/O
Ethoxylated Amides -2	10.1*	W/O Emulsifier	0.02 $\mu\text{S}/\text{cm}$ [20.9 °C ]	W/O

### 2.4.3 Emulsion Thermal Stability Test

To investigate the thermal stability of the formed emulsion a seal case high temperature test tubes were used to conduct stability tests for all formed emulsions by monitoring the separated volume fraction of the oil and water phases versus time at constant temperature. Such a test can give an indication about emulsion quality.

In this paper, the possibility of employing commercial surfactants as alternative emulsifier in forming stable W/O emulsion for high temperature and high salinity

applications in oilfields is investigated. From operational point of view the thermal stability of the emulsified system plays important role in the success of the placement job. For instance, in emulsified acid no separation for a specific period of time is required. Similarly, designed separation time is necessary for the water shut-off applications. Therefore, the thermal stability of various emulsions is investigated at high temperature to enhance the current understanding of the effect of surfactant concentration on the stability of the emulsion (emulsion quality).

Cross-linked polymeric gels, especially PAM gels, are widely used in the petroleum industry to minimize water production during oil and gas exploration and production. Aqueous polymer gels are usually emulsified in oil and then injected in the water zones. The emulsion should be injected as one component. Then, it will separate into oil phase and water phase. The water phase contains the (polymer mixture) gelant which gels up in a portion of the pore space to reduce permeability to water. The oil phase remains mobile to secure a path for oil to flow (Stavland et al., 2006). Surfactants are usually used to emulsify the aqueous gel solution in oil. Accordingly, the complete separation of emulsified system is important for water shut-off treatment.

Thus, in this study we attempted designing an emulsified system with controllable separation time to meet the operation requirement. The time needed for gelling solution placement was reported to be about 55 minutes at 150°C (302°F) (Al-Muntasheri et al., 2010). Consequently, the emulsified gel system should be stable for at least one hour. De-emulsification and gelation of the system should start afterward. Usually, pre-flush is injected prior the treatment to cool down the reservoir from 150°C (302°F) to 116°C

(240.8°F). Therefore, the thermal stability of all formed emulsions was investigated at 120°C.

The emulsion stability is presented by using phase changes diagram (volume fraction versus time). This graph illustrates the percentage of the phases at specific time. Initially, the emulsion is within the sample before it starts to break. The single phase water and oil phases at the start are 0% as the separation is yet to start. However, exposing the emulsion to a particular temperature over time leads to de-emulsification of the emulsion. Then, the percentage of water and oil phases increases. The volume percentage of oil and water phases keeps changing until reaching a plateau or the emulsion is entirely separated.

In all emulsions covered in this study, the total volume was 30 ml, 70 % of which was water phase (brine), the rest 30% was hydrocarbon phase (the mixture of emulsifier and the diesel). The diesel percentage was in the range of 24–29.5%, while the emulsifier percentage was in the range 0.5% - 6%. All emulsions were prepared at room temperature at 2000 rpm mixing speed for 5 minutes. Then, the thermal stability was examined in bulk at 120°C (248°F) for 12 hours using the oil heating bath. The emulsion stability is presented by using phase changes diagram (volume fraction versus time). This graph illustrates the percentage of the phases at specific time. Initially, the emulsion is homogeneous and with time the emulsion starts to break. The separation of the emulsion into water and oil phases increases with time and temperature.

### **Polyethylene Glycol-2 Ether**

2 vol% of Polyethylene Glycol-2 Ether were used as emulsifier and the balance is diesel and brine as described earlier. However, 9% of the water phase has separated after

4 minutes. After 6 minutes, 62% of the water and 7% of oil have separated. Complete separation has taken place after 8 minutes as shown in **Figure 2.3**. By increasing the emulsifier dose to 4 vol% the water phase starts separating (7%) after 9 minutes. After 14 minutes, the separation of water has reached 44% and only 2% of the oil has separated. Complete separation has occurred after 20 minutes as shown in **Figure 2.4**. Finally, the surfactant dosage has been increased to 6 vol% and resulted in water phase initial separation of 3% after 9 minutes which was continued until it completely separated after 22 minutes (**Figure 2.5**). The oil phase separation did not take place before 22 minutes.

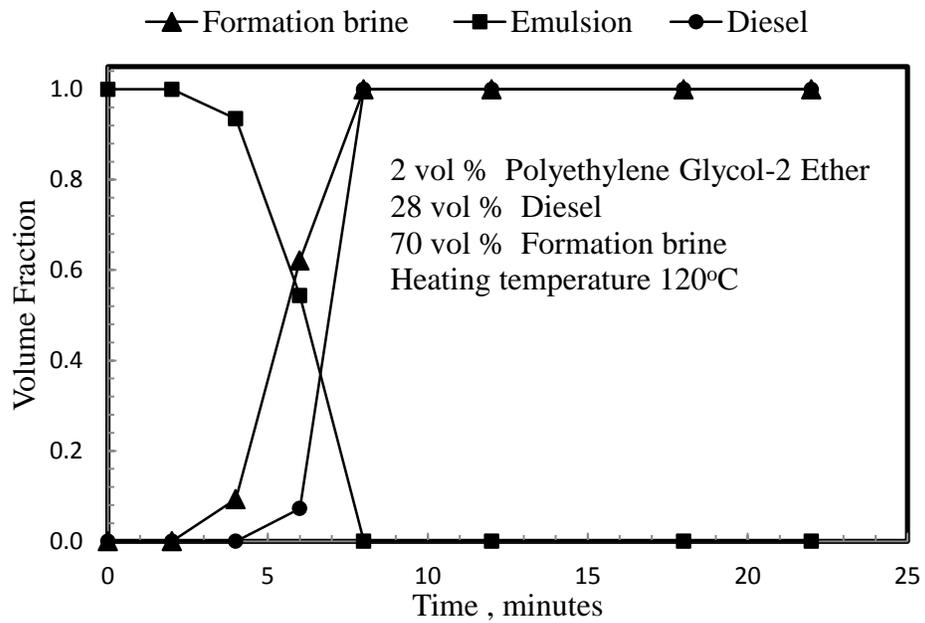
### **Polyethylene Glycol-3 Ether**

The emulsion of Polyethylene Glycol-3 Ether, using 2 vol% of emulsifier at 120°C, resulted in a separation of 91% in the water phase and 93% in the oil phase after 1 minute. The experiment was stopped after 6 minutes of heating because no more changes were noticed (**Figure 2.6**). The surfactant concentration was increased to 4 vol% before placing the sample in the oil bath. The total volume was 25 ml and the volume was reduced by 4 ml due to the formation of foam. After 1 minute of heating, water started to separate (9%) and after 2 minutes the sample size reduced by 5 ml. As shown in **Figure 2.7**, the separation of the oil phase started after 6 minutes, the sample was kept inside the oil bath for 225 minutes. After 88 minutes, 71% of the water phase and 60% of the oil were separated. These values did not change until the end of the test.

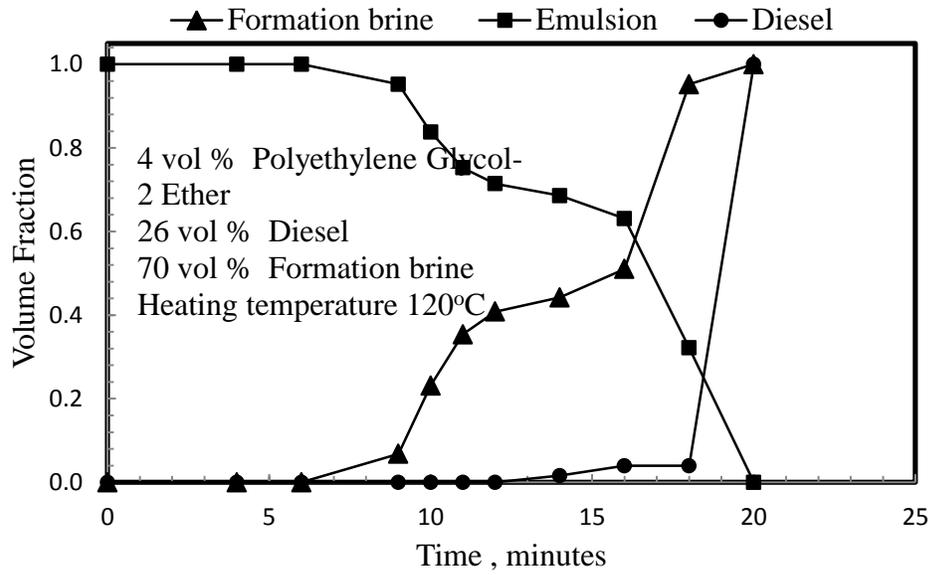
### **Ethoxylated Amides-2**

At low concentration of Ethoxylated Amides-2 (1 vol %), water started to separate in less than 6 minutes. In about 30 minutes 97% of the water and oil were

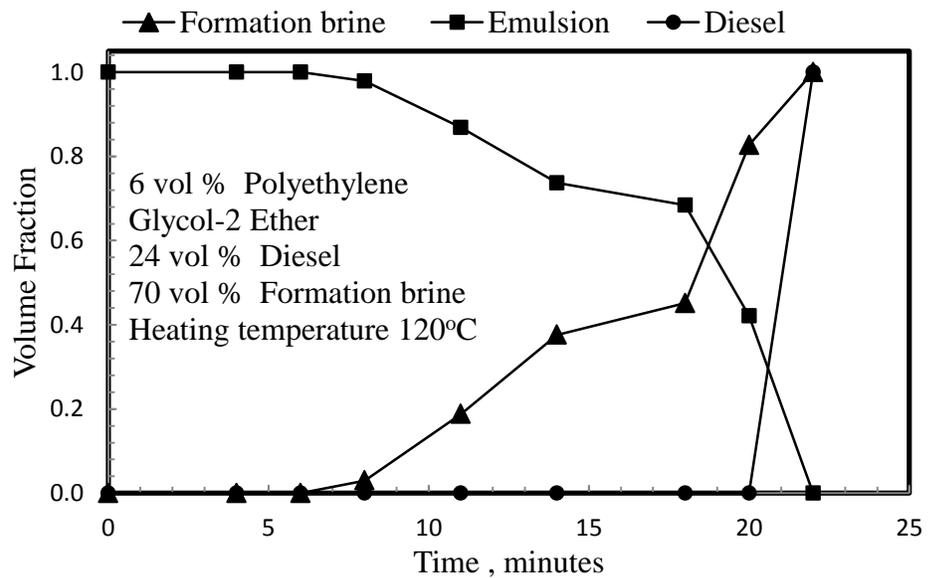
separated. This ratio did not change for another 150 minutes. Then the test was stopped. The same behavior was observed when 2 vol%, 3 vol% and 6 vol% were used. However, with the increase in emulsifier concentration the breaking of the emulsion took longer time. **Figures 2.8 – 2.10** show the positive impact of the surfactant concentration on the stability of the emulsion.



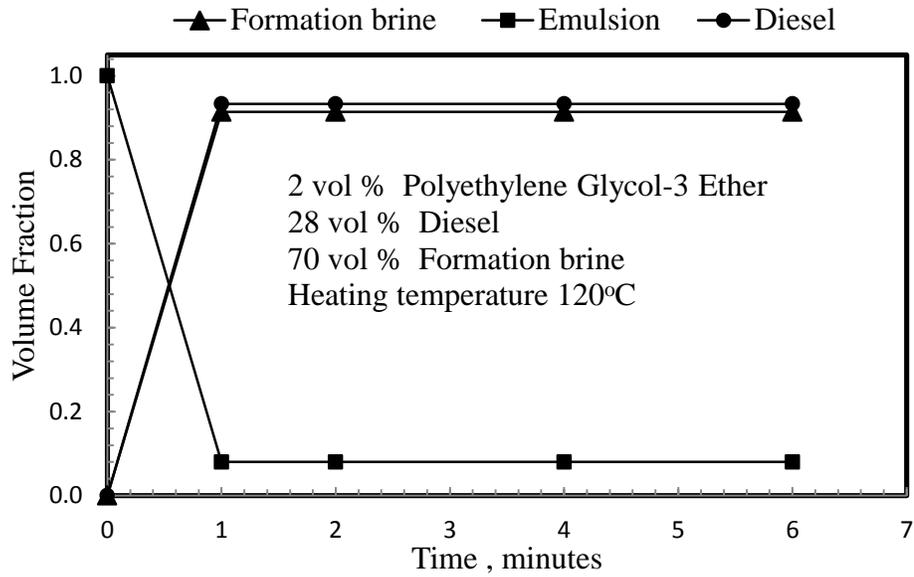
**Figure 2.3** Volume fraction for the emulsion system, 2 vol % Polyethylene Glycol-2 Ether at 120°C (248°F)



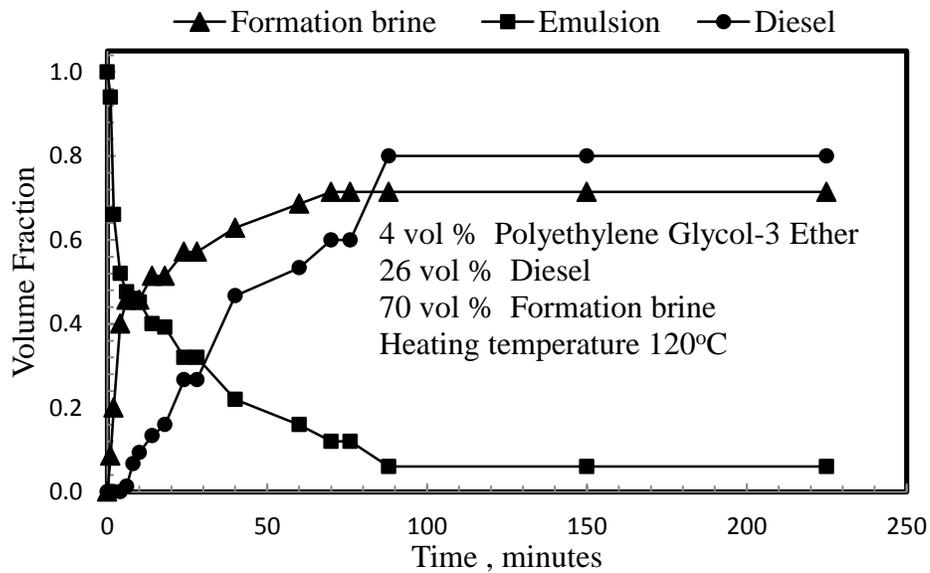
**Figure 2.4** Volume fraction for the emulsion system, 4 vol % Polyethylene Glycol-2 Ether at 120°C (248°F)



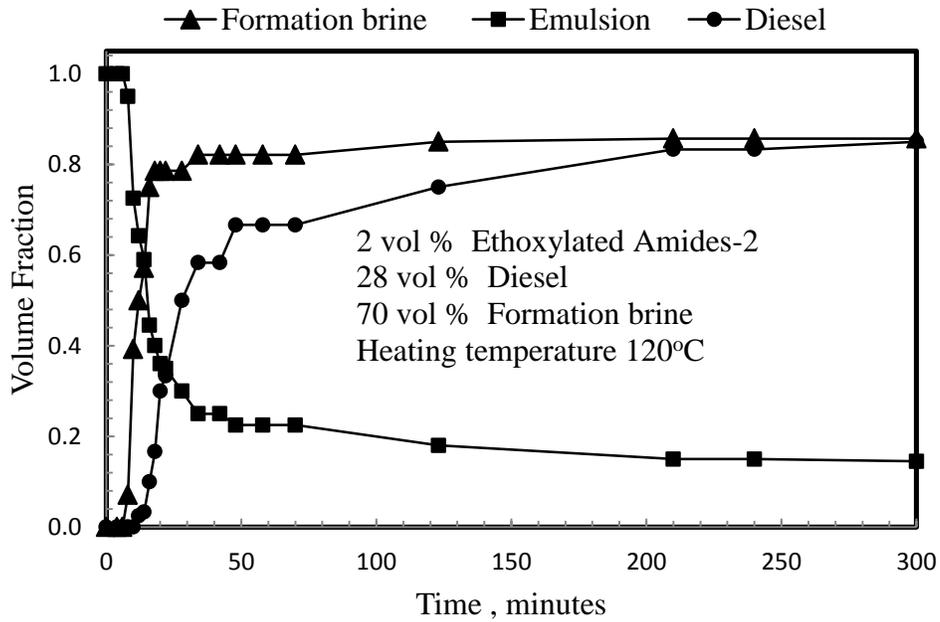
**Figure 2.5** Volume fraction for the emulsion system, 6 vol % Polyethylene Glycol-2 Ether at 120°C (248°F)



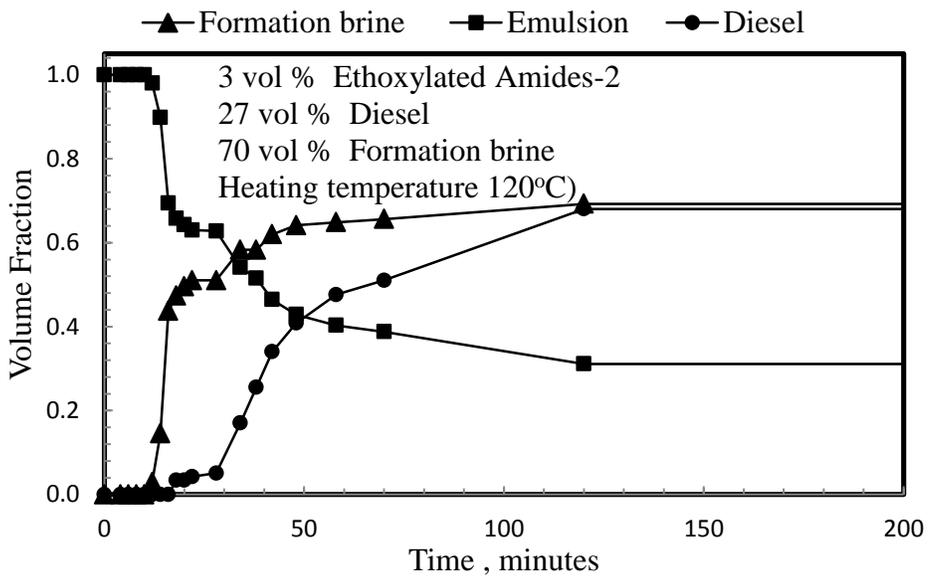
**Figure 2.6** Volume fraction for the emulsion system, 2 vol % Polyethylene Glycol-3 Ether at 120°C (248°F)



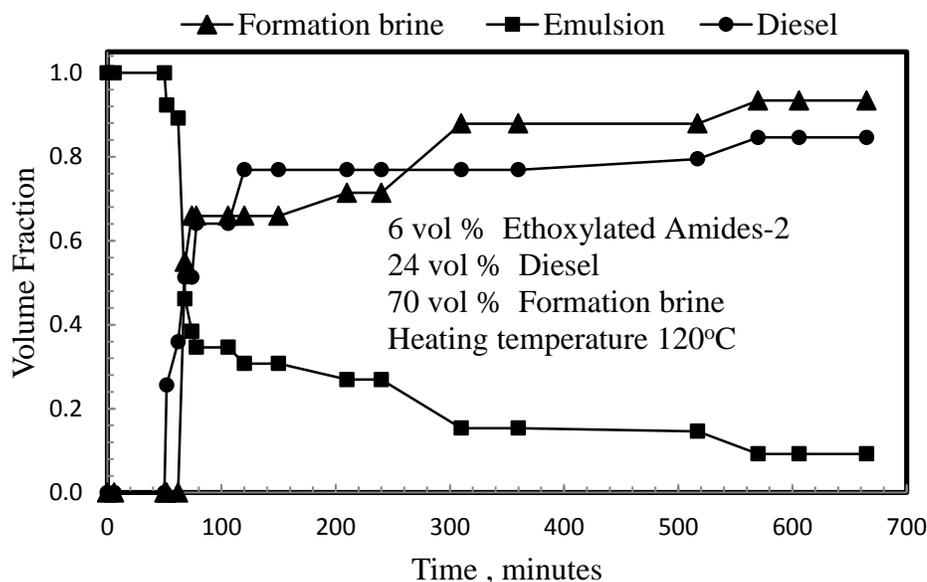
**Figure 2.7** Volume fraction for the emulsion system, 4 vol % Polyethylene Glycol-3 Ether at 120°C (248°F)



**Figure 2.8** Volume fraction for the emulsion system, 2vol % Ethoxylated Amides -2 at 120°C (248°F)



**Figure 2.9** Volume fraction for the emulsion system, 3vol % Ethoxylated Amides -2 at 120°C (248°F)



**Figure 2.10** Volume fraction for the emulsion system, 6vol % Ethoxylated Amides -2 at 120°C (248°F)

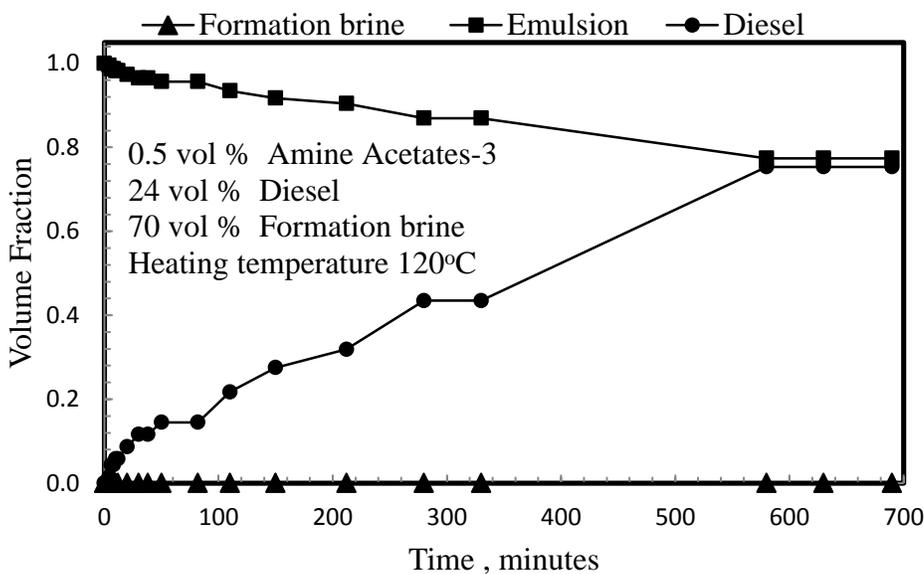
From the above observations it is clear that Polyethylene Glycol-2 Ether and Polyethylene Glycol-3 Ether do not secure the desired separation time (1 hour) at 120°C (248°F) with up to 6 vol% of surfactant. However, when 3 vol % of Ethoxylated Amides-2 was used the desired separation time was almost achieved. Polyethylene Glycol-2 Ether, Polyethylene Glycol-3 Ether and Ethoxylated Amides-2 are appropriate for applications involving emulsifying water soluble materials at low temperatures only.

### **Amine Acetates-3**

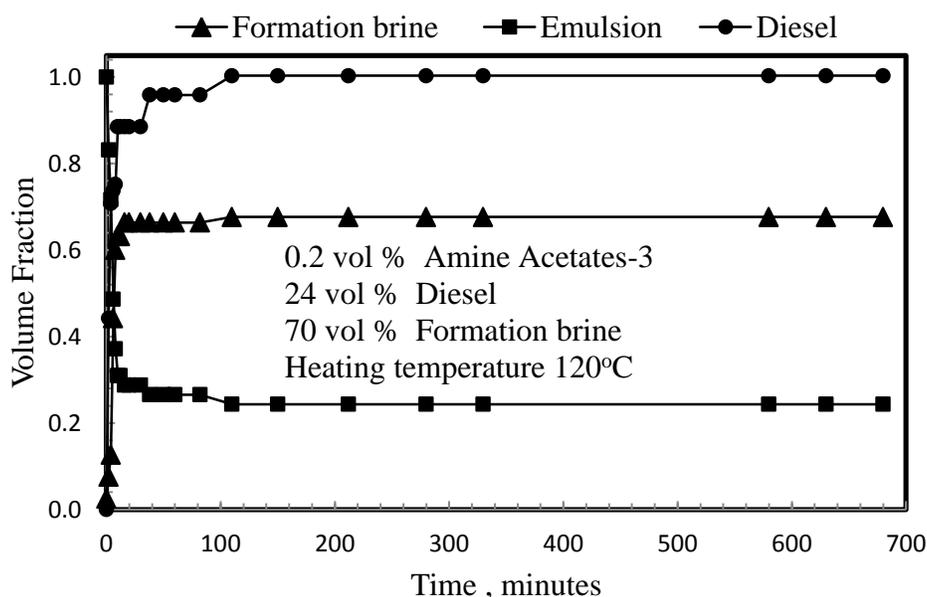
To exploit Amine Acetates-3 as emulsifier, different concentrations were used starting with 2 vol%. The emulsified system was very viscous (cream like) even when 1vol% was used. These doses are not good from operation point of view (pumping and handling operation). Consequently, the dose was reduced to 0.5 vol% and 0.2 vol% to monitor the phase behavior of the emulsion in the condition of the study (120°C). The use of 1 vol% and 0.5 vol% of the emulsifier produced flowable emulsion. The emulsion

behavior here is different to what was noted earlier in Polyethylene Glycol-2 Ether, Polyethylene Glycol-3 Ether and Ethoxylated Amides-2. Here, the oil starts to separate first in less than 5 minutes in both experiments. This behavior continued without any water separation **Figure 2.11-2.12**. Therefore, Amine Acetates-3 may be suitable for other applications that require fast release of the oil phase.

In addition, it has been perceived that the amount of diesel separated depend on the surfactant dosage. Low level of separation took place at low surfactant concentration. Further reduction (0.2 vol% ) in emulsifier concentration resulted in initial separation of both oil and water phases, in less than 4 minute , until the emulsion completely separated as shown in **Figure 2.12**.



**Figure 2.11** Volume fraction for the emulsion system, 0.5 vol % Amine Acetates-3 at 120°C (248°F)

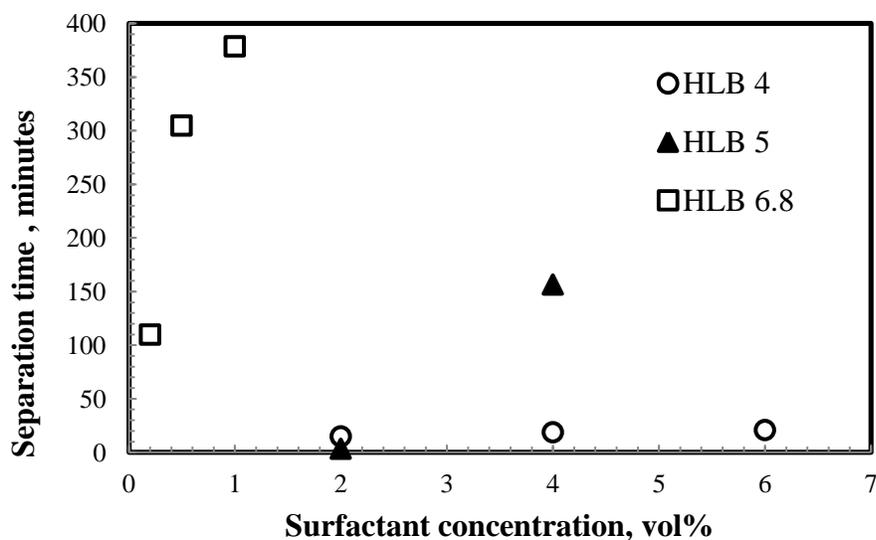


**Figure 2.12** Volume fraction for the emulsion system, 0.2 vol % Amine Acetates-3 at 12°C(248°F)

## 2.5 Reflections on HLB and Emulsion Stability

By definition, the HLB of a surfactant is a measure of the degree to which it is hydrophilic or lipophilic. Hence, authors think that an ideal emulsifier has the hydrophilic part equivalent (equal) to lipophilic portion. This may allow for equal (balanced) distribution of the emulsifier in the water and oil phases, which may lead to more stable emulsion. This hypothesis will be examined by correlating the emulsion stability to HLB. Generally, to create stable (W/O) emulsion, the HLB for specific emulsifier, must be in a certain range as described earlier by Griffin (1949, 1954). However, **Figure 2.13** suggests that more stability of W/O emulsions is achieved at higher HLB. For instance, when an emulsifier with HLB of 6.8 was used at very low concentration (0.5 vol %), the emulsion took 310 minutes to completely break down. While in the case of the emulsifier with HLB of 4 the separation time was 20 minutes, although a higher concentration (6 vol

%) was used. In addition, in **Figure 2.13** it has been noticed that the Polyethylene Glycol-3 Ether with HLB of 5, formed more stable emulsion compared to Polyethylene Glycol-2 Ether, with HLB of 4. By comparing the physical and chemical properties of the two emulsifiers (see **Table 1**) the only difference is the C/H ratio which is higher in the case of Polyethylene Glycol-2 Ether (more unsaturations in the molecule). Here we like to postulate that this behavior is likely related to the C/H in the surfactant. Higher C/H indicates the presence of more unsaturation which will influence the polarity and the surfactant may favor one phase over the other. Keeping in mind that the water phase contains cations, while the oil phase may contain acidic components. Most likely that the reduced stability is due to the unbalanced distribution of the emulsifier between the two phases as a result of the change in polarity.



**Figure 2. 13** Separation time as function of surfactant concentration, at different HLB at 120°C(248°F)

## 2.6 Conclusions

In general, this work was successful in developing stable emulsified water in oil systems that can tolerate high temperature high salinity environments using scientific approaches. In addition, HLB approach was used for surfactant selection and new insights on structure-emulsion stability relationships beyond the HLB approach were provided. The findings of this work would open more avenues for future research.

Here are the main conclusions of this article:

1. HLB was used as a criterion for surfactant selection.
2. HLB was found to work well for many surfactants of different structures. This approach is expected to reduce the time and resources needed for screening.
3. The solubility of the surfactant has been postulated to play a vital role in the type of the formed emulsion, this argument was found not Necessary true.
4. Surfactant with higher HLB value inside the recommended range for water in oil emulsion resulted in more stable emulsion. For surfactants with similar structure and physical properties, it was found that the surfactant with higher C/H ratio formed less stable emulsion. The authors postulated that this result is likely due to unbalanced distribution of surfactant as a consequence of the difference in polarity.
5. A set of new cost effective emulsifiers, suitable for emulsified water phase (polymeric gels/acids) in oil phase, were identified. The formed water in oil emulsion is very stable at high temperature and high salinity conditions.
6. The general trend is that the separation time increases with the increase in emulsifier concentration, or vice versa. The increase in stability is likely due to the decrease in interfacial tension with the increase in emulsifier concentration and the consequent delay in the coalescence of the droplets.

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## CHAPTER 3

### **Organoclay as emulsifier for Water in Oil Polymeric Gel Formulations used in water shut-off applications**

#### **Abstract**

The produced water in oil and gas wells causes serious problems. Such as; loss of productivity, corrosion, scale and environmental concerns. Generally, polymer gels are well suited for water shut-off; nevertheless without a proper placement, there is a risk of significant reduction in hydrocarbon production. In recent work, new approach has been developed, which has the advantage of selectively reducing the water production without considerably damaging the hydrocarbon recovery. Emulsifying water soluble polymer gels into Oil phase, this emulsified polymeric gels, designed to separate into a water phase and an oil phase in the porous media at reservoir conditions. In the pore space the water phase, which contains the polymer mixture (gelant), gels up while the oil phase remains mobile. The breaking of the emulsified system and then the gelation are a function of temperature, time, salinity of mixing water and concentration of the different phases. Accordingly, Organoclay (OC) has been proposed as a substitute for classical surfactants used in such application. Currently, many nanomaterials have been developed for several applications in various fields of endeavors. Layered silicate clay minerals are one of the most well-known nanomaterials due to their high surface area of the dispersed nano-sized particle, availability, low-priced and more importantly environmentally friendly. Also, the new emulsifier is expected to enhance the properties of emulsified gel solutions and most importantly improving the gel strength. The new emulsifier can form high quality water in oil (W/O) emulsions and improve the thermal

stability of emulsified polymers or acid solution. The stability of the emulsion can be controlled by controlling emulsifier concentration; the emulsion system can withstand high salinity much better than current surfactants used in oilfields. These emulsifiers will be appropriate for wellbores having high pressure and high temperature (120°C) with high salinity field water (221,673 ppm).

### **3.1 Introduction**

Emulsions are widely used in various fields such as pharmaceutical (Nielloud and Marti, 2000), hydraulic fluids (Greaves et al., 2009), polymerization (Anderson and Daniels, 2003), paints (Osemeahon, 2011) and food industries (McClements, 2009 and Friberg, 2003). Recently, the emulsification technique gained momentum in the oil and gas industry, it has been extensively applied in oil industry in applications such as drilling fluid formulations (Lawhon et al., 1967; Patel, 1999; Ebeltoft et al., 2001), well stimulation treatment (Al-Anazi et al., 1998; Nasr-El-Din et al., 2000; Nasr-El-Din et al., 2001; Fatah and Nasr-El-Din 2010; Sayed et al., 2013) and quite recently for the application of excessive water production treatment (Stavland et al., 2006).

An emulsion consists of two or more, completely or partially immiscible liquids (Tadros et al., 1983), such as oil and water, where one liquid (the dispersed phase) exists in the form of droplets suspended in the other (the continuous phase). Because the surface of each droplet is an interface between hydrophobic and hydrophilic molecules, it is inherently thermodynamically unstable (Weiss, 2002). An emulsion is formed when two immiscible liquids are mechanically stirred during the stirring process both liquid tend to form phases (Rieger, 1976; Tamilvanan, 2010). If a surfactant is added to a 2-phase system, it tends to stabilize and form a continuous and a dispersed phase, since it slow

down the breaking of emulsion such as coalescences and creaming (Becher, 1983). Stability of the emulsion depends on different factors including physical nature of the interfacial film, presence of steric barriers on the droplets, viscosity of the continuous phase, droplets size, oil/water ratio, temperature, and mixing time (Joshi et al., 2012). Emulsion stability is also related to the amount of surfactant that is adsorbed at the interface. With the adsorption of more surfactant, the interfacial tension is decreased and the surfactant molecules act as a barrier delaying the coalescence of droplets (Becher 1983; Joshi et al., 2012; Rai and Pandey, 2013).

New nanomaterials showed high performance in polymer nanocomposites due to their high aspect ratio and the high surface area of the dispersed nano-sized particles. Various nanomaterials are currently being developed; however, clay minerals are the most popular due to their availability (natural source), low cost and more importantly their being environmentally friendly (Al-Yaari et al., 2014). Of particular interest, organically modified clay mineral showed significant enhancement of a large number of physical properties (Sinha Ray et al., 2005; Sinha-Ray and Bousmina, 2005). The main reason for these improved properties in clay polymer nanocomposites (CPN) is the high surface area of the organically modified clay mineral particles as opposed to conventional fillers (Chen et al., 2002). The application of OC for emulsified acid system resulted in cost effective systems for reduction of surface treating pressures (Al-Yaari et al., 2014). As well, further research in the application of OC as an alternative emulsifier and reinforcement agent, for application such as emulsified polymeric gels for water control may result in cost effective and environmentally friendly solution.

The objective of this paper is to investigate the possibility of utilizing OC materials in forming stable water in oil emulsion for high temperature and high salinity applications in oilfields treatments.

## **3.2 Experimental Setup and Procedure**

### **3.2.1 Materials**

Organoclay was provided by Southern Clay Products, Inc, has been employed for this work. The chemical and physical properties are shown in **Table 3.1**. The surfactants used in this study were supplied by Sigma-Aldrich® , as presented in **Table 3.2** and **Table 3.3**, formation water (brine) served as water phase, the chemical analysis of the brine is given in Table 4, diesel from local gas stations which is representative of that used in the field by local industry for preparing emulsified acids have been used. Two polymer solutions were used in this study. Polyacrylamide (PAM) was delivered by SNF Florger as an aqueous solution and used without further treatment. PAM solution was 20 wt% active and has a molecular weight within the range 250 to 500 kg/mol (as disclosed by the supplier). Polyethylenimine (PEI) was used as a cross-linker in a solution form. Its activity and molecular weight were 30wt% and 70 kg/mol, respectively. Salts used in this study include Sodium and calcium chloride as presented in **Table 3.4**. All these salts were ACS grade. L-glutamic acid-N, N-diacetic acid (GLDA) is a Chelating agent that was used in this work and supplied by AkzoNobel. The molecular weights, protonation and metal stability constants of GLDA are shown in **Table 3.5** (LePage et al., 2011 ).

**Table 3.1** Organoclay, physical and chemical properties

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<b>Characteristics</b>	
Product name	Ditallowdimethylammonium Salts with Bentonite
Appearance	Cream powder
Specific density / Gravity	1.6 – 1.8
Solubility	Oil soluble

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**Table 3.2** Polyethylene Glycol-2 Ether, physical and chemical properties

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<b>Characteristics</b>	
Type	Nonionic
Molecular formula	$C_{18}H_{35}(OCH_2CH_2)_nOH$ , n~2
Molecular weight (MW)	Mn ~357
Appearance	liquid , yellow
Refractive index	n 20/D 1.462(lit.)
Relative density	0,912 g/cm <sup>3</sup> at 25 °C
HLB	4

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**Table 3.3** Polyethylene Glycol-3 Ether, physical and chemical properties

---

<b>Characteristics</b>	
Type	Nonionic
Molecular formula	$C_{16}H_{33}(OCH_2CH_2)_nOH$ , $n \sim 2$
Molecular weight (MW)	$M_n \sim 330$
Appearance	Solid , white
Refractive index	$n_{20/D} 1.466(\text{lit.})$
Relative density	0,978 g/mL at 25 °C
HLB	5

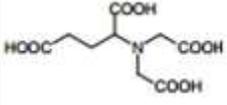
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**Table 3.4** Chemical analysis of the formation brine

<b>Ion</b>	<b>Concentration, mg/L</b>
$Na^+$	59,300
$Ca^{2+}$	23,400
$Mg^{2+}$	1,510
$SO_4^{2-}$	110
$Cl^-$	137,000
$HCO_3^-$	353
(TDS)*	221,673

\*Total dissolved solids determined by addition.

Table 3. 5 Chelate molecular weights, protonation and metal stability constants

Chelate		Molecular weights		pK <sub>s</sub> value				Log K	
Abbreviation	Structure	Acid	Sodium salt	pK <sub>1</sub>	pK <sub>2</sub>	pK <sub>3</sub>	pK <sub>4</sub>	Ca <sup>2+</sup>	Fe <sup>3+</sup>
GLDA		263	351	9.36	5.0	3.5	2.6	5.9	11.7*

\*value is not listed in the national institute of sciences and technology standard reference database 46 version 7.0 for critically selected stability constants of metal complexes. Experimental results indicate that Fe<sup>3+</sup> the stability constant of GLDA is comparable to NTA.

### 3.2.2 Equipment

The emulsion were formed utilizing high performance dispersing instrument Ultra-Turrax T 50 Basic provided by VWR International, the homogenizer is equipped with a variable speed drive with different 6 speeds available 500 – 10000 RPM. CDC401 Conductivity meter provided by HACH with range 0.01 to 200,000 μS/cm, the device can handle total dissolved solid in the range 0 to 50 mg/L as NaCl, operation temperature -10 to 110 °C (14 to 230 °F), minimum sample depth 45 mm (1.77 in), the meter exploited to classify the emulsion type whether it is water in oil or oil in water. GL-18 high temperature disposable test tubes, soda-lime-glass (18 x 180 mm) of approximate volume of 32 ml and operation temperature of 180°C were used. The high temperature tubes were sealed with a screw-cap and a rubber seal case to prevent evaporation. The fact that no evaporation is taking place was assured by comparing the initial and final volumes of the sample at the end of the experiment. HAAKE FISIONS hot oil bath Model N3, with temperature range: ambient to 300 °C was employed to study the emulsion separation: separated volume fraction of the phases versus time.

### 3.2.3 Emulsion Preparation

Several emulsion systems with varying emulsifiers (organoclay and composite system of organoclay/surfactant) and emulsifier concentrations, were prepared in a systemic way to ensure the reproducibility of the water in oil emulsions. Emulsion type depends more on the nature of the emulsifying agent than on the relative proportions of oil or water present or the methodology of preparing emulsion. One of the first empirical rules developed to describe the type of emulsion that could be stabilized by a given emulsifier was proposed by Bancroft's rule, which states that the phase in which an emulsifier is more soluble constitutes the continuous phase. Hence, a water soluble emulsifier forms O/W emulsions, whereas an oil soluble emulsifier stabilizes forms W/O emulsions (Langmuir, 1996).

To further support our claim, water in oil emulsion was prepared by first dissolving the emulsifier (at specific concentration) into diesel, the emulsifier was given enough time to mix in the diesel thoroughly, followed by subjecting the mixture to agitation for 5 minutes. Afterwards, a desired volume of the water phase (brine) was gradually added to the hydrocarbon phase (diesel and emulsifier mixture). The emulsification process was performed using the high power homogenizer; the speed of agitation was 2000 rpm. Dilution test was conducted to confirm that the formed emulsion is water in oil since it did disperse in diesel. In furtherance to ensure that the produced emulsion is water in oil, conductivity test was used to check the external phase of this emulsion. The result showed that there was no dispersion in water phase and the emulsion had no conductivity ( $0\mu\text{S}/\text{cm}$ ). It is important to add the water phase droplets

slowly and uniformly throughout the mixing. Note that the rate of the addition of the dispersed phase to the continuous phase and the intensity of mixing are critical to the produce emulsion. The coarsest emulsion will be produced when all the dispersed phase is added at once to the continuous phase and then shaken by hand. On the contrary, the finest emulsion will be produced when the dispersed phase is atomized with a spray bottle to the continuous phase in a blender at a very high mixing speed (Al-Mutairi 2008).

### **3.2.4 Emulsion Thermal stability Test**

To investigate the thermal stability of the formed emulsion, a high temperature test tube was used to conduct stability tests for all formed emulsions by monitoring the separated volume fraction of the oil and water phases versus time at constant temperature. Such a test can give an indication about emulsion quality by relating the emulsifier concentration to the thermal stability.

From operational point of view, the thermal stability of the emulsified system is playing crucial role on the success of any treatment. For instance, in emulsified acid no separation for specific time is required. Similarly, designed separation time is necessary for the application of water shut-off treatments. Therefore, the thermal stability of various emulsions were investigated at high temperature, to enhance the current understanding of the effect of surfactant concentration on the stability of the emulsion (emulsion quality). Cross-linked polymeric gels especially polyacrylamide gels are widely used in petroleum industry to minimize water production during oil and gas exploration and production. Aqueous polymer gels are usually emulsified in oil and then injected in the water zones. The emulsion should be injected as one component, and then it will separate into oil

phase and water phase. The water phase contains the (polymer mixture) gelant which will gel-up in a portion of the pore space to reduce permeability to water, the oil phase remains mobile to secure a path for oil to flow (Stavland et al., 2006). Surfactants are usually used to emulsify the aqueous gel solution in oil. Accordingly, the complete separation of emulsified system is important for water shut-off treatment,

Thus, the study designed up based on controllable separation time as the desired property of the produced emulsion to meet the operational requirement (treatment placement). The time needed for gelling solution placement was reported to be about 55 minutes at 150°C (302°F) (Al-Muntasheri et al., 2010). Consequently, the emulsified gels system should be at least stable for an hour. Breakage and gelation of system should start afterward. Usually, pre-flush injected prior the treatment to cool down the reservoir from 150°C (302°F) to 116°C (240.8°F). Therefore, the thermal stability of all formed emulsions was investigated at 120°C.

In all emulsions prepared the total volume were 30 ml, 70 % of which was water phase (brine) , the rest 30% was hydrocarbon phase (the mixture of emulsifier and the diesel). The diesel percentage was in range of 24–28%, while the emulsifier percentage was in range of 2% - 6%, all emulsions have been prepared at room temperature under 2000 rpm. Then, the thermal stability was examined in bulk at 120°C (248°F) for 12 hours using the oil heating bath.

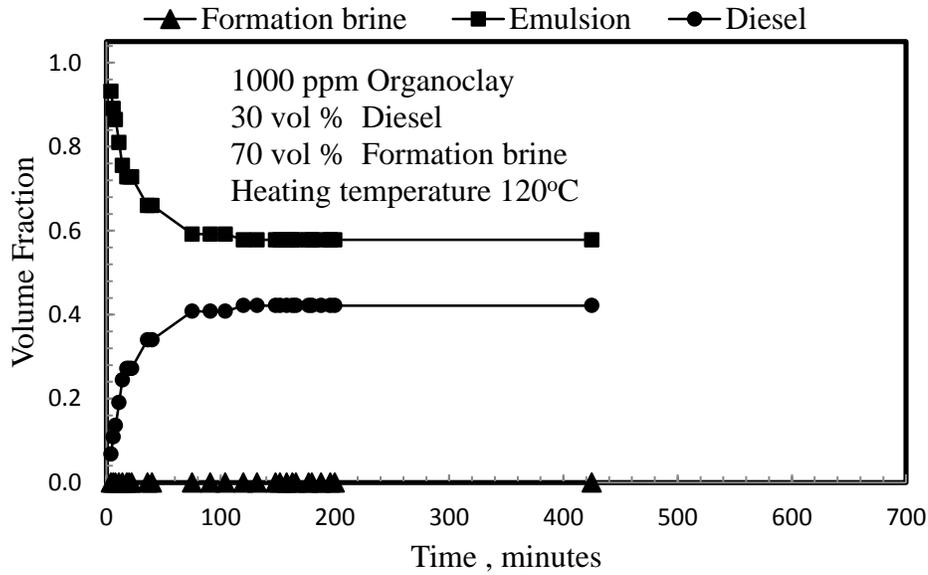
### **3.3 Results of The Thermal Stability**

#### **3.3.1 Organoclay**

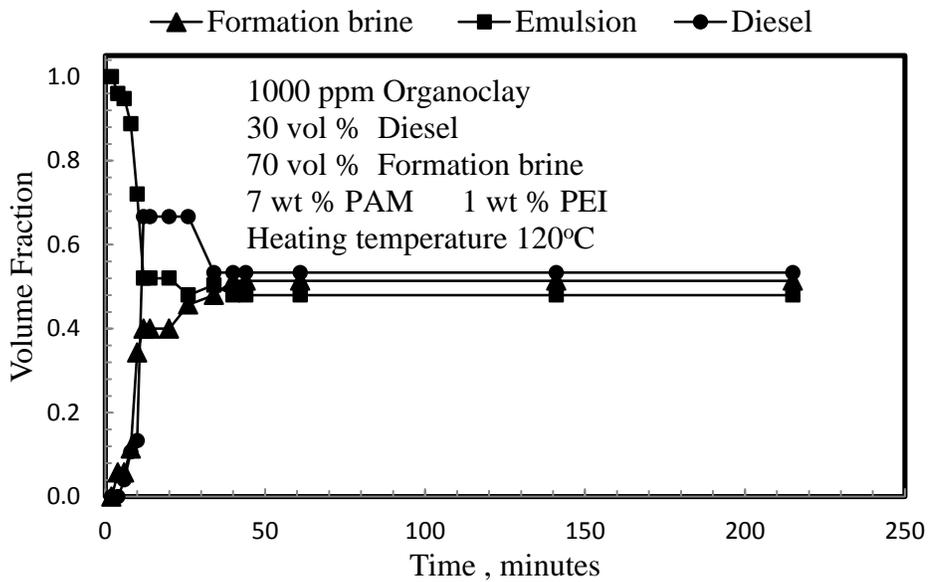
The emulsion formed by use of 1000 ppm Organoclay , insignificant separation of the oil phase has been measured after 4 minutes of heating the emulsion, this percentage

kept on increasing to 42% at 2 hours, no additional separation has been observed until the completion of the test, whereas water phase did not separate at all. Interestingly an expansion of 25 ml has been witnessed in the original volume of the sample. This volume kept on increasing until it reached 30 ml by the end of the experiment **Figure 3.1**. This emulsion system may be utilized as delivering media for oil soluble material. It is crystal clear that this formula is very stable after 6 hours. A smaller concentration of 600 ppm Organoclay has been used to study the effect of OC concentration on stability, different manner of the emulsion breakage have been detected in a less than 3 minutes and oil started to separate, while the water phase separation happened late after 24 minutes, both of the phases separation continued up until the maximum separation after 278 minutes of heating. Remarkably, the emulsion began to shrink after 3 hours with increase in the brine volume as shown in **Figure 3.3**. Further reduction in concentration (300 ppm) of the Organoclay has been used in attempt to gain more control of the emulsion separation, but this low dosage was not enough to form an emulsion. in general terms, some of emulsions produced by utilizing the Organoclay alone as emulsifier are very stable or not controllable in term of separation, consequently using Organoclay by itself as emulsifier is not optimum choice. Therefore, chelating agent has been purposed to address this issue, evidently the effect of the chelating agent on the emulsion system can be seen in **Figure 3.4**, and less stable emulsion have been formed, the oil phase start separating after 2 minutes, then water phase separation occurred after 30 minutes. In the prepared emulsion with 1000 ppm Organoclay and 2vol% GLDA, specimen quick separation of the oil-phase spotted at the beginning in less than 6 minutes after heating. Accurately the stability of the emulsion reduced due to the ability of the chelating agent of isolating the

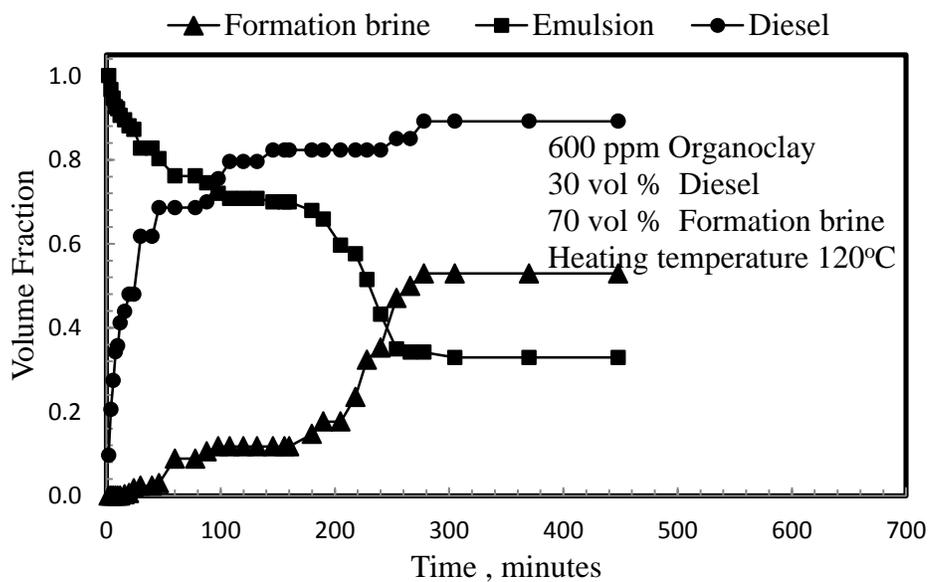
salt in the water phase which is considerably affecting the emulsion stability. Moreover, adding PAM/PEI to the water phase decrease the emulsion separation time and this behavior could be explained by the fact that some of the emulsifier absorbed by the polymer **Figure 3.1** and **3.2**, which has been observed elsewhere (Arne et al., 2006)



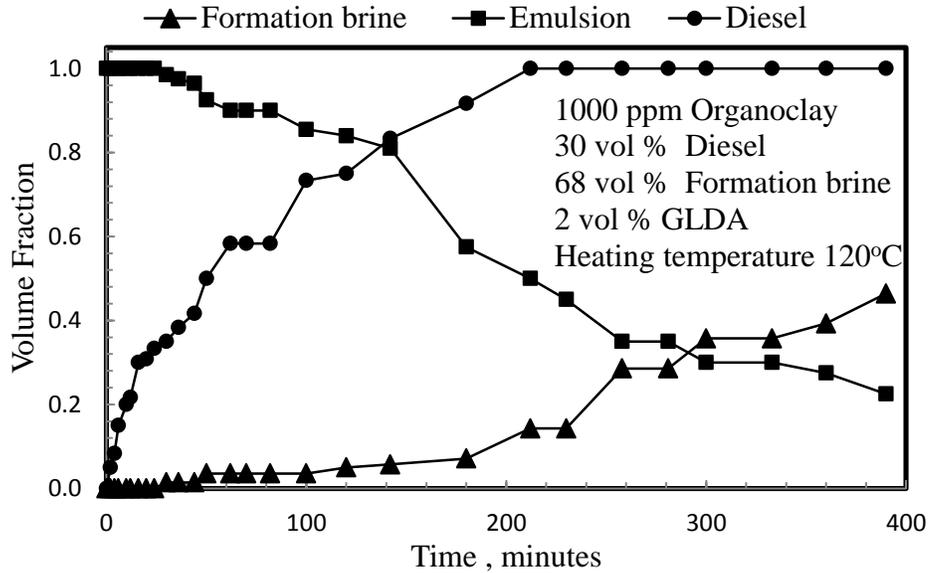
**Figure 3.1** Volume fraction for the emulsion system, 1000 PPM Organoclay at 120°C (248°F)



**Figure 3.2** Volume fraction for the emulsified (7/1) wt% (PAM/PEI), 1000 PPM Organoclay at 120°C (248°F)



**Figure 3.3** Volume fraction for the emulsion system, 600 PPM Organoclay at 120°C (248°F)

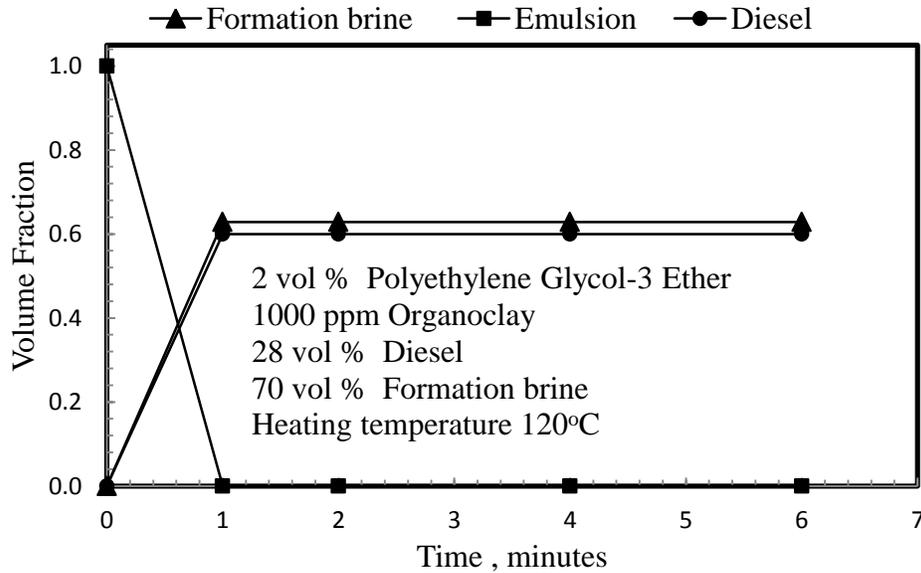


**Figure 3.4** Volume fraction for the emulsified 2 vol % GLDA, 1000 PPM Organoclay at 120°C (248°F)

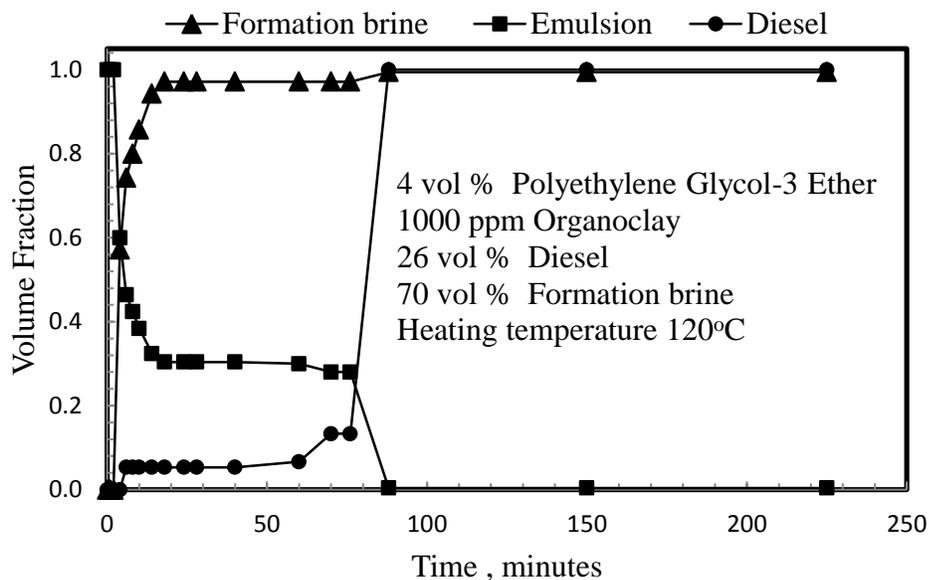
### 3.3.2 Organoclay/Surfactant Composite

The combinations of surfactant and Organoclay mixed together at different concentrations have been tested. Firstly, the system of Polyethylene Glycol-3 Ether + Organoclay similar behavior to Polyethylene Glycol-3 Ether alone with slight improvement in the emulsion stability (longer separation time), however compared to using only Organoclay as emulsifier the emulsion stability significantly reduced **Figure 3.5-3.6**. similar trend have been witnessed in the system Polyethylene Glycol-2 Ether + Organoclay, a low surfactant concentration such as 2 vol% **Figure 3.7-3.9** added to different Organoclay concentrations (300 , 600 and 1000 ppm ) it is found not enough to break the emulsion completely and a high concentration (6 vol%) form very stable emulsion **Figure 3.13-3.15**. In this coupled system even a low concentration 300 ppm of Organoclay can form emulsion. Remarkably in the coupled system no noteworthy when

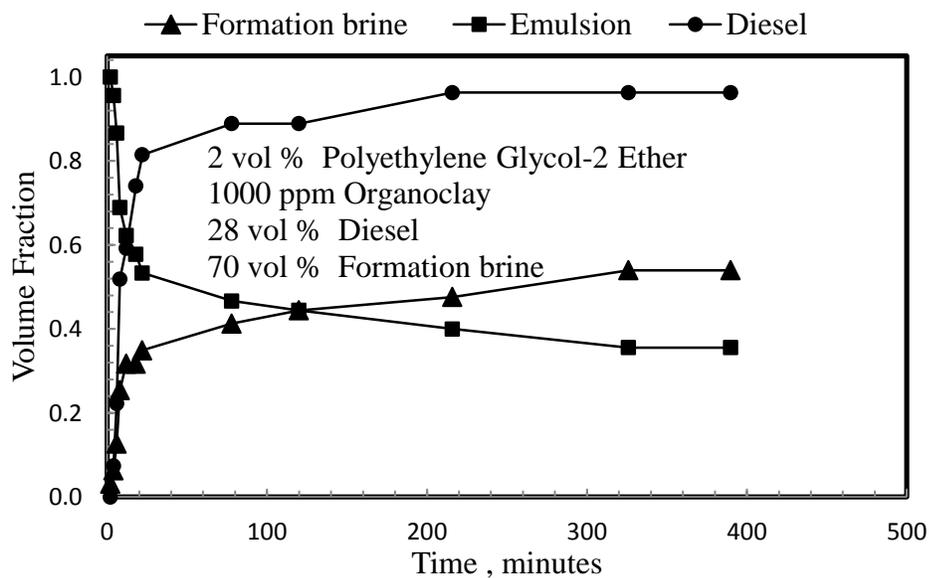
changing the concentration of Organoclay from 600 ppm to 300 ppm similar affect detected .finally 4 vol% of Polyethylene Glycol-2 Ether plus 300 ppm (mg/L) of Organoclay found to be the optimum recipe which, can accomplish 1 hour of stability and complete controllable separation **Figure 3.10-3.12**.



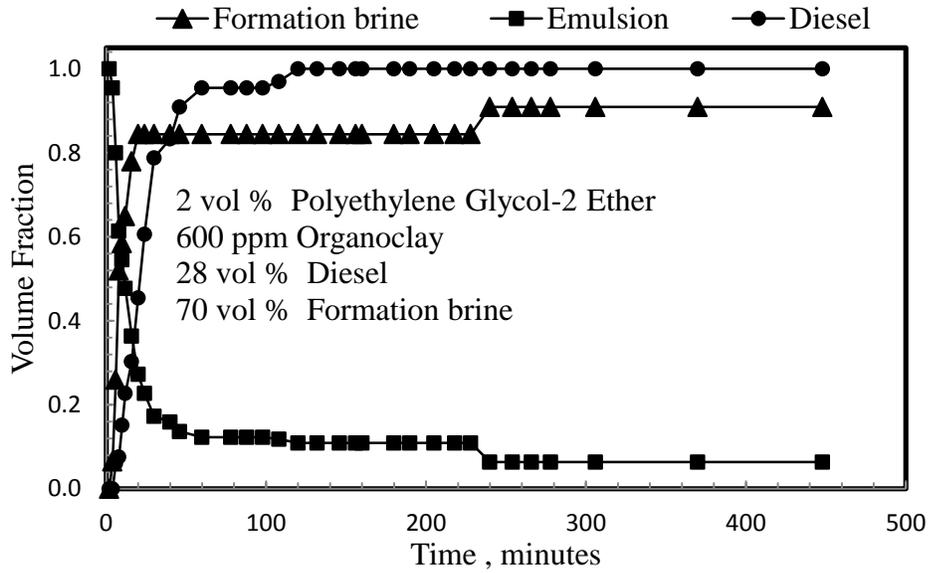
**Figure 3.5** Volume fraction for the emulsion system, 2 vol % Polyethylene Glycol-3 Ether + 1000 ppm Organoclay at 120°C (248°F)



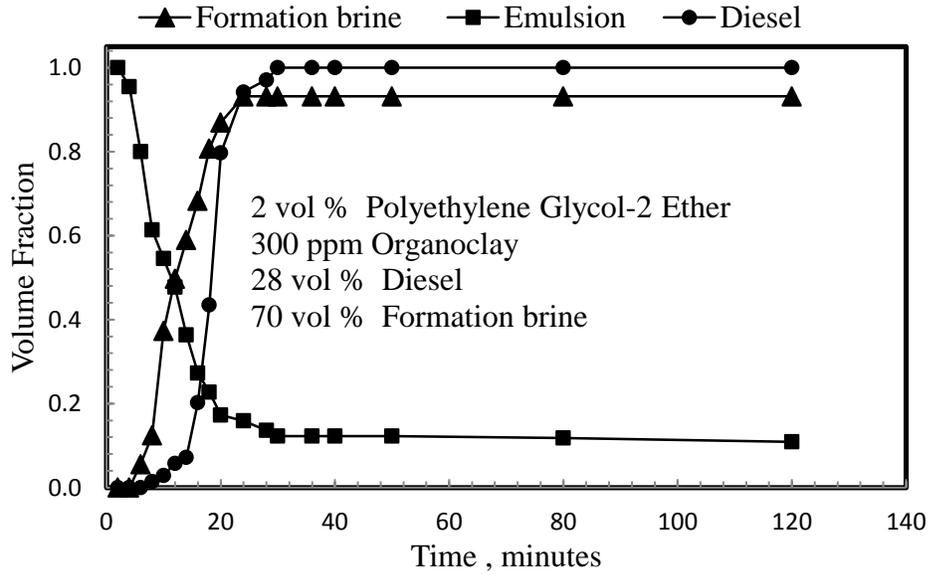
**Figure 3.6** Volume fraction for the emulsion system, 4 vol % Polyethylene Glycol-3 Ether + 1000 ppm Organoclay at 120°C (248°F)



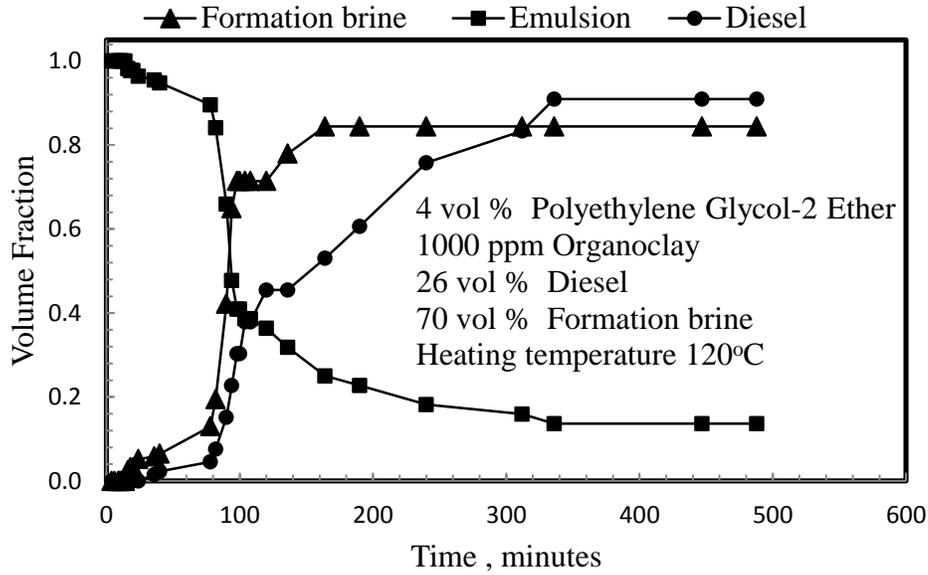
**Figure 3.7** Volume fraction for the emulsion system, 2 vol % Polyethylene Glycol-2 Ether + 1000 ppm Organoclay at 120°C (248°F)



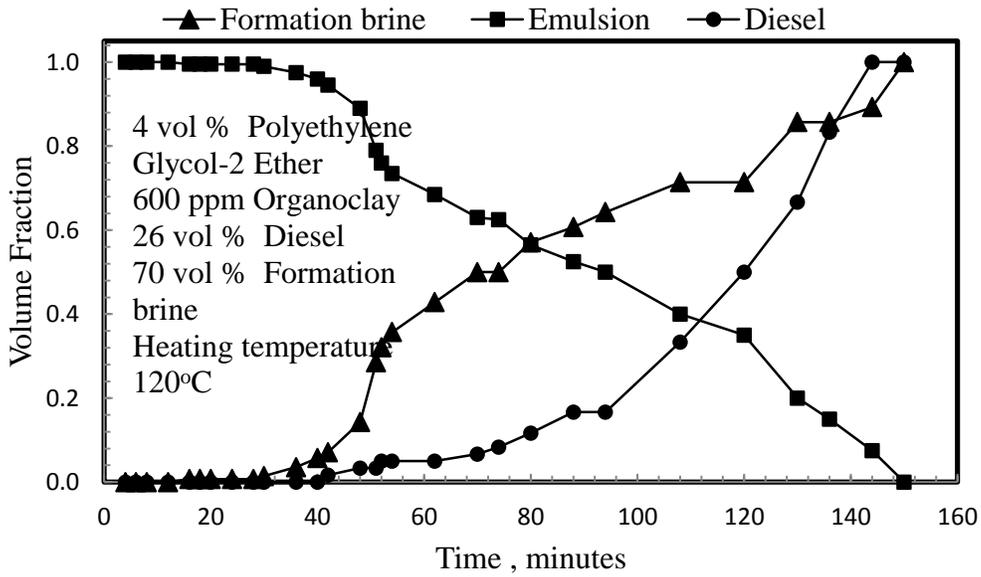
**Figure 3.8** Volume fraction for the emulsion system, 2 vol % Polyethylene Glycol-2 Ether + 600 ppm Organoclay at 120°C (248°F)



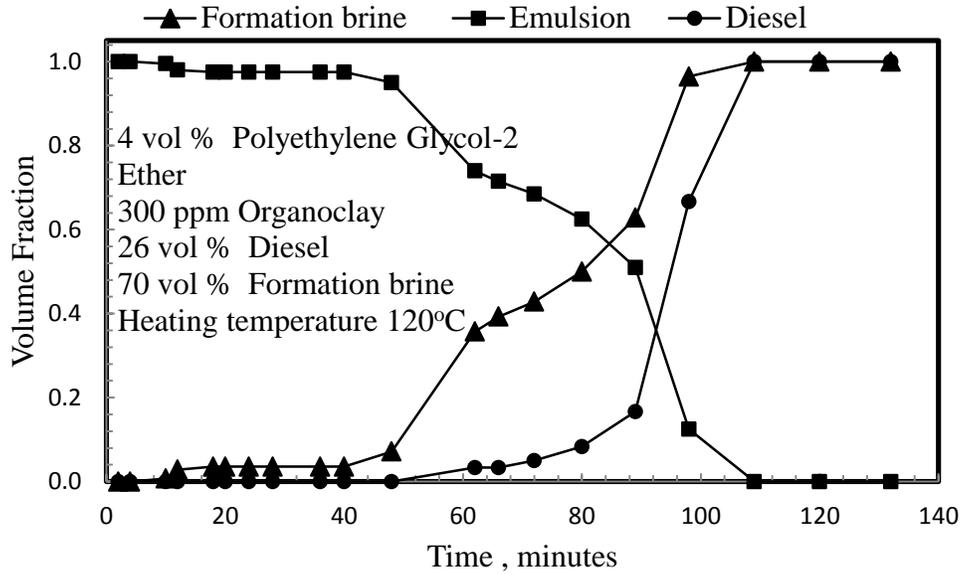
**Figure 3.9** Volume fraction for the emulsion system, 2 vol % Polyethylene Glycol-2 Ether + 300 ppm Organoclay at 120°C (248°F)



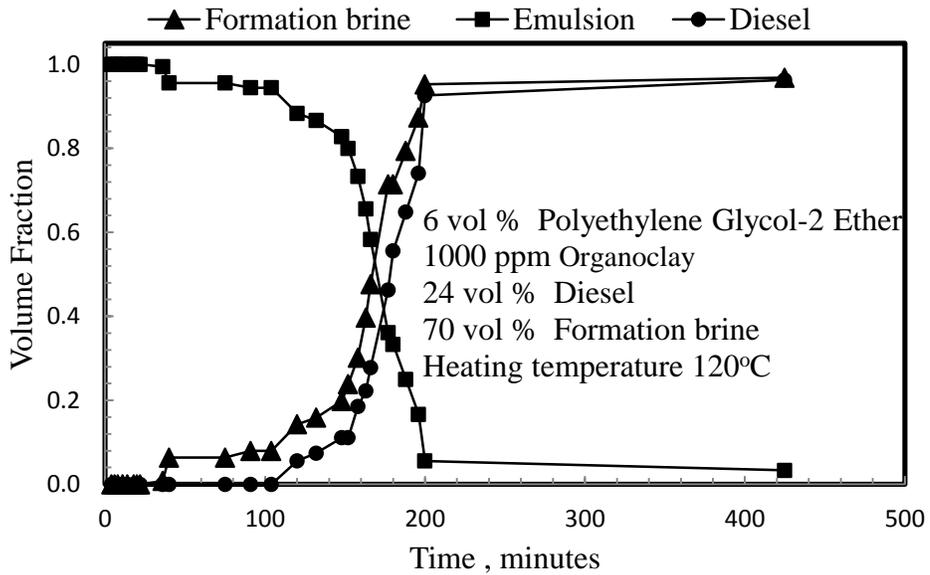
**Figure 3.10** Volume fraction for the emulsion system, 4 vol % Polyethylene Glycol-2 Ether + 1000 ppm Organoclay at 120°C (248°F)



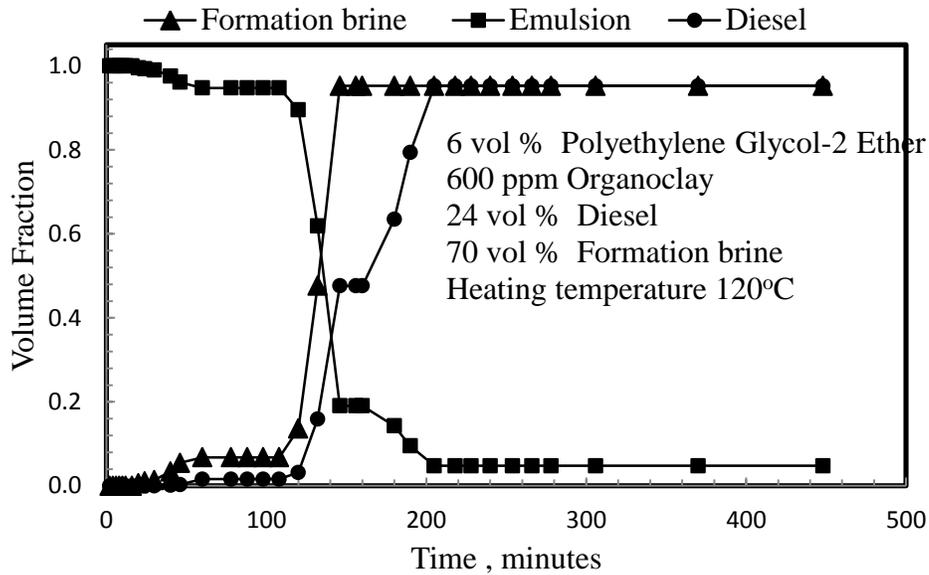
**Figure 3.11** Volume fraction for the emulsion system, 4 vol % Polyethylene Glycol-2 Ether + 600 ppm Organoclay at 120°C (248°F)



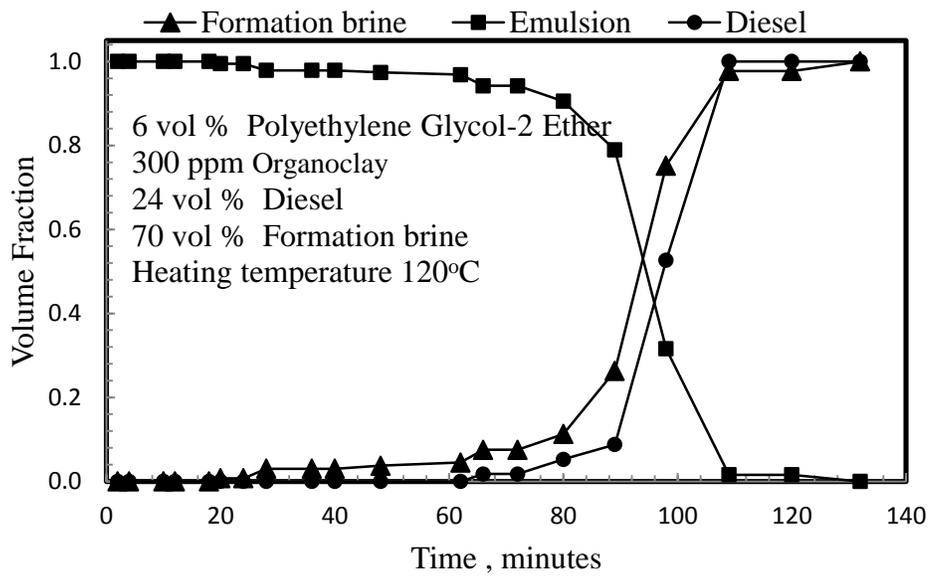
**Figure 3.12** Volume fraction for the emulsion system, 4 vol % Polyethylene Glycol-2 Ether + 300 ppm Organoclay at 120°C (248°F)



**Figure 3.13** Volume fraction for the emulsion system, 6 vol % Polyethylene Glycol-2 Ether + 1000 ppm Organoclay at 120°C (248°F)



**Figure 3.14** Volume fraction for the emulsion system, 6 vol % Polyethylene Glycol-2 Ether + 600 ppm Organoclay at 120°C (248°F)



**Figure 3.15** Volume fraction for the emulsion system, 6 vol % Polyethylene Glycol-2 Ether + 300 ppm Organoclay at 120°C (248°F)

### 3.4 Conclusions

1. The emulsion produced by utilizing the 1000 ppm Organoclay alone as emulsifier is very stable, and it requires more optimization for near wellbore application, however, for the deep reservoir profile modification it is expected to meet the desired stability.
2. The system of coupled emulsifiers (Organoclay/Surfactant Composite), the surfactant worked as destabilizer to break down the emulsion produced by utilizing Organoclay. The formed emulsion is controllable in term of separation, nevertheless the concentration of the (surfactant and Organoclay) play critical role in the emulsion stability.
3. At low concentration of the emulsifier (Organoclay / Surfactant system) and low oil phase fraction (30 volume %), the formed water in oil emulsion is very stable (2 hours) at high temperature high salinity reservoir conditions.
4. Chelating agent (GLDA), at low concentration showed high possibility to be employed as emulsion destabilizer, due to their inherently property of Sequestering metallic ions in water ( $\text{Ca}^{2+}$ ,  $\text{Mg}^{2+}$ ).
5. The emulsion stability was slightly improved by replacing the formation brine with polymers mixture (PAM/PEI).
6. The general trend is that the separation time is decreased with increasing temperature and decreasing emulsifier concentration. For all systems the emulsion was regained if agitation was turned on.
7. The organoclay is cost effective emulsifiers, suitable for emulsifying water phase (polymers/acids) in oil phase, appropriate to high temperature and high salinity applications.

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## CHAPTER 4

### **Surfactant Stabilized Emulsified Gels of polyacrylamide /polyethylenimine: Influence of different Parameters**

#### **Abstract**

Emulsification has been widely employed in the oil industry. The thermal stability of the emulsified systems, such as emulsified gels or acids, is very critical for the emulsified system successes, particularly in the case of emulsified acid. Early separation of this system in well tubular leads to corrosion. In this study, the stability of emulsified polyacrylamide /polyethylenimine gels was investigated at high temperature and high salinity conditions. The influence of different parameters, such as water and oil phase fractions, salinity, intensity of mixing, surfactant concentration and temperature, on the droplet size and the thermal stability of the emulsion was studied. Emulsified gel droplet size decreases and the separation time increases with the increase in mixing speed, surfactant concentration, salinity and water fraction. Emulsion droplet size has been correlated to thermal stability. Emulsions with smaller droplet size were found to be more stable. Conclusively, this work was successful in developing the current understanding of how to control emulsion stability through different parameters to withstand high temperature high salinity environments. The emulsion stability has improved with the increase in surfactant concentration, salinity, mixing intensity and water/oil ratio. Increase in temperature was found significantly reduce the stability; this may be due to the high rate of coalescence.

## 4.1 Introduction

Emulsification techniques were utilized for long time in various fields (Nielloud and Marti, 2000; Greaves et al., 2009; Anderson and Daniels, 2003; Osemeahon, 2011; McClements, 2009; Friberg, 2003). Likewise, in the oil industry emulsification has been broadly applied in applications such as drilling fluid formulations (Lawhon et al., 1967; Patel, 1999; Ebeltoft et al., 2001), well stimulation treatment (Fatah and Nasr-El-Din 2010; Sayed et al., 2013), drag reduction in multiphase flow (Al-Yaari et al., 2014) and recently for water shut off (Arne et al., 2006).

An emulsion is a colloidal dispersion of two or more completely or partially immiscible liquids (Tadros et al., 1983), where a dispersed phase exists in the form of spherical droplets suspended in a continuous phase. It is naturally thermodynamically unstable (Weiss, 2002), due to an interaction between hydrophobic and hydrophilic molecules at the surface of each droplet. An emulsion is formed when two immiscible liquids are mechanically stirred during the process both liquids tend to form different phases (Rieger, 1976; Tamilvanan, 2010). If a surfactant is added to a 2-phase system, it tends to stabilize and form a continuous and a dispersed phase, since it slows down the breaking of emulsion such as coalescences and creaming (Becher, 1983; Guo et al., 2006; Binks and Rocher 2009). Droplets coalesce by creating a cross linked three dimensional networks of aggregates on the droplet surface. Emulsifiers are believed to be able to form a viscoelastic barrier (Guo,et al., 2006; Binks and Rocher 2009). Emulsions' rigid interfacial films on the dispersed droplets surface are reported to have the ability to prevent the coalescence process (Kokal, 2005). Stability of the emulsion depends on

different factors including physical nature of the interfacial film, presence of steric barriers on the droplets, viscosity of the continuous phase, droplets size, oil/water ratio, temperature, and mixing time (Joshi et al., 2012).

Emulsion stability is also related to the amount of surfactant that is adsorbed at the interface. With the adsorption of more surfactant, the interfacial tension is decreased and the surfactant molecules act as a barrier delaying the coalescence of droplets (Becher, 1983; Joshi et al., 2012; Rai and Pandey, 2013). Moreover, the droplet size and its specific surface area were found to increase with the increase in surfactant concentration and decrease with the increase in acid volume fraction (Al-Mutairi et al., 2008). Additionally, water salinity play important role in the stability , an increase in the external phase (water) salinity ( $\geq 5,000$ ), resulted in smaller double layer indicated by a lower interfacial tension (Aveyard et al., 1989), further increase resulted in phase inversion from oil in water (O/W) to water in oil (W/O) (Winsor, 1948). A nonhomogeneous distribution of the dispersed droplets (oil phase) were noticed, when salinity increased from zero ppm to 5,000 ppm, which has been related to a negative interaction between the emulsifier and the external phase (water) charges (Al-Yaari et al., 2013). Conversely, at high salinity ( $\geq 20,000$  ppm), an enhancement was observed in water in oil emulsion viscosity in addition to repulsive forces between the droplets of the dispersed phase (water). This enhancement has led to increase in water droplets double layer (Al-Yaari et al., 2013). This has been proposed due an increase in the interfacial tension (Aveyard et al., 1989). Also, emulsifier is more soluble in external phase (oil) in (W/O) emulsions, consequently, the medium hydrophilicity will be an increase with salinity decreases leading to increase emulsion stability (Strassner, 1968; Fortuny et al.,

2007). It has been postulated that the increases in (water) dispersed droplets film rigidity is expected , when the aqueous phase salinity increase (McLean and Kilpatrick 1997) , this argument agree with what have been reported in the literature (Al-Yaari et al., 2013). Emulsion stability is also linked to the intensity of mixing; low shearing was found to produce coarse emulsions, whereas high shearing produced fine emulsions (Al-Mutairi et al., 2008).

Emulsification techniques were introduced in the oil industry through the use of emulsified acids in 1933. Emulsified acids were invented to address corrosion problems rather than improve the stimulation job (De Groote, 1933). As a result, many researchers comprehensively studied this technique for further understanding of advantages and disadvantages of emulsified acids (Dill et al., 1961; Knox and Lasater 1964; Davis et al., 1965; Knox et al., 1965; Crenshaw and Flippen 1968; Nierode and Kruk 1973; Navarrete et al., 1998; Al-Anazi et al., 1998; Nasr-El-Din et al., 2000). Moreover, extensive study on micro level to develop better understanding of the effect of droplet size, emulsifier concentration, and acid volume fraction on the rheological properties and stability of emulsified acids were reported (Al-Mutairi et al., 2008; Sayed et al., 2011). Recently, the emulsification technique gained momentum in the oil industry. Emulsification has been employed for different applications such as emulsified acids for matrix-acid treatments of water injectors, and water-disposal wells (Al-Anazi et al., 1998; Nasr-El-Din et al., 2000), acid-fracturing treatments of deep hot gas wells (Nasr-El-Din et al., 2001), a cost-effective emulsified xylene to remove asphaltene deposition and enhance well productivity (Fatah and Nasr-El-Din 2010) and an innovative emulsified chelating agents for permeability enhancement of Indiana limestone core (Sayed et al., 2013). In addition

to the well stimulation applications, a new application of emulsification technique in the oilfield is proposed recently as a method for water control with bullhead injection. In this case disproportionate permeability reduction (DPR) or relative permeability modifier (RPM) takes place. DPR will be effective in multilayered reservoirs without crossflow and with some zones producing clean oil or in treating coning problems (Liang and Seright, 1993; Stavland et al., 1998; Botermans and Van Batenburg, 2001). The existence of DPR fluids is well known (Schneider, 1982; Sparlin 1976; Zaitoun, 1999; Seright, 2009; Liang and Seright, 1992, Kalfayan and Dawson, 2004). In a patent, Stavland and Nilsson suggested injection of the gelant as an emulsion for RPM field application (Stavland and Nilsson, 1999). In Stavland work (2006), a water based gelant is emulsified in oil and injected into the formation. The emulsion is designed to separate into a water phase and an oil phase at static conditions in the formation. The water phase gels up while the oil phase remains mobile. It has been found that the controlling parameter for DPR is to control the fraction of gel occupying the porous media (saturation of the gel in the pore space). The water fraction in the emulsion controls the reduction in the relative oil and water permeability (Arne et al., 2006).

Emulsions are thermodynamically unstable (Weiss, 2002), forming stable emulsion to meet the requirements of oil field applications is not simple practice, coupled with the fact that applications are becoming increasingly demanding, necessity to develop deep understanding of the emulsification mechanism and how to stabilize it. The objective of this paper is to study the impact of different factors on the thermal stability of the emulsified gel. Furthermore, the relationship between the thermal stability and the emulsified system droplet size was investigated.

## 4.2 Experimental Setup and Procedure

### 4.2.1 Materials

The surfactant (Ethoxylated Amides-2) was supplied by AkzoNobel, was used as emulsifier, its chemical and physical properties as shown in **Table 4.1**. Sea water, field mixing water (FMW) and formation brine were used as the water phase and the concentration of dissolved ions is shown in **Table 4.2**. Diesel ( $814.6 \text{ kg/m}^3$ ), which is representative of that used in the field for preparing emulsified acids, was procured from the local gas stations. Polyacrylamide (PAM) and Polyethylenimine (PEI) polymer solutions were used in this study. The aqueous PAM solution, which is 20 wt % active and has a molecular weight in the range 250 to 500 kg/mol with a pH of  $\sim 4.0$  (according to the supplier), was obtained from SNF Floriger and used without further treatment. The PEI solution with an activity of 30 wt % and a molecular weight of 70 kg/mol was used as a cross-linker.

**Table 4.1** Ethoxylated Amides-2, Chemical and Physical properties

<b>Characteristics</b>	
IUPAC	BIS (2- Hydroxyethyl) Letyl Amine
Appearance, 20°C	liquid
Viscosity, 20°C	150 mPa s
Density, 20°C	905 kg/m <sup>3</sup>
HLB	10.1*

**Table 4.2** Chemical analysis of water used in the experiments

Ion ,	Water type Concentration, mg/L (ppm)		
	Formation brine	Sea water	FMW
Na	59,300	18,300	175
Ca	23,400	650	46
Mg	1,510	2,082.729	112
SO <sub>4</sub>	110	4,290	377
Cl	137,000	32,200	266
HCO <sub>3</sub>	353	120	146
Total Dissolved Solids*	221,673	57,642.729	1,122

\*Sum of the concentration of the ions

#### 4.2.2 Instrument

High performance dispersing instrument Ultra-Turrax T50 Basic provided by International, will be utilized to form the emulsion , the homogenizer is equipped with a variable speed drive with different 6 speeds available 500 – 10000 RPM. The droplet size measurement of the dispersed phase was performed through Leica DM2000 microscope and FRITSCH Laser particle size analyzer, to understand how the droplet size affects the emulsion stability. GL-18 high temperature disposable test tubes, soda-lime-glass (18 x 180 mm) of approximate volume of 32 ml and operation temperature of

180°C were used. The high temperature tubes were sealed with a screw-cap and a rubber seal case to prevent evaporation. The fact that no evaporation is taking place was assured by comparing the initial and final volumes of the sample at the end of the experiment.. Fisher Isotemp Series 300 Laboratory Oven model 350G, Temperature range: ambient to 300°C. will be used to study the emulsion separation: separated volume fraction of the phases versus time.

#### **4.2.3 Procedure / Preparation**

Polymer gels and emulsified polymer gel systems were prepared in a systematic manner to ensure reproducibility. The Polymer gels were prepared by adding a specific amount of PAM to water (either sea, field or formation brine) over a period of 2 minutes while stirring. Then the required amount of the cross-linker (PEI) was added drop wise, and the mixture was continuously stirred for an additional 10 minutes to obtain a homogenous solution. This mixture is identified as the gelant. In this study, the emulsified systems were prepared by the addition of the emulsifier (at a specific concentration) to diesel, giving it sufficient time to mix with diesel thoroughly. Then the desired volume of the water phase (gelant) was slowly added to the hydrocarbon phase (diesel containing the emulsifier), while continuously agitating for about 5 minutes until a homogenous emulsion is obtained.

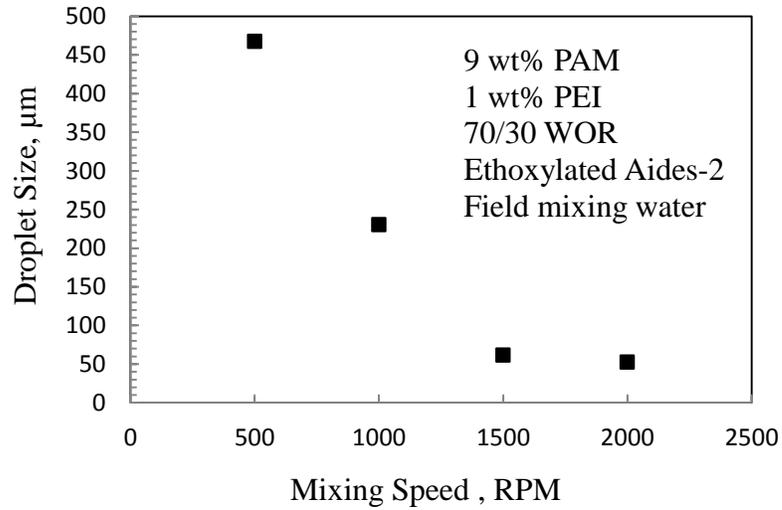
#### **4.3 Results and Discussion**

To investigate the impact of different parameters on the droplet size and the thermal stability, emulsified gels samples were prepared at the ambient temperature (26°C), specimen of each samples was placed in the particle size analyzer and the microscope.

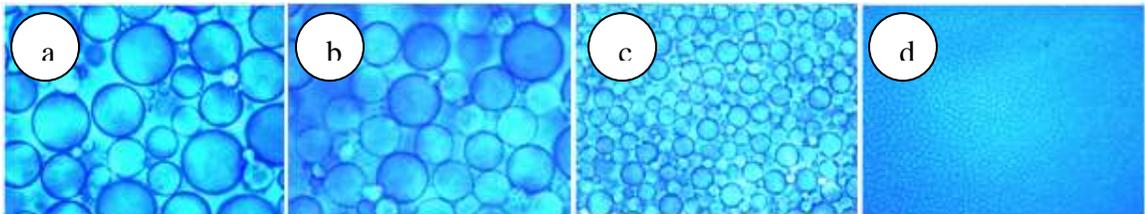
Simultaneously, the seal case high temperature test tube was used to study the stability, the separated volume fraction of oil and water phases was observed at specific temperature. It should be mentioned that no water separation was noticed after 1 week in any of the samples.

#### **4.3.1 Effect of Mixing Intensity**

To study the influence of mixing speed, four emulsified gels samples were prepared at different mixing speed in the range 500 to 2000 rpm. As shown in **Figures 4.1&4.2**, it was observed that the droplet size has decrease with the increase in intensity of mixing. Droplet size decreased from 467.67 to 61.65  $\mu\text{m}$  (i.e.  $\sim 87\%$  decrease) or a factor of 7.6 when the mixing speed was increased from 500 to 1500 rpm. However, when the mixing speed was increased from 1500 to 2000 rpm, slight decreased was observed in droplet size from 61.65 to 52.58  $\mu\text{m}$  (i.e.  $\sim 15\%$  decrease) or a factor of 1.2. **Figure 4.3** indicates that the emulsified system stability has increased with the increase in intensity of mixing; no separation took place, whereas 18% of the diesel separated when 500 instead of 2000 rpm used to prepare the sample. This enhancement in the stability may be due to low interfacial tension at smaller droplet size, which perceived when 2000 rpm was utilized to create the emulsified system as shown in **Figure 4.2**.



**Figure 4.1** Droplet size for the emulsified gels at different mixing speeds at (26°C)



**Figure 4.2** Effect of mixing speed on the Droplet size, after one week at (26°C)

(a) 500 RPM, (b) 1000 RPM, (c) 1500 RPM and (d) 2000 RPM

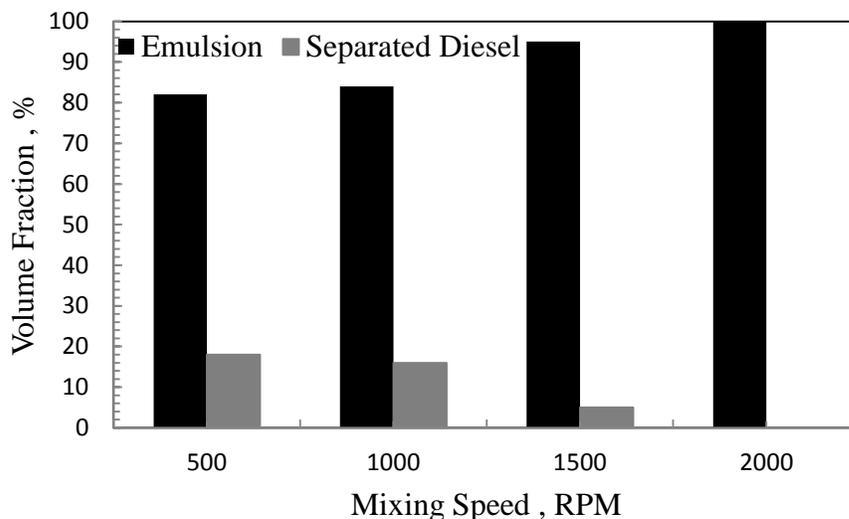
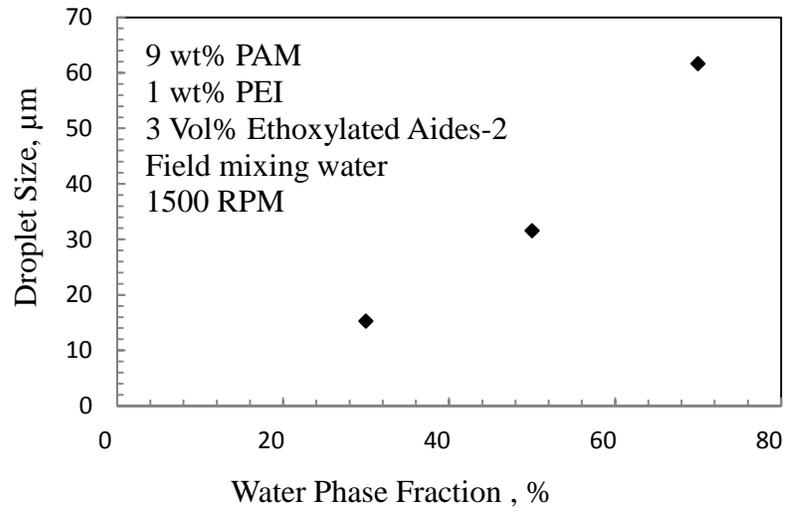


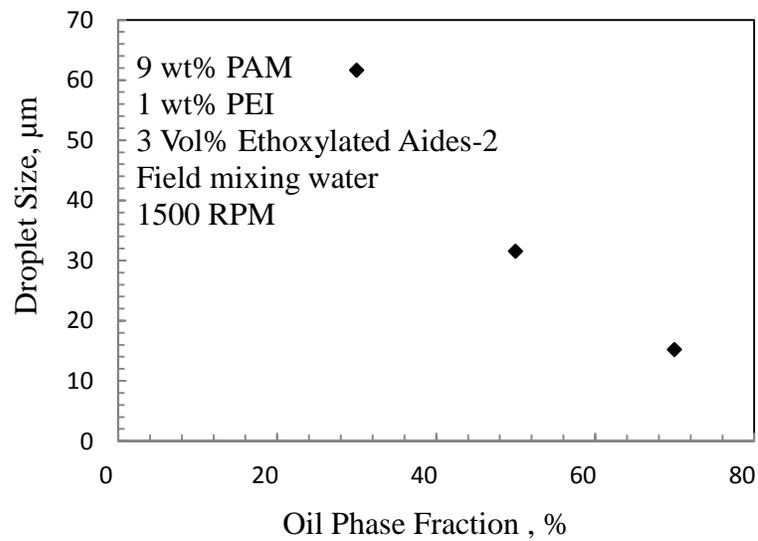
Figure 4.3 Volume fraction for the emulsified gels at different mixing speeds, after one week at (26°C)

#### 4.3.2 Effect of Water fraction

To examine the impact of Water oil ratio, three emulsified gels samples were prepared, 9 wt% PAM and 1 wt% PEI were used in the preparation of the gelant at different phase fraction in the range 30 to 70 %. As shown in **Figures 4 (a) & (b)**, it was notice that the droplet size has increased with the increase in water phase fraction and decrease of oil phase fraction. Droplet size increased from 15.24 to 61.65  $\mu\text{m}$  (i.e.  $\sim 25\%$  increase) or a factor of 4, when the water phase fraction was increased from 30 to 70 % (the oil phase fraction was decreased from 70 to 30 %). **Figures 5 & 6** states that the emulsified gel stability has increased with the increase in water phase fraction and decrease of oil phase fraction, 5 % of the diesel separated, when 70 / 30 water oil ratio used. While 65 % separation was observed as 30/70 employed to form the system.

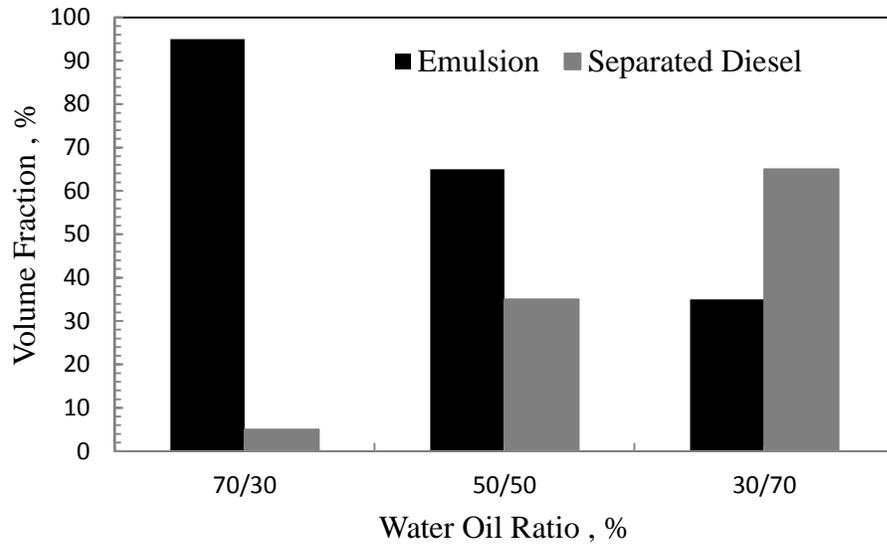


(a)

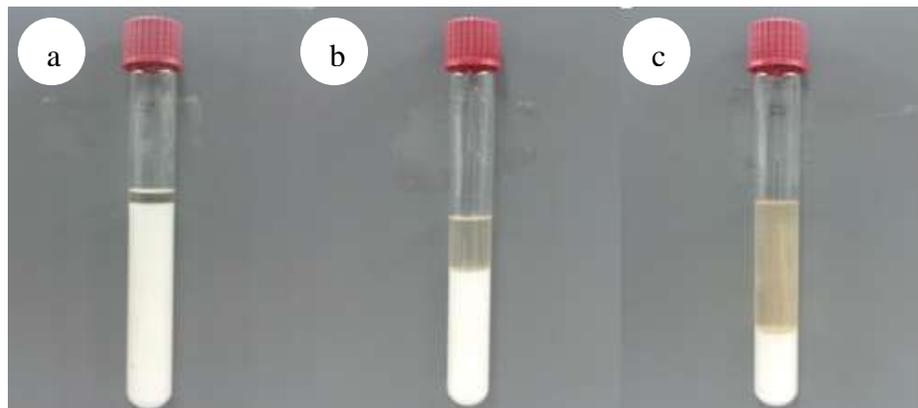


(b)

**Figure 4.4** size for the emulsified gels at different phase fraction at (26oC), (a) Water Phase Fraction, (b) Oil Phase Fraction



**Figure 4.5** Volume fraction for the emulsified gels at different Water Oil ratio, after one week at (26°C)

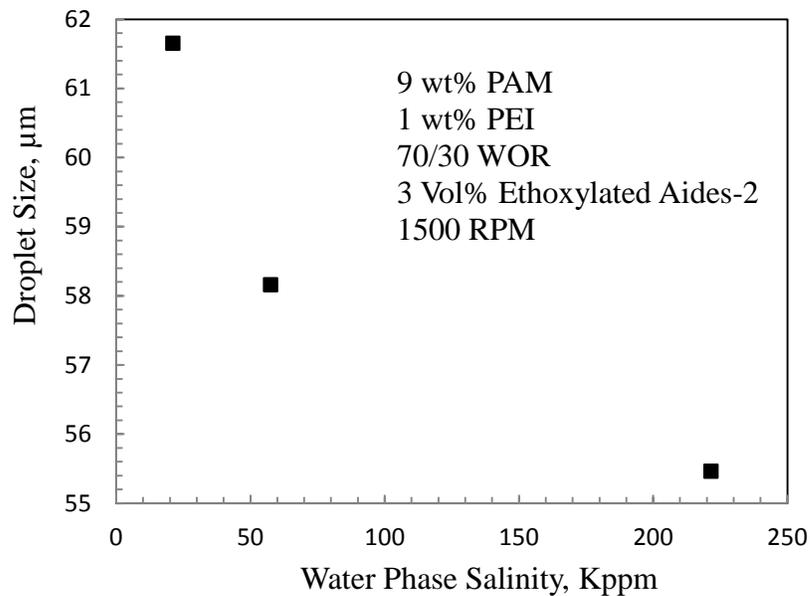


**Figure 4.6** Effect of Water Oil ratio on the stability after one week at (26°C), 70/30 WOR, (b) 50/50 WOR and (c) 30/70 WOR

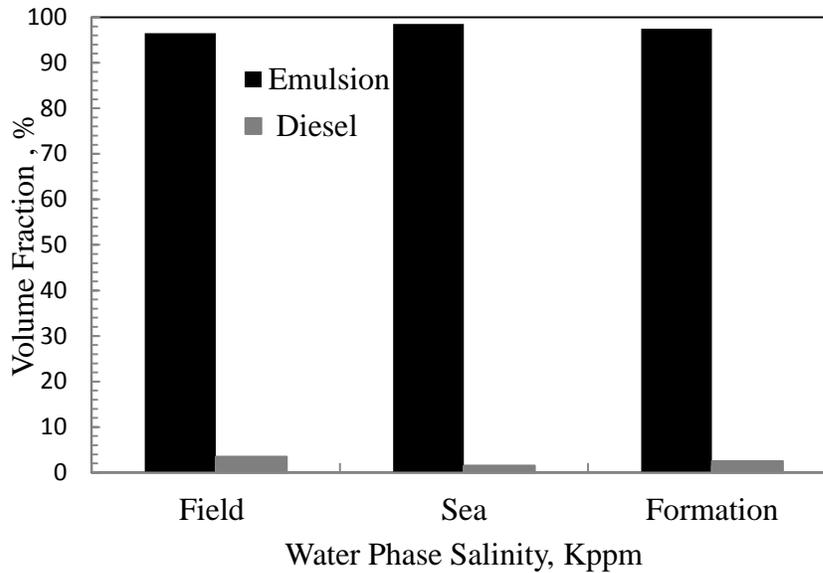
### 4.3.3 Effect of Salinity

Representative compositions of field, sea and formation water were used to investigate the effect of water phase salinity. However, the field water salinity was not enough to produce (W /O) emulsion, that why 2 wt% KCl was added to the field water, which resulted in increase of salinity from 1,122 mg/l to 21,122 mg/l. Three emulsified gels

were formed utilizing different water phase salinity in the range 21,122 to 221,673 mg/l. As appears in **Figure 4.7**, it was clear that the droplet size has slightly decreased with the increase in salinity. Droplet size decreased from 61.65 to 55.46  $\mu\text{m}$  (i.e.  $\sim 10\%$  decrease) or a factor of 1.1, when the water phase salinity was increased from 21,122 (field) to 221,673 mg/l(formation). From **Figure 4.8** it was apparent that insignificant increase in the stability will be realized, if the formation brine is used in place of the field water.



**Figure 4.7** Droplet size for the emulsified gels at different salinities at (26°C).

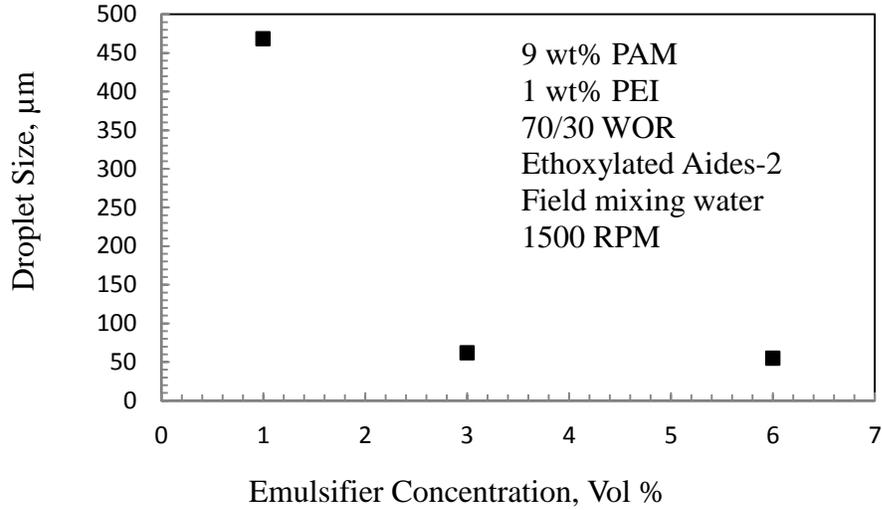


**Figure 4.8** Volume fraction for the emulsified gels at different salinities, after one week at (26°C).

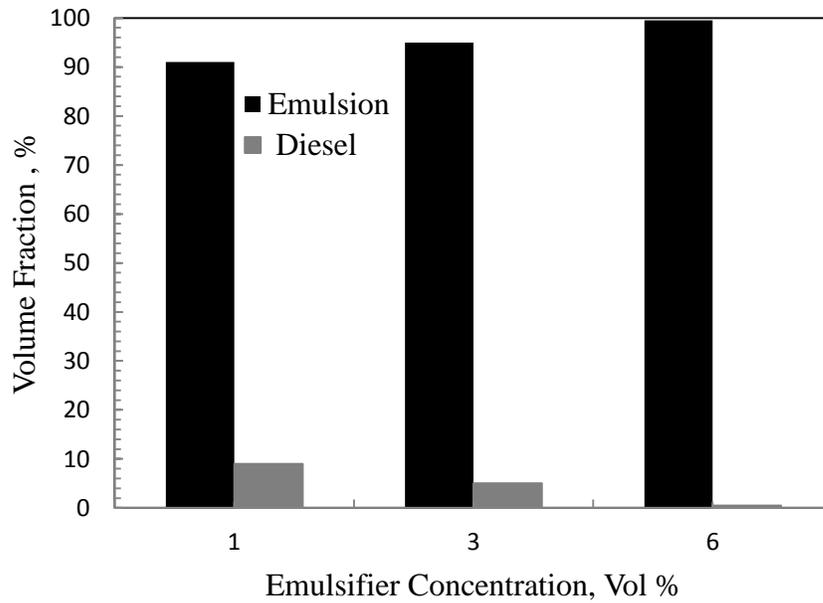
#### 4.3.4 Effect of Surfactant concentration

The impact of the surfactant concentration was studied through employing Ethoxylated Aides-22 as emulsifier; three emulsified gels models were produced applying different surfactant concentration in the range 1 to 6 vol %. As shown in **Figure 9**, it was attained that the droplet size has decrease with the increase in surfactant concentration , droplet size decreased from 467.98to 61.65  $\mu\text{m}$  (i.e.  $\sim 87\%$  decrease) or a factor of 7.6 , as the surfactant concentration was increased from 1 to 3 vol %, this led to 56% decrease in the volume the separated diesel, In contrast, trivial decrease was attained (i.e.  $\sim 11\%$  decrease) ,when the surfactant concentration was increased from 3 to 6 vol %, which cause 1% decrease in the separated diesel fraction **Figure 10**. The increase in stability could be explained by the amount of emulsifier that is adsorbed at the interface. More

emulsifier adsorbed, leads to decreased interfacial tension and emulsifier molecules act as a barrier slowing the coalescence of droplets.



**Figure 4.9** Droplet size for the emulsified gels at different emulsifier concentrations at (26°C)



**Figure 4.10** Volume fraction for the emulsified gels at different emulsifier concentrations, after one week at (26°C).

### 4.3.5 Effect of Temperature

The investigation of influence of the temperature on the stability, four solutions containing PAM/PEI (9/1) wt% were prepared at room temperature (26°C). Afterward, the effect of temperature was examined at various temperatures in range 26.7° and 120°C (80 to 248°F). **Figure 11** indicates that the emulsified system stability decreased with increase in the temperature, almost 3 vol % of the diesel separated after 1 hour, no water phase separation was observed, when the oven temperature increased from 26.7°C (80°F) to 60°C (140°F). While, 30 vol % of the diesel and 70 vol % of the water phase was separated after 1 hour, as the temperature increased from 60°C (140°F) to 120°C (248°F), this represent 91% increase in the fraction of the separated diesel (or a factor of 11.4), which is reflected negatively on the stability. This may be due to the rate of coalescence, which is slow at low temperature. An increase of temperature results in a progressive increase in coalescence and sedimentation as molecules been desorbed from interfaces.

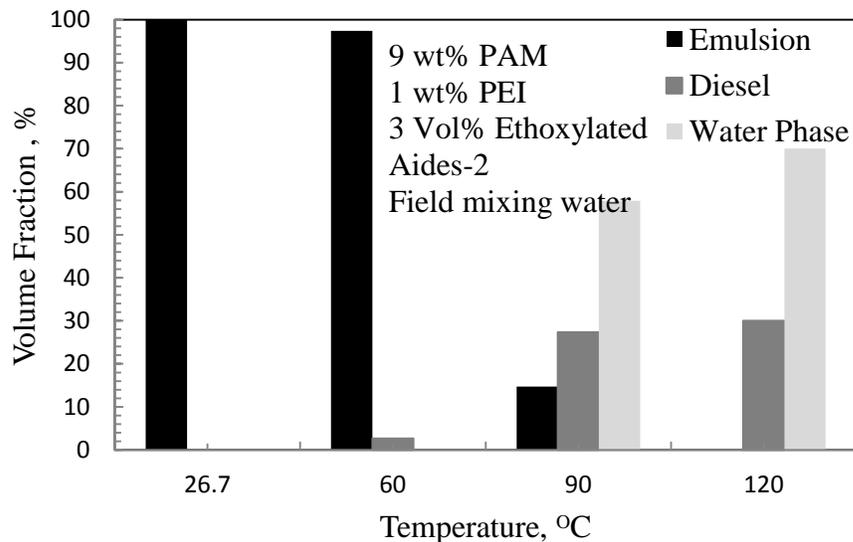


Figure 4.11 Volume fraction for the emulsified gels at different temperatures, after 1 hour

#### 4.4 Conclusions

In general, this work was successful in developing an insight into the factors that influence the droplet size and stability of the emulsified water in oil systems. Moreover, the relation between the droplet size and stability was investigated.

7. The general trend is that the stability is increased with decreasing in the droplet size, which agree with what have been reported in the literature. This could be due to low interfacial tension at smaller droplet size.
8. Droplet size is found to decrease with the increase in intensity of mixing, 87% decrease was achieved, when the mixing speed was increased from 500 to 1500 rpm. However, slight decreased (15% decrease) was observed, as the mixing speed increased beyond 1500 rpm.
9. Stability is found to increase with the increase in intensity of mixing, no separation occurred, whereas 18% of the diesel separated when intensity amplified from 500 to 2000 rpm.
10. Droplet size is established increased with the increase in water/oil ratio. Furthermore, the increase in the water oil ratio resulted in increase in the stability, 65 % of the diesel separated as 30/70 employed to form the system instead of 70/30 water oil ratio.
11. Insignificant alteration in the droplet size and the stability was realized, when the formation brine is used in place of the field water with, which implies a salinity of 21,122 mg/l (field water ) could be applied to seize same result instead of using high salinity of 221,673 mg/l (formation brine).
12. The increase in surfactant concentration is accomplish to increase stability and decrease the droplet size , 87% decrease was attained , as the concentration was

increased from 1 to 3 vol % ,which led to 56% decrease in the separated diesel, Inversely, slight decrease by 11% ,when the concentration increased from 3 to 6 vol %, caused 1% decrease in the separated diesel. This could be related to the amount of emulsifier that is adsorbed at the interface.

13. Emulsified system stability was realized to decreased with increase in the temperature, as the temperature increased from 60°C (140°F) to 120°C (248°F), 91% increase in the separated diesel after I hour .In contrast, No significant separation happened at low temperature  $\leq 60^{\circ}\text{C}$  (140°F). This may be due to the low rate of coalescence.

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## CHAPTER 5

### **Gelation of Emulsified PAM/PEI System at High Temperature and High Salinity Conditions: Rheological Investigation**

#### **Abstract**

In this study, an emulsified gel has been proposed to provide a method for disproportionate permeability reduction for oil and gas applications. This emulsified system separates into water phase and oil phase. Then, the water phase forms gels that block water flow while the diesel phase leaves an open channel for the hydrocarbon flow. The purpose of this work is to study the gel strength of the organically cross-linked polyacrylamide (PAM) cross-linked with polyethylenimine (PEI) emulsified into diesel. Several parameters were investigated. These included: the type of emulsifier, temperature and salinity of brine. Emulsified PAM/PEI was found to have lower rate of cross-linking (gelation) in comparison to PAM/PEI. This effect is more pronounced when stable emulsified PAM/PEI was used instead of emulsified PAM/PEI with complete separation within one hour where the elastic modulus reduced from 746 Pa to 343.6 Pa ( ~ 54% decrease). The elastic modulus of the emulsified PAM/PEI increased by about 32% when the temperature was increased from 120°C (248°F) to 150°C (266°F). In general, elastic modulus decreased in the presence of salts. High water salinities resulted in low gel strength and longer gelation time. NH<sub>4</sub>Cl is found to be more efficient than NaCl in the retardation of the gelation process. This is due to the fact that NH<sub>4</sub>Cl is more effective than NaCl in screening negative charges on the carboxylate groups.

## 5.1 Introduction

Water production is an inevitable consequence of the hydrocarbon recovery operations, nonetheless it is considerably the major excessive stream allied with hydrocarbon exploration and production (Khatib and Verbeek 2003; Burnett 2007; Veil and Clark, 2009). When produced water from a specific field (is no longer economically acceptable) exceeds economic limits, this fact necessitate developing a technique by which water production is controlled. The production of water was reported to be in the order of 210 million barrels per day globally in the year 1999 (Veil et al., 2004). Bailey et al., (2000) reported the same figure for the year 2000. This amount increased to 249, 000,000 BD in the year 2005 (Khatib, 2007), similar number was recorded in 2007, for an oil water ratio roughly 1:3, this figure is anticipated to rise to greater than 300 million BD by 2012 (Dal Ferro and Smith 2007). Approximately, \$40 billion is spent annually to handle the unwarranted produced water from oilfields (Bailey et al., 2000; Seright et al., 2003; Dal Ferro and Smith 2007). More recent publications indicate that this number has increased to \$45 billion in the year 2002 (Mercado et al., 2009; Boye et al., 2011). The disposal of produced water affects the environment seriously especially if the produced water contains mercury, arsenic and other salts (Hibbeler and Rae, 2005). Water is also responsible for most of the corrosion and scale problems in the oilfield (Donham, 1991; Merdhah and Yassin, 2009; Al-Tolaihy and Bukhari, 2010). Consequently, there is a need for a remediate technique that totally shuts off or reduces the water production to some acceptable extend.

Polymer and polymer gels are well suited for total blockage of water production zones (Alqam et al., 2001; Vasquez et al., 2003). The use of polymeric gels results in reducing water relative permeability during oil and gas production (Zaitoun and Kohler 1988; Liang and Seright 1995) and improving injection wells sweep efficiency (Lei and Nasr Eldin 2011). Inorganic cross-linked gels (Sydansk 1990; Lockhart 1994) and organically cross-linked gels (Morgan et al., 1997; Moradi-Araghi 2000) are the most common systems used in oilfields. Literature reports revealed that organically cross-linked gels were more thermally stable in comparison with inorganic gels (Moradi-Araghi 1991; Albonico et al. 1994; Hutchins et al. 1996; Hardy et al. 1999), which makes it more suitable for high temperature applications. Nevertheless, there exists a risk that they reduce oil flow appreciably, together with water. Additionally, the shortage of means to optimally set a plugging sort (barrier) obstruction, accompanied with the high operational costs, the need arise for developing selective technique, which can primarily obstruct or block the water flow, resulting in slight or no restriction to oil flow. Consequently, the undertaken risk will be minimized.

In general, gelants or polymers are used as selective techniques, by developing a hydrophilic layer, when adsorb on the rock surface, which decrease mobility of water and no unique placement method involved (Vinson, 1986; McCool et al., 1991; Liang et al. 1995, Seright 1995; Liang and Seright 1997; Nilsson et al. 1998; Al-Sharji et al. 1999; Willhite et al., 2002; Sydansk and Seright 2007). This phenomenon is known as Relative Permeability Modification (RPM) or disproportionate permeability reduction (DPR). DPR fluids are widely used in oil and gas fields (Sparlin 1976; Hejri et al., 1993; Bybee 1999; Zaitoun 1999; Kalfayan and Dawson 2004; Cozic 2009; Seright 2009). Different

water problems could be handled efficiently through DPR (Stavland et al., 1998; Kantzas et al., 1999; Botermans and Van Batenburg 2001). When accurate zone isolation is required, but it is unattainable or unfeasible, the disproportionate permeability reduction is desirable (Liang et al. 1993; Sydansk and Seright 2007). Under current capabilities DPR is favourable, when dealing with wells that interconnect a fissure or fissure sort of character (Seright et al., 1995, 2002; Amaury et al., 2002; Leal et al., 2005; Borodin et al., 2008). However, numbers of scholars are very interested in employing DPR to minimise produced water from un-fractured wells. In countless production wells, bull-heading of gelants and polymers has established to be a robust process, by which unwarranted water production was prevented (Mofitt, 1993; Zaitoun et al., 1999). The optimistic scenario is to significantly decrease the water productivity index without notably damaging oil and gas productivity, by developing a system, that can be pumped into production well without isolating hydrocarbon productive zones.

Recently, emulsified gel is proposed as a smart method for shutting off unwarranted water produced from oilfields (Stavland and Nilsson 2001; Stavland et al., 2006). The injection of emulsified gels into near wellbore formation has the advantage of selectively reducing the relative permeability of water more significantly than the hydrocarbon phase. Here, bullhead placement technique is used without the need of zone isolated routine, which leads to restricting water flow and improves hydrocarbon recovery. Thus, it can be applied in oil wells without risking their productivity unlike the case where a rigid gel is used, in which the risk of blocking the oil producing zones is high.

A mixture of polymer solution (gelant) is generally emulsified in oil phase utilizing an appropriate surfactant (emulsifier). The system is created to break up into water and an oil phases in the porous media at reservoir conditions. In the pore space, the water phase, which contains the gelant, gels up forming a viscoelastic gel, while the oil phase remains mobile, the time required for the system to separate and gels up is a decisive factor for treatment placement. Consequently, appropriate separation and longer gelation time are necessary especially for high temperature reservoirs. Usually, a number of salts (retarders) are used to delay the gelation and slow down the cross-linking process in order to keep the gelant flow-able until it reaches the target zone. The breaking of the emulsified system and then the gelation are a function of temperature, time and salinity of mixing water and concentration of the different components.

The rheological measurements of polymer gels/emulsified gels were reported. First, the gelation time at which the 3-D structure is formed is determined. The accurate determination of gelation time is a vital factor in gelant placement. Then, the gel strength, which reflects the gel ability to withstand the water flow, is obtained. To the best of authors' knowledge no reports are available on the correlation of elastic modulus with lifetime of the gel. However, it is speculated that the higher the modulus the higher the stored energy and resistance to small deformations. Gel strength depends mainly on the elasticity which can be evaluated by measuring the elastic properties (storage modulus) through dynamic shear testing. The storage modulus for different types of polymer gels utilized for water control, reported in literature can be find elsewhere (Karsani et al., 2014), **Table 5.1** provides a summary of the storage modulus for polymer gels and emulsified gels used in this study.

Dynamic (oscillatory) shear was applied on the emulsified system, and the dynamic shear measurements data were collected. The elastic and viscous behaviors are interpreted through the storage and loss modulus, respectively. The storage modulus ( $G'$ ) reflects the stored recoverable energy of the material, whereas, the loss modulus ( $G''$ ) counts for the mechanical energy dissipated into heat due to viscous forces. The ratio of ( $G''/G'$ ) determines the shift angle ( $\tan \delta$ ) between the stress and strain (Karsani et al., 2014). Gelation kinetics can be determined by monitoring the evolution of the storage and loss moduli with time (Grattoni et al. 2001). More fundamental details of dynamic oscillatory testing can be found elsewhere (Kakadjian et al. 1999; Liu and Seright 2001; Calvet et al. 2004; Al-Muntasheri et al. 2007; Koohi et al. 2010; Karsani et al., 2014).

All of the previous dynamic rheological measurements had comprehensively focused on studying the cross-linked gel (polymeric gel), with either organic or inorganic cross-linkers. No extensive investigation of the emulsified gels has been reported in the literature to the best of the authors' knowledge. Stavland et al., in 2006 studied the emulsification of acrylamide and tert-butylacrylate (TBA) cross-linked with PEI into diesel. The gelant was heated to 90°C for a given time, then the water phase viscosity was calculated at ambient temperature (25°C). The rate of gelation was evaluated against a reference cross-linked polymer (non-emulsified). Slightly longer gelation time was observed with the emulsified gels. Moreover, a slightly increase in the gel strength was perceived, when the standard cross-linked polymer was used instead of the emulsified polymers, which may be (explained by) due to dissolving some of the cross-linker (PEI) into the diesel (Stavland et al., 2006). Whereas, in the case of polymeric gels the focus

was on studying the inorganically cross-linked gels (Kakadjian et al. 1999; Liu and Seright 2001; te Nijenhuis et al. 2003).

**Table 5.1** Summary of storage modulus for polymer gels and emulsified gels

System	Polymer Type	Cross-linker Type	Curing Temp. (°C)	Curing Pressure, Pa	Measurement Temperature (°C)	$G_e'$ , Pa	Reference
Polymer gels	PAM (9 wt%)	PEI (1 wt%)	120	$3.45 \times 10^6$	120	885	Present study
Emulsified gels	Acrylamide and t-butyl acrylate	PEI	25	N/A	90	N/A	Stavland et al. (2006)
	PAM (9 wt%)	PEI (1 wt%)	120	$3.45 \times 10^6$	120	703	Present study
	PAM (9 wt%)	PEI (1 wt%)	150	$3.45 \times 10^6$	150	1035	Present study

Rheology of organically cross-linked gel was reported by Al-Muntasheri et al. 2007. Polyacrylamide tert-butylacrylate (PAtBA) was cross-linked with polyethylenimine (PEI) at temperatures ranging from 100 to 150°C (212 to 302°F). Bear in mind that these dynamic measurements were performed at ambient temperature using ready-formed gels. These gels were cured under high temperature and pressure conditions. Higher elastic modulus was reported by the authors for PAtBA/PEI system in comparison with inorganically cross-linked gels. Higher temperature (> 100°C), higher polymer and cross-linker concentrations lead to higher elastic modulus. However, increasing the cross-linker

concentration to 1.2 wt% resulted in gel syneresis and the equilibrium elastic modulus decreased at 150°C (302°F). Increasing the salinity of the mixing water caused a negative impact on elastic moduli. PAtBA / PEI system showed a higher thermal stability (Hardy et al. 1998). Moreover, it was successfully applied at high temperatures and low temperatures in different reservoir lithologies; carbonate and sandstone reservoirs (Polo et al. 2004).

Organically cross-linked polyacrylamide (PAM) cross-linked with polyethylenimine (PEI) was reported by Karsani et al., 2014, dynamically tested at high temperatures up to 130°C (266°F) and high pressure (500 psi). It was found that the elastic modulus (G) has increased with temperature in the range 120 to 130°C (248 to 266°F). Polymer concentration has a stronger impact on (G') in comparison with the cross-linker. Salinity of mixing water has a negative impact on G'. High G' was observed in distilled water (1044 Pa) in comparison with field water (725 Pa) at 130°C (266°F). Additionally, samples prepared at alkaline and acidic conditions produced stronger gels compared to samples prepared at neutral conditions. However, the gelation time is longer at a pH of 7. Ammonium chloride is found to be very effective retarder in comparison with NaCl. Gels with 7/0.3 and 5/0.3 wt% PAM/PEI gave pressure gradients of 155.5 kPa/m (55.2 psi/m) and 3,572 kPa/m (518 psi/m), respectively (Karsani et al., 2014). Recent research revealed that more cost-effective polyacrylamide (PAM) homopolymer could substitute PAtBA (Al-Muntasheri et al. 2007; Karsani et al., 2014). The cross-linking between PAM and PEI was also thought to be through a nucleophilic substitution in which the imine nitrogen in PEI will replace the amide group at the carbonyl carbon of PAM (Al-Muntasheri et al. 2007).

Thus, this work is intended to examine the potential use of PAM /PEI in preparing emulsified gels to produce thermally stable gels for high temperature high salinity reservoirs. Moreover, impact of different factors on the strength of the PAM / PEI system through dynamic shear testing at high temperatures. These parameters include: impact of polymer concentration, emulsifier, and emulsified gel formulation (emulsified gel separation time), salinity of mixing water, retarders and temperature on gel strength. Most of the previous dynamic rheological investigations on either polymeric gels or emulsified gels were performed on matured gels. In this work, the development of the gel and gel strength were observed via high pressure rheometer for the duration of the gelation process up to the equilibrium state. In this work, the different parameters were varied to come up with a composition that provides the highest gel strength at the lab level. The optimized gel composition (high strength) will be recommended for testing in core-flooding experiments at high temperatures (~150°C) before application in the field. Here we studied the gel strength in the temperature range 120 to 150°C which represents the temperature range of the target reservoirs.

## **5.2 Experimental Setup and Procedure**

### **5.2.1 Materials**

Two surfactants were used in this study: Ethomeen T/12 (Ethoxylated Amides) and ANSC (CRV) RD (Amine Acetates). Sea water (SW) and field mixing water (FMW) were used for the water phase; **Table 5.2** shows their chemical analysis. Diesel from local gas stations which is representative of that used in the field for preparing emulsified acids is used. 2- Polymer liquids were used. Polyethylenimine (PEI) was used as a cross-linker

as an aqueous solution. Its molecular weight and activity were 70 kg/mol and 30wt.%, correspondingly. Polyacrylamide (PAM) was offered by SNF Florger in a liquid form. PAM solution 20 wt.% was active. All Salts used in this study were American Chemical Society (ACS) grade.

**Table 5. 2** Make-up brine chemical analysis

Ion	Water type, mg/l	
	Field	Sea
Na	175	17,085
Mg	46.2	2,200
Ca	112	1,040
Cl	377	31,267
SO <sub>4</sub>	266	4,308
TDS*	976.2	55,900

\* Total dissolved solids (TDS) were determined by addition.

### 5.2.2 Procedure / Preparation

Systematic routine was used to prepare polymer gels and emulsified polymer gels systems to guarantee the reproducibility. The Polymer gels were formed by adding a

specific quantity of PAM to water (either SW or FMW) while stirring. Afterward the required quantity of cross-linker (PEI) was added drop wise, the mixture kept under continuous stirring for an additional 10 minutes to acquire a homogenous solution. This blend is referred to as gelant. The emulsified system was prepared with two different surfactants. The emulsifier (at a specific concentration) was added to the diesel. Sufficient time was maintained for the emulsifier to thoroughly mix (dissolve) in the diesel. Then, the desired volume of the water phase gelant (70 vol %) was gradually added to the (30 vol %, emulsifier and diesel solution), while continuous agitation was performed for an extra 5 minutes until a homogenous emulsion obtained.

NaCl and / or NH<sub>4</sub>Cl were added to SW and/or FMW before the addition of the polymer and the cross-linker to investigate how the retarders influence the gelation time in addition to the gel strength. Two emulsified gel formulations (different separation time) were prepared in SW and/or FMW, to investigate the impact of separation time on the gel strength and gelation time, in the first formula, the emulsified gel did not break down to its original components (water and oil phase) throughout the test time. The second formula completely separated after an hour. Afterward, the model was studied on the rheometer equipped with high pressure high temperature cell. Distilled water has not been used, due to limitation of the minimum salts concentration required to form stabile W/O emulsified system (Al-Yarri et al., 2013).

### **5.2.3 Instrument**

All rheological tests were performed in a high pressure cell geometry mounted on rheometer. The geometry with bob and cup of diameter 26 and 28 millimeters, correspondingly. All tests were performed at a pressure of 34.47 bar (500 psi), and

temperature ranges from 120 to 150°C (248 to 302°F). The setup has a torque ranging from 100  $\mu\text{N}\cdot\text{m}$  to 0.2 Nm and functioning temperature in the range -10 to 150°C (14 to 302°F). The maximum applied pressure was 138 bar (2,000 psi). The tests were conducted at 500 psi which was much higher than the vapor pressure of water at 150°C (~70 psi). Therefore, water is in the liquid phase. Since the role of the pressure is to keep the liquid in solution, we do not expect an effect of pressure on the strength of the gels. In order to perform dynamic oscillatory testing, the strain used should be inside the linear viscoelastic range. The dynamic measurements were carried out at fixed strain of 10% and frequency of 1 Hertz (Hz), which was proven to be in the linear viscoelastic range for the PAM/PEI (Karsani et al., 2014).

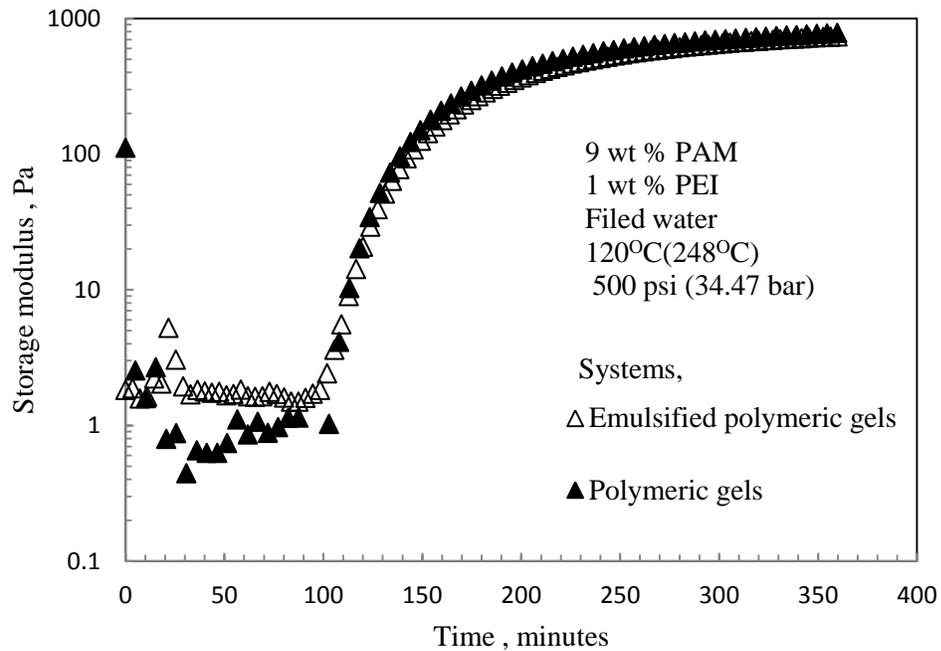
### **5.3 Results and Discussion**

The purpose of this work is to examine the gel strength of the emulsified form of organically cross-linked polyacrylamide (PAM) with polyethylenimine (PEI) into diesel. The influence of several parameters was investigated. These included: the type of emulsifier, PAM and PEI concentration, emulsified gel formula, temperature, salinity of brine and retarder type. This study is first of its kind; no measurements on the emulsified gel strength have been reported to the best of our knowledge. The methodology presented in this study simulates the actual gelation process in the reservoir.

#### **5.3.1 Effect of Emulsification**

To study the impact of emulsification on gel strength, two systems namely a polymeric gel and emulsified gel were prepared at ambient temperature, each containing PAM/PEI (9/1) wt%. Then, the effect of emulsification was investigated at 120° (248°F). From **Figure 5.1** three distinctive behaviors (regimes) can be identified. An induction

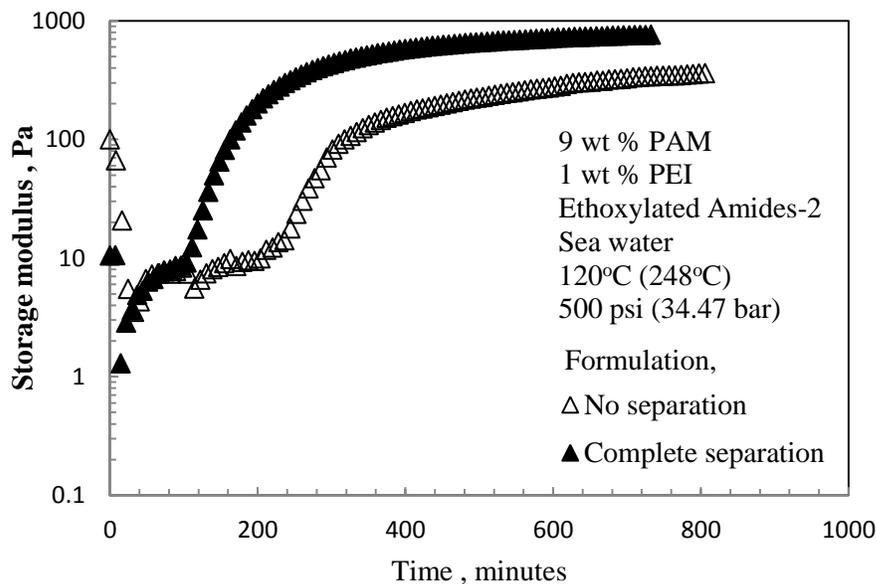
phase in which  $G'(t)$  oscillates around 2 Pa. Very low values of storage modulus are obtained throughout this period, which is due to the low elasticity of the sample. A higher strain, within the linear viscoelastic regime, was used. However, it appears that the primary character of the solution (60% water) is not within the torque limits of the machine. It should be mentioned that the 0 time is measured as the time at which the sample reaches the particular temperature. For instance, it took the sample 16 minutes to heat up at 120°C (248°F) from the ambient temperature. There were more fluctuations in the polymeric gel data compared to the emulsified gel during this period. The subsequent period illustrated an inflection in  $G'(t)$  after which it increases significantly. The gelation time has been related to the inflection point, which was observed during the increase in elasticity versus time. As seen in **Figure 5.1**, the shape of this period differs with the system.



**Figure 5.1** Elastic modulus of polymer gels and emulsified gels

As shown in **Figure 5.1** the inflection point (gelation time) for polymeric gel was ~72 minutes, whereas the emulsified gel took more time (~98 minutes). This hindrance can be explained through the kinetics of the cross-linking reaction. It has been reported that the gel strength, which is reflected in  $G'$ , depends on the cross-links density. The gel strength was predicted to increase with the increase in temperature (Kakadjian et al. 1999; Calvet et al. 2004; Al-Muntasheri et al. 2007; Karsani et al., 2014). This is due to the increase in the cross-linking density; hence, more cross-links could be formed. In case of the emulsified system, presence of the PAM/PEI as emulsified into the oil phase may lead to less heat been conducted to the gelant. As a result, the cross linking density will be less. This will be the case until breakage of the emulsified system; thereafter higher cross-linking density will be achieved. In another way, emulsification slows down the cross-

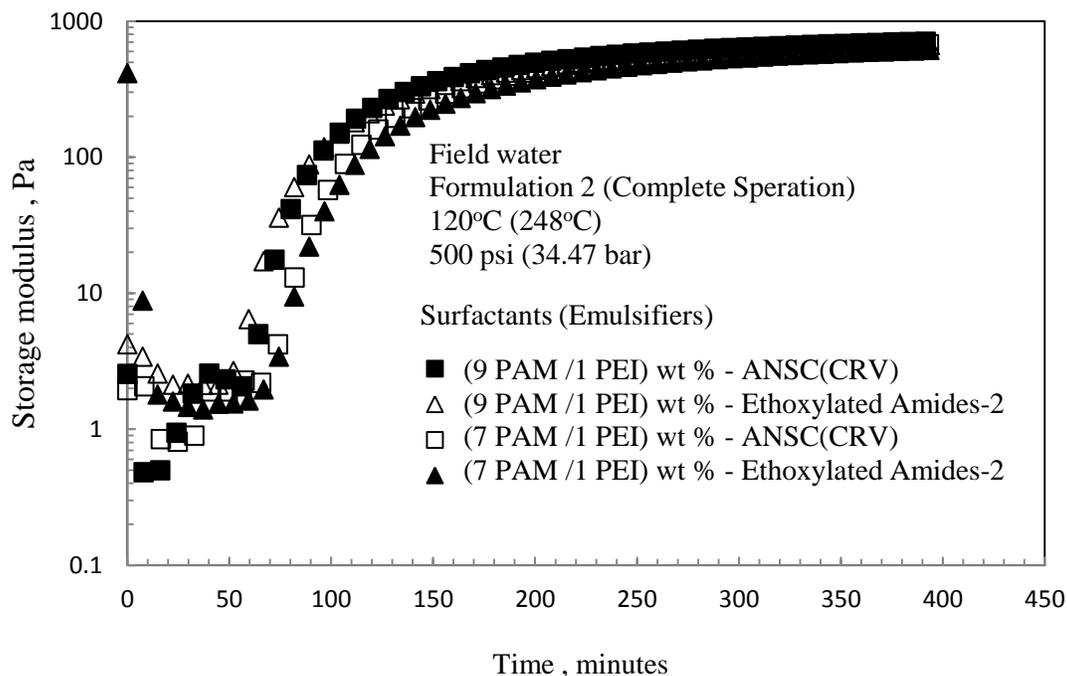
linking process. A slight increase in  $G'(t)$  was detected in the last period, in which a plateau (final equilibrium value) is accomplished. It was observed that the equilibrium elastic modulus ( $G_e'$ ) has decreased with emulsification.  $G_e'$  decreased from 749 Pa to 715 Pa (i.e. ~ 5% decrease). As shown in **Figure 5.2**, this effect of the emulsification is more pronounced when more stable emulsified system was studied (longer separation time). Two emulsified gels were prepared and each one has a different separation time. The first formulation did not separate during the test period while the second formulation has completely separated after one hour. The equilibrium elastic modulus ( $G_e'$ ) has decreased for the first formulation where the gelant was emulsified into the oil phase throughout the test period. However, the emulsified system separated into gelant and oil phase within one hour.  $G_e'$  decreased from 746 Pa to 343.6 Pa (i.e. ~ 54% decrease). Conclusively, it could be concluded that emulsification slows down the gelation rate (longer gelation time) and reduces the gel strength. However, if the emulsified system completely breaks, the final gel strength will not be affected.



**Figure 5.2** Effect of emulsification (separation time) on elastic modulus

### 5.3.2 Effect of Emulsifier

To study the influence of emulsifier type, two different surfactants were used to form emulsified gel. Ethomeen T/12 of 3 vol% and ANSC (CRV) of 0.35 vol% were used to emulsify the gelants into the diesel. These concentrations were found to be the minimum dose that will form stable W/O emulsion with a separation time of ~ one hour at 120°C (248°F). The gelants were prepared at different concentrations of the PAM and PEI of 9/1 and 7/1 wt%. It is clear from **Figure 5.3** no significant change was noticed, when ANSC (CRV) was used to form the emulsion system in comparison to Ethomeen T/12. At gelant concentration of 9/1 wt%, increase in  $G_e'$  from 633.9 to 672.8 was obtained, when ANSC (CRV) was used instead of Ethomeen T/12. At gelant concentration of 7/1 wt%, increase in  $G_e'$  from 597.2 to 630 was achieved, when ANSC (CRV) was utilized in place of Ethomeen T/12. This slight increase may be related to the emulsifier type and concentration.

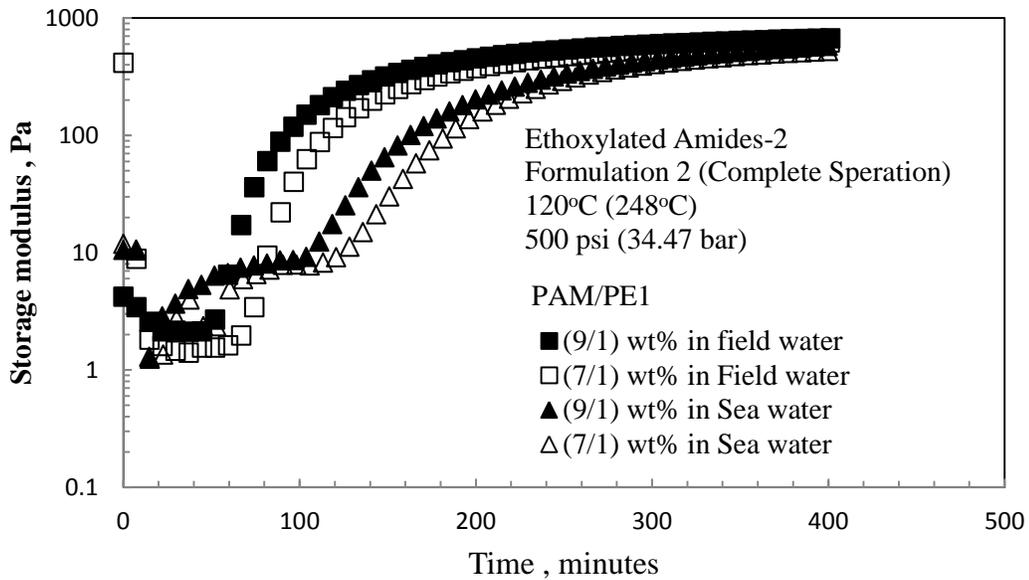


**Figure 5.3** Effect of emulsifier on elastic modulus, at different polymer concentration

### 5.3.3 Effect of Polymer Concentration

It was reported in the literature that  $G_e'$  depends on polymer and cross-linker concentration in both organically (Al-Muntasheri et al. 2007; Karsani et al., 2014) and inorganically cross-linked polymer gels (Grattoni et al. 2001; Omari 1995). To study the impact of polymer concentration, two different gelants were prepared in FMW and SW with PAM of 9 and 7 wt%, with PEI of 1 wt%. A higher  $G'(t)$  was observed with the increase in PAM concentration. This increase was associated with the fact that more cross-linkable sites will be accessible for PEI. As shown in Figure 5,  $G_e'$  increased with increasing polymer concentration, which in conformity with the data noted for inorganically cross-linked gels (Sydansk 1990; Liu and Seright. 2001; Cai and Huang. 2001) and organically cross-linked systems (Al-Muntasheri et al. 2007; Karsani et al.,

2014) as well. From Figure 5, in case of field water, when PAM concentration was increased from 7 to 9 wt%,  $G_e'$  increased from 579 to 634, whereas, in sea water containing 7 and 9 wt% PAM showed  $G_e'$  of 465 and 508 Pa, respectively. Hence, the production of a gel with higher  $G_e'$  requires higher PAM loading. This is likely due to the more cross-linkable sites offered with high PAM concentration. However, higher PAM concentrations resulted in shorter gelation times. So, in treating deeper reservoirs (deep profile modification) in which higher gelation time is required, these two effects should be taken into account.

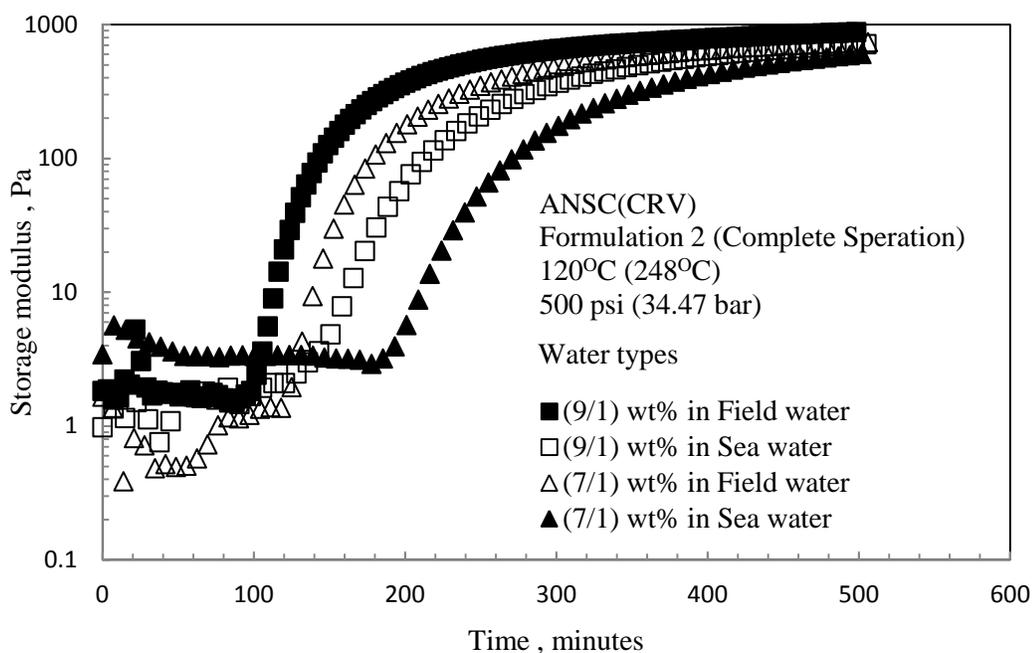


**Figure 5.4** Effect of polymer concentration on elastic modulus, at different salinity

### 5.3.4 Effect of Salinity

Representative compositions of field and sea water were used to examine the impact of salinity. PAM of 7 and 9 wt% and PEI of 1 wt% were used in the preparation of the gelant. It has been perceived that the increase in water salinity resulted in the

elastic modulus decreased. As illustrated in **Figure 5.5**, in the case of 9/1 (PAM/PEI) wt%, the  $G_e'$  values were 654.5 Pa and 842.3 Pa for sea and field water samples, respectively. Whereas, in 7/1 (PAM/PEI), the  $G_e'$  values were 510 Pa and 697 Pa for sea and field water, in that order. This indicates that sea water reduces  $G_e'$  by a factor of almost 1.3. This is likely due to the known shrinkage in polymer chain caused by salts (Nasr-El-Din et al. 1991). Such shrinkage leads to a decrease in the number of cross-linkable sites and consequently low elasticity. Generally, the gelation time was increased by increasing water salinity. This observation was confirmed in previous literature reports (Kakadjian et al. 1999; Broseta et al. 2000; Romero-Zerón et al. 2008, karani et al., 2014). The causes for the increase in the gelation time and the decrease in gel strength ( $G_e'$ ) are related to the impact of salts on the PAM degree of hydrolysis. These salts tend to slow the rate of hydrolysis which will eventually increase the gelation time due to reduction in the cross-linking rate. The negative impact of salinity on  $G'$  was also noticed in inorganically cross-linked gels. In the case of divalent and monovalent cations existence the  $G'$  is decreased when a copolymer of 2-acrylamido-2-methyl-propanesulphonic-acid (AMPS) and acrylamide was cross-linked with  $Cr^{+3}$  acetate (Koohi et al. 2010). It was suggested that the cations compete with  $Cr^{+3}$  leading to low cross-links.



**Figure 5.5** Effect of mixing water salinity on elastic modulus , at different polymer concentration

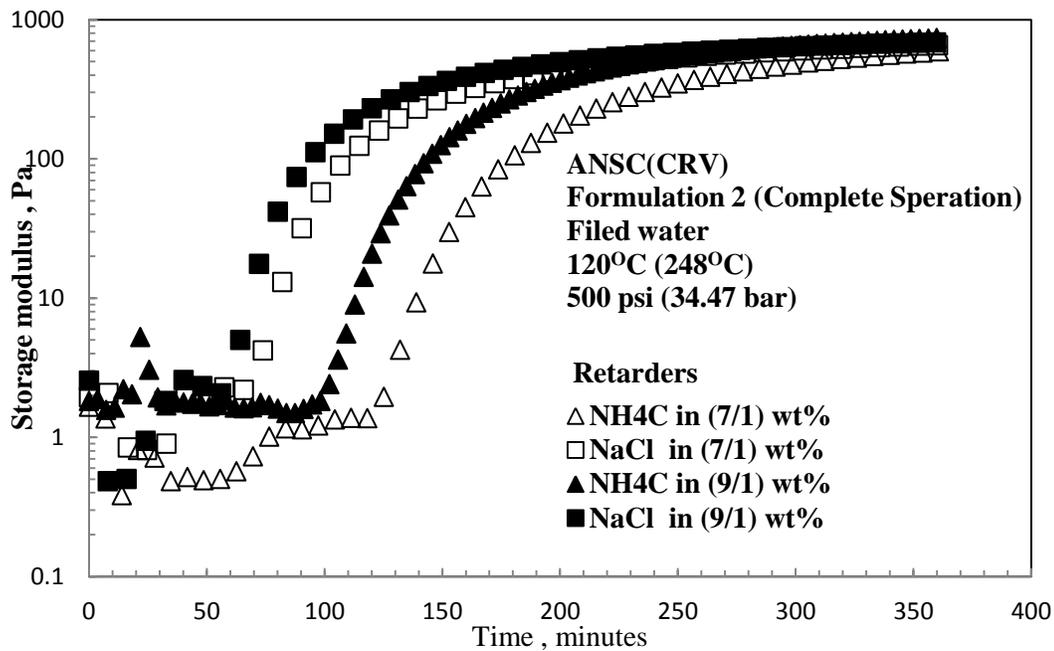
### 5.3.5 Effect of Retarder

The influence of retarders on gel strength was investigated for different salts at several concentrations by our research group (Karsni et al., 2014), high salt concentration leads to longer gelation time and a weaker gel in comparison with salt-free environment at the given time. This is likely due to charge screening effect by salt cations on carboxylate groups resulted from PAM hydrolysis (Tam and Tiu 1989; Nasr-El-Din et al. 1991; Ghannam 1999). Therefore, salts delay the gelation process and consequently reduce gel strength and longer heating times may be needed to reach the same ultimate gel strength. Furthermore,  $\text{NH}_4\text{Cl}$  is found to be more efficient than  $\text{NaCl}$  in the retardation of the gelation process (Karsni et al., 2014). This is due to the fact that  $\text{NH}_4\text{Cl}$

is more effective than NaCl in screening the negative charges on the carboxylate groups. Consequently, it reduces the sites on the polymer available for cross-linking with PEI.

### **Effect of Salt Type**

For the influence of salt type, the same concentration of NaCl, and NH<sub>4</sub>Cl (50 lb / 1000 gal) was added to a polymer solution containing of 9 wt% PAM and 1 wt% PEI. The effect of salts was examined in field water as presented in **Figure 5.6**. G<sub>e</sub>' of 703 Pa was measured, when 6,000 mg/L of NaCl was added where almost no change was observed (638 Pa), When the same amount of NH<sub>4</sub>Cl was added. However, NH<sub>4</sub>Cl was observed to be very effective in delaying the gelation, which concurs with what was described in the literature (Karsani et al., 2014). The main reason for this phenomenon could be, tentatively, the strong efficiency of NH<sub>4</sub>Cl in screening the negative charges on the carboxylate groups on the PHPA resulted from the hydrolysis of PAM. This is because Na<sup>+</sup> was reported to have weaker bondage to carboxylate groups compare to NH<sub>4</sub><sup>+</sup> (Kherb et al. 2012).

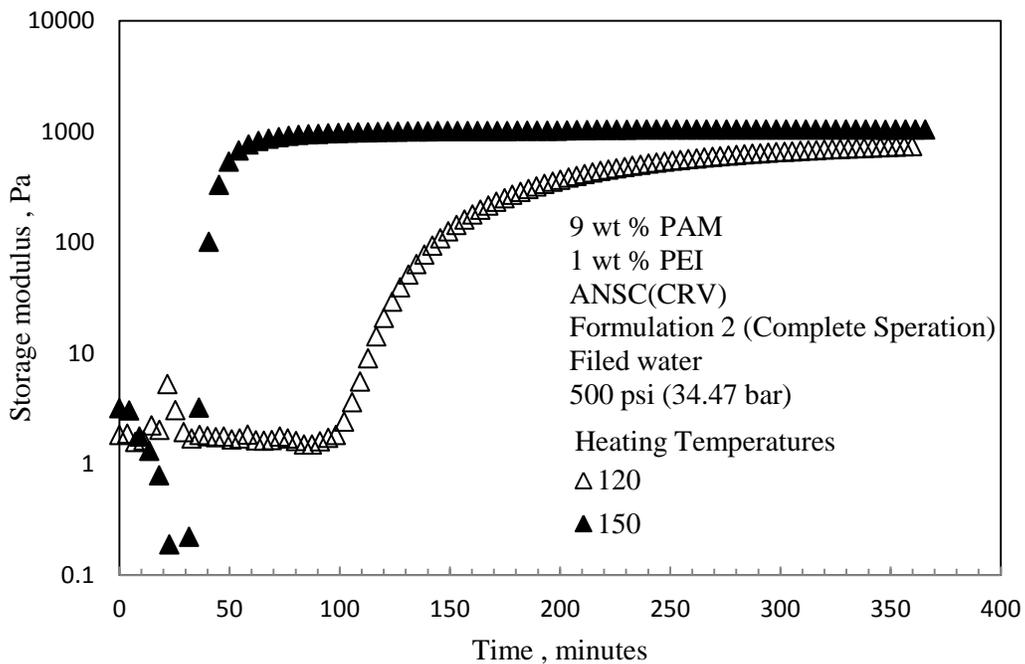


**Figure 5.6** Effect of retarder on elastic modulus, at different polymer concentration

### 5.3.6 Effect of Temperature

To examine the temperature effect on gel strength, two solutions were prepared at ambient temperature containing 9 wt% PAM / 1 wt% PEI. Then, the effect of temperature was investigated at 120° and 150°C (248 to 302°F). The gel strength, which is reflected in  $G'$ , depends on the cross-links density. The gel strength was predicted to increase with temperature (Kakadjian et al. 1999; Calvet et al., 2004; Al-Muntasheri et al., 2007). As shown in **Figure 5.7**, the shape of the second period differs with temperature. The shoulder shape weakens with increasing temperature. The same trend was observed in PAM/PEI in the same range of temperature (Karsani et al., 2014) and PAM /  $Cr^{+3}$  cross-linked gels (Sydansk 1990) in which the gelation was studied in the temperature range

24-60°C (75-10°F). This can be explained through the kinetics of the cross-linking reaction. Higher temperatures could lead to an increase in molecular mobility; hence, more cross-links could be formed. Consequently, the reaction rate will be enhanced. In another way, higher temperatures could lead to an increase in PAM hydrolysis which accelerates cross-linking. Another possible interpretation is the formation of new cross-links at higher temperatures. It was noticed that with the raise in temperature increase in the equilibrium elastic modulus ( $G_e'$ ) was observed.  $G_e'$  increased from 703 Pa to 1035 Pa (i.e. ~ 32% increase) or a factor of 1.5 as the temperature was raised from 120°C (248°F) to 150°C (266°F). This increase in  $G_e'$  with temperature is due to the increase in the rate of cross-linking.



**Figure 5.7** Effect of temperature on elastic modulus

## 5.4 Conclusions

The influence of emulsification, emulsifier, separation time, polymer concentrations, temperature, salinity of mixing water and salts on gel strength of emulsified PAM / PEI system were studied at high temperatures ( $>100^{\circ}\text{C}$ ). The gel strength was measured using dynamic shear measurements. This study is the first of its kind on the gel strength of the emulsified gels. The main findings of this work as follows:

1. Emulsification slows down the cross-linking process.
2. Emulsified PAM/PEI was found to have lower rate of cross-linking (gelation) in comparison with un-emulsified PAM/PEI. This effect is more pronounced when stable emulsified PAM / PEI (9/1) wt% was used instead of unstable emulsified PAM / PEI (9/1) wt% with complete separation within one hour, The elastic modulus decreased from 746 Pa to 343.6 Pa (i.e.  $\sim 54\%$  decrease).
3. No significant impact was observed when ANSC (CRV) was used instead of Ethomeen T/12 as emulsifier.
4. The elastic modulus of the emulsified PAM / PEI (9/1) wt% system was found to increase by about 32%, when the temperature was increased from  $120^{\circ}\text{C}$  ( $248^{\circ}\text{F}$ ) to  $150^{\circ}\text{C}$  ( $266^{\circ}\text{F}$ ).
5. Generally, elastic modulus decreased in the presence of salts. High water salinities resulted in low gel strength and longer gelation time.
6.  $\text{NH}_4\text{Cl}$  is found to be more efficient than  $\text{NaCl}$  in the retardation of the gelation process. This is due to the fact that  $\text{NH}_4\text{Cl}$  is more effective than  $\text{NaCl}$  in screening the negative charges on the carboxylate groups. Consequently, it reduces the available sites on the polymer to cross-link with PEI.

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## CHAPTER 6

### Conclusions and Recommendations

#### 6.1 General Conclusions

1. This work was successful in developing stable emulsified water in oil systems that can tolerate high temperature high salinity environments using scientific approaches.
2. In addition, HLB approach was used for surfactant selection and new insights on structure-emulsion stability relationships beyond the HLB approach were provided. The findings of this work would open more avenues for future research.
3. The cost effective organoclay as emulsifiers, was found suitable for emulsifying water phase (polymers/acids/ polyethylenimine) in oil phase, appropriate to high temperature and high salinity applications.
4. The influence of different parameters on the stability of emulsified polyacrylamide /polyethylenimine gels was extensively investigated at high temperature high salinity conditions. Emulsion droplet size has been correlated to thermal stability. Emulsions with smaller droplet size were found to be more stable.
5. The influence of emulsification, emulsifier, separation time, polymer concentrations, temperature, salinity of mixing water and salts on gel strength of emulsified PAM / PEI system were studied at high temperatures ( $>100^{\circ}\text{C}$ ). The gel strength was measured using dynamic shear measurements. This study is the first of its kind on the gel strength of the emulsified gels.
6. The proposed emulsified PAM/PEI system was found to offer adequate gel strength at high temperature using field mixing water.

## 6.2 Recommendations

Even though significant work was performed throughout this study, nevertheless still there are some parts that require further investigation. The following points summarize the recommendations for future research:

1. Impact of different oil phase and its properties such as viscosity and pH on the emulsion droplet size and thermal stability.
2. Waste oil from oilfield should be considered as cost effective oil phase, to substitute the commercial diesel in forming the emulsified PAM/PEI.
3. Effect of factors such as pH, water oil ratio and oil phase on gel strength and gelation time of the emulsified PAM/PEI should be studied.
4. Evaluation of emulsified PAM/PEI system through core-flow experiments at high pressure and high temperature.
5. Since, the treatment was proposed to control the saturation of the gelant in the pore space, through water fraction, different water oil ratio should be considered to evaluate this hypothesis.
6. The area of nanotechnology should be introduced to the application of polymer gel systems in shutting water in deep reservoirs. Fractures with high permeability need particles which can swell much more than the order of magnitude.

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## **Publications and Recent Researches**

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