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1

## Abstract

3 The first ever field pilot on Alaska North Slope (ANS) to validate the use of polymer floods for heavy oil
4 EOR is currently ongoing. One of the major concerns of the operator is the effect of polymer on oil-water
5 separation efficiency after polymer breakthrough. This work investigates the influence of polymer on
6 separation behavior of heavy oil emulsions and evaluates the performance of emulsion breakers (EBs). In
7 this study, two types of heavy oil emulsions were prepared and tested at 20% and 50% water cut (WC),
8 respectively. The bottle test method was employed in the experiments, in which the separated water
9 volume with time, the separated water quality and the volume fraction of phases were recorded. Results
10 showed that polymer accelerated the oil-water separation acting as emulsion inhibitor at 20% WC but
11 tended to impede the water separation at 50% WC. Regardless of WC, polymer resulted in poor water
12 quality and the formation of a stable intermediate o/w emulsion, owing to the increased viscosity of the
13 water phase. The performance of EBs showed a complex dependency upon the WC, the type of demulsifier
14 and dosage, and the polymer concentration. Despite the varied conditions encountered in the heavy oil-
15 water-polymer-demulsifier system, a compound emulsion breaker, achieved satisfactory demulsification
16 performance, showing the highest potential for deployment in the current ANS polymer flooding pilot.
17 This paper systematically studied the potential influence of polymer breakthrough on the separation
18 behavior of heavy oil emulsion on ANS for the first time. The findings of this study will provide practical
19 guidance in advance for produced fluid treatment of the ongoing first ever polymer flooding pilot on
20 Alaska North Slope.

21

## Introduction

23 Alaska North Slope (ANS) contains vast viscous and heavy oil resources ranging between 20-25 billion
24 barrels, which are primarily concentrated in West Sak (also called Schrader Bluff) and Ugnu reservoirs
25 (Targac et al. 2005). The development pace of these resources has been slow due to various factors such
26 as high costs, low oil recovery using conventional techniques, and the inapplicability of thermal methods
27 due to the presence of continuous permafrost. Polymer flooding has a great potential to improve oil
28 recovery from ANS' heavy oil reservoirs due to better mobility control and higher oil sweep efficiency

1  based on initial scoping studies. Currently, the US Department of Energy and Hilcorp is sponsoring the
2  first ever advanced polymer flooding pilot test in the Schrader Bluff viscous oil reservoir with an in-situ
3  oil viscosity of 330 cP and the current concentration of the injected polymer is 1,700 ppm. However, the
4  use of polymers in heavy oil EOR presents a potential problem, as this could upset the separation facilities
5  and disrupt existing field operations by negatively influencing the efficiency of oil-water separation after
6  polymer breakthrough into production systems.
7      With the worldwide application of polymer flooding, the oil-water separation characteristics after the
8  polymer breakthrough have been extensively addressed by field engineers and researchers (Feng et al.
9  1994, Deng et al. 2002, Wang et al. 2009, Zheng et al. 2011, Wylde et al. 2013, Al Kalbani et al. 2014,
10 Chen et al. 2015, Liu et al. 2015). Two common emulsions, both water in oil (w/o) and oil in water (o/w)
11 emulsion, have been studied to illustrate the potential problems of polymer flooding. As for the o/w
12 emulsion, it is generally believed that the presence of polymer can result in highly stable emulsion by
13 increasing produced water viscosity, electronegativity and the strength of interfacial film between oil and
14 water, thus preventing coalescence of oil droplets (Wu et al. 1999, Argillier et al. 2014, Chen et al. 2015,
15 Liu et al. 2015). Moreover, polymer molecules and the suspended particles, such as clay, carried by
16 polymer flooding can synergistically absorb on the oil-water interface to further stabilize the o/w emulsion
17 (Wang et al. 2012, Li et al. 2014, Liu et al. 2014). However, the influence of polymer on the stability of
18 w/o emulsion is much more complicated, depending on various factors such as the crude oil composition,
19 property of polymer, and the presence of surfactant. For example, the studies of Kang et al. (2011) and
20 Liu et al. (2015) showed that polymer enhances the stability of w/o (light oil) emulsion by forming a more
21 rigid oil-water interfacial film. In addition, Dalmazzone et al. (2012), Argillier et al. (2013) and Sjoblom
22 et al. (2017) found the polymer itself had no significant influence on the stability of w/o (heavy oil)
23 emulsion since they determined that the polymer had no interaction with the surface-active agents at the
24 oil-water interface. It was also found that, in the presence of surfactant, the polymer can contribute to the
25 stable intermediate w/o emulsion at low water cut (Dalmazzone et al. 2012, Argillier et al. 2013). Some
26 studies reported that especially the hydrophilic polymer could favor oil-water separation by reducing the
27 stability of the emulsion (Wu et al. 1999, Lin et al. 2008, Argillier et al. 2014, Al-Kayiem and Javed 2017).
28 The unpredictable impact of polymer on w/o emulsion brings a significant challenge in evaluating the
29 influence of polymer on actual oil-water separation in oilfield production systems since the actually
30 produced fluids are composed of both w/o emulsion and o/w emulsion. Furthermore, in some studies (Wu
31 et al. 1999, Lin et al. 2008, Argillier et al. 2013), the use of solvent-diluted crude oil or synthetic water
32 excluding some chemical additives used in oilfield such as drilling fluid additive, corrosion inhibitor, etc.
33 may not represent the separation behavior of actual crude oil emulsion. Therefore, the real oil-water
34 separation issues should be investigated as a whole using the on-site crude oil, produced water, and the
35 injected polymer under specific oilfield conditions to obtain reliable conclusions.
36     Treating produced liquid from polymer flooding has become a great challenge in oilfields. Many new
37 techniques, such as electrical dehydrator coupled with gravity settling (Liu et al. 2009, Liu et al. 2015),
38 novel crossflow oil-water separator (Deng et al. 2002), new hydrocyclone (Liu et al. 2007) and new
39 flotation device (Chen et al. 2015), have been developed to solve the oil-water separation problems.
40 However, chemical methods, i.e., demulsifiers and water treatment chemistries, are still the most popular
41 techniques due to their effectiveness, ease of implementation, and low cost. Fang et al. (2014) evaluated
42 the demulsification efficiency of cationic surfactants, i.e., alkyltrimethylammonium bromides (CTAB),
43 which were applied to treat produced fluids directly obtained from a heavy oil polymer flooding project
44 in China. They found $C_{14}TAB$ and $C_{16}TAB$, can effectively break both w/o and o/w emulsions existing in
45 the produced fluids since they were found to be able to reduce interfacial film strength and neutralize the
46 surface charge. Also, researchers have been making an effort to develop new demulsifiers to treat the
47 chemical EOR induced emulsions. For example, Duan and his group (Duan et al. 2014, Zhang et al. 2015)
48 developed a new type of non-ionic demulsifier which could effectively treat the o/w emulsion directly
49 produced from an offshore polymer flooding project. Li et al. (2016) found a novel polyether demulsifier,
50 TPEA19920, which exhibited an excellent performance to treat the produced heavy oil emulsions. Even

1 though the development of demulsifiers has made significant progress, there are still no demulsifiers with
2 universal applicability to process the produced fluids. In general, targeted demulsifiers need to be
3 developed or selected through extensive evaluation tests since they are highly sensitive to the properties
4 of the crude oil, produced water, applied chemicals, and the actual operating conditions. However, most
5 of the studies focused on investigating the same type of demulsifiers and mainly used separation efficiency
6 or water clarity to evaluate the demulsification performance (Duan et al. 2014; Fang et al. 2014; Li et al.
7 2016).
8 　　Extensive studies have been conducted to investigate the emulsification and demulsification
9 phenomenon. However, few studies are reported to investigate the effect of polymer on the separation
10 behavior of heavy oil emulsion from ANS. Herein lies the purpose of this work. In this paper, the
11 traditional bottle test method has been employed to investigate the influence of polymer on the separation
12 of produced liquid prepared in the lab using actual heavy crude oil, produced water, and injected polymer
13 obtained from the pilot test site on ANS and to evaluate the performance of several commercial
14 demulsifiers. Various influence factors, including WC, polymer concentration, demulsifier type and
15 concentration, and compound demulsifier, have been investigated. Additionally, multiple parameter
16 indicators are developed to evaluate the performance of different types of demulsifiers. A radar chart
17 composed of demulsification efficiency, separation speed, water clarity, and optimized dosage has been
18 developed to evaluate the demulsification performance. Finally, the most applicable demulsifier has been
19 proposed for field applications.
20
21 ## Experimental Method
22 **Materials**
23 The produced fluid was sampled directly from the wellhead of a production well on polymer flooding
24 pilot site, which was initially separated by thermal settling. The upper heavy oil was further dehydrated
25 by centrifuge until no water separated, whereas the bottom produced water was filtered by 0.2 µm water-
26 wet filter paper (Tianjin Jinteng Experimental Equipment Co., China) through the vacuum filtration
27 method to remove the suspended oil and particulate matter. The properties of heavy oil and produced
28 water are listed in **Table 1** and **Table 2**, respectively. The polymer used, Flopaam 3630 having a molecular
29 weight of 18-20 MM Dalton and 30% hydrolysis, was supplied by SNF, Inc. Commercial emulsion
30 breakers, E12085A, E18276A, N1691, and R01319 which are the product codes, were used in this study.
31 The names of the four emulsion breakers are also abbreviated as E12, E18, N16, and R13, respectively.
32 All chemical reagents such as petroleum ether, methanol, and xylene (VWR International) were used as
33 received.
34
35

Table 1–Properties of heavy oil

| Density (g/cm$^3$, 22 °C) | In-situ Density (g/cm$^3$) | Viscosity (cP, 22 °C) | In-situ Viscosity (cP) |
|---|---|---|---|
| 0.9557 | 0.9176 | 3,500 | 330 |

36
37

Table 2–Properties of produced water

| TDS (ppm) | pH | Conductivity (µS/m) |
|---|---|---|
| 6,645 | 5.61 | 8,128 |

38
39 **Polymer solution preparation**
40 A polymer mother solution of 1,000 ppm concentration was prepared by dissolving a certain amount of
41 polymer powder into the filtered produced water under gentle stirring at room temperature for 24 hours
42 until no fish eyes were remaining. The mother solution was diluted with the filtered produced water to
43 obtain the desired polymer solution with concentrations of 150 ppm, 400 ppm, and 800 ppm. The polymer
44 concentrations were determined to cover the potential viscosity range of produced water which would be
45 produced from the pilot well. The apparent viscosity of each polymer solution was measured by Brookfield
46 viscometer (Brookfield Engineering Laboratories Inc., USA) as a function of shear rate at 130 °F.

**Demulsifier solution preparation**
10,000 mg/L demulsifier original solution was prepared by dissolving a certain amount of demulsifier into a specific solvent. Oil-soluble demulsifiers, E12085A, E18276A, and R01319, were dissolved into xylene, and water-soluble demulsifier, N1691, was dissolved into methanol.

**Emulsion preparation**
The separated heavy oil and the aqueous phase (produced water or polymer solution) were added to a beaker according to designed ratios (20% WC and 50% WC) and preheated to 130 °F in the water bath to mimic actual field conditions. The WC is defined as the volume ratio of the aqueous phase to the total volume of emulsion. The IKA Ultra-Turrax T18 Digital homogenizer was used to stir the mixture at 5,000 rpm for 3 min to prepare the emulsion.

**Microscopic observation**
As for oil-continuous emulsion, to obtain high-quality microscopic images, the prepared emulsion was first diluted with white oil by 50 times. Subsequently, a small drop of the diluted emulsion was immediately transferred by a syringe onto a glass slide for taking the microscopic image without using the cover slide. As for water-continuous emulsion, a small drop of the prepared emulsion was immediately transferred by a syringe onto a glass slide, and a cover slide was placed on the top of the emulsion before taking the microscopic image to avoid the evaporation of the aqueous phase. The Olympus BX60 microscope was used to observe the micromorphology of the prepared sample. Several images on each slide were captured to ensure uniformity.

**Bottle test method**
In gravitational separation tests, the emulsion was transferred into a graduated tube immediately after preparation. The tube was placed into the water bath to observe the separation characteristics of emulsion under the action of gravity. In chemical demulsification tests, after transferring the prepared emulsion, a certain amount of demulsifier solution was added to the test tube based on the volume of the emulsion. The tube was shaken by hand for 3 minutes to mix the emulsion and demulsifier thoroughly and then kept in the water bath for the chemical separation test. All the separation tests were performed at the temperature of 130 °F. During the separation process, the separated water volume and the volume fraction of each phase (oil, emulsion and aqueous phase) were recorded with respect to time. In addition, the sharpness of the interface between the oil phase and the separated water phase and the clarity of the separated water was observed. Eventually, the oil content in separated water (OIW) was measured after 24 hours using Genesys 10s UV-Vis spectrophotometer (Thermal Fisher Scientific Inc., USA).

# Results and Discussion
**The viscosity of polymer solutions**
The viscosity of prepared polymer solutions as a function of shear rate is shown in **Figure 1**. Polymer solution at each concentration can be characterized as non-Newtonian fluid showing shearing-thinning behavior as the viscosity of polymer solution decreased with the shear rate. The viscosity-shear rate decline trend clearly complies with the power-law model, which is consistent with the study of Gao (2013). It is also obvious that higher polymer concentration led to higher viscosity.

**Gravitational separation behavior**
The micromorphology and separation behavior of heavy oil emulsions were studied. During the microscopic observation, the impact of the water cut was evaluated. In the study of separation behavior, water separation kinetics, oil content in the separated water (OIW) and volume fraction of the separated phases were analyzed at various water cut and polymer concentration.
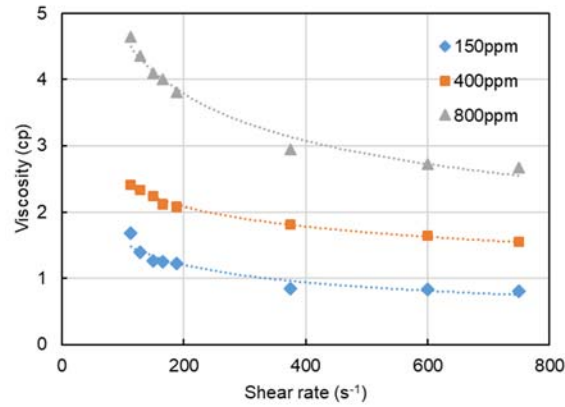
Figure 1–The viscosity of polymer solutions as a function of shear rate

**Micromorphology of emulsion. Figure 2** shows the micromorphology of emulsion generated at 20% WC and 50% WC with no addition of polymer. At 20% WC, w/o emulsion was observed with water droplets dispersed in the oil phase as seen from Figure 2(a). At 50% WC, the droplets in forms of w/o emulsion were trapped in the water phase, forming complex water in oil in water (w/o/w) emulsion as indicated by Figure 2(b).
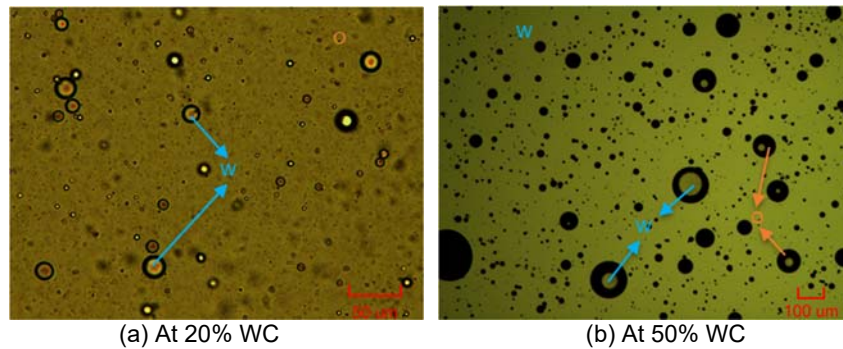


(a) At 20% WC          (b) At 50% WC

Figure 2–Microscopic images of emulsion (a) at 20% WC and (b) at 50% WC

**The effect of polymer on separation kinetics.** Water separation kinetics can be used to describe the emulsion stability; the faster the water can separate, the less stable the emulsion is (Nguyen and Nick, 2011). **Figure 3** shows the impact of polymer concentration on separation kinetics at 20% and 50% WC, in which the markers are the measured data points, and the corresponding regression curves represent the separation trend. To better characterize the separation behavior, the influence of polymer on OIW and volume fraction of the separated phases are shown in **Figure 4** and **Figure 5**, respectively.



(a) At 20% WC          (b) At 50% WC
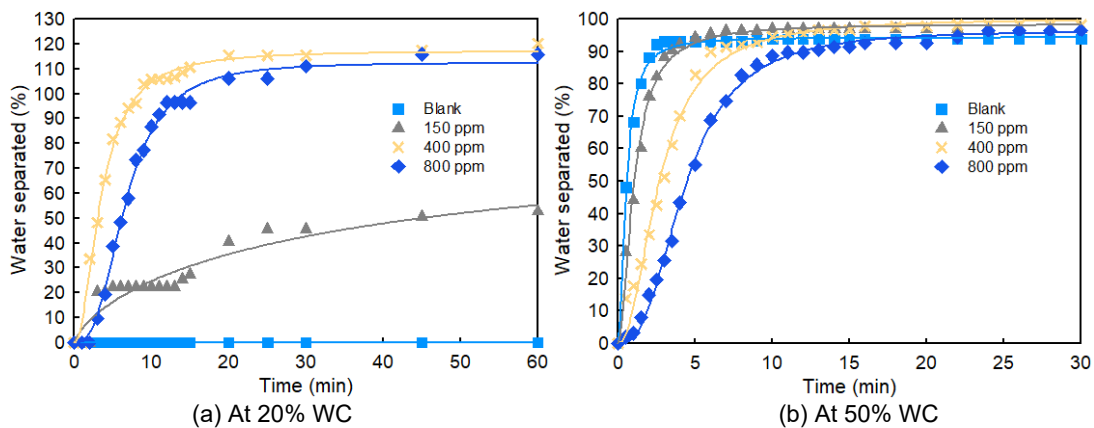
Figure 3–The effect of polymer on separation kinetics

1    With no addition of polymer (blank sample), the emulsion generated at 20% WC was much more stable
2    than that at 50% WC. The w/o emulsion generated at 20% WC was stable for at least 24 hours (not shown
3    in the plot but was observed); however, the w/o/w emulsion generated at 50% WC was quite unstable,
4    separating into two layers in less than 5 min.
5        For emulsions at 20% WC, as shown in Figure 3(a), the water separation was accelerated in the presence
6    of polymer compared to the blank sample. The destabilization effect of polymer for w/o emulsion has
7    been previously reported due to the increased coherent energy of polymer molecules (Wu et al. 1999). It
8    could also be attributed to the increased density of polymer solution (Sjoblom et al. 2017). According to
9    the Stokes equation:

10  $$\nu = \frac{\Delta\rho g d^2}{18\eta} \tag{1}$$

11   Where $\nu$ is the sedimentation or creaming rate, $\Delta\rho$ is the density difference between oil and water, $d$ is the
12   diameter of the dispersed droplets, and $\eta$ is the viscosity of the continuous phase. As the viscosity for the
13   continuous oil phase is constant, the increased density of polymer solution contributes to larger $\Delta\rho$,
14   facilitating the sedimentation of water droplets. To be noted in Figure 3(a) is the water separation in excess
15   of 100% at 400 ppm and 800 ppm polymer concentration, which is attributed to the intermediate layer (it
16   is believed to be an o/w emulsion layer, see **Figure 5**) that was included in the separated water volume
17   since the interface between the water layer and the intermediate layer cannot be well defined.
18       It is also noteworthy that although the water separation was enhanced with the addition of polymer at
19   20% WC compared to the blank sample, the amount of separated water at first increased with increasing
20   polymer concentration until a critical point of 400 ppm was reached and then decreased. Even though such
21   critical point has not been reported previously, this trend may be due to the phase inversion (the w/o
22   emulsion could be converted to o/w emulsion) resulting from the increase of polymer concentration
23   (Preziosi et al. 2013, Liu et al. 2015). Thus, in this study, water continuous emulsion could be generated
24   starting from the polymer concentration of 400 ppm at 20% WC. And then, the reduced water separation
25   after the critical point could be attributed to the increased viscosity of the continuous phase (i.e., water
26   phase).
27       For water continuous emulsion at 50% WC, as shown in Figure 3(b), the presence of polymer impeded
28   the phase separation, which could be attributed to the increasing viscosity of polymer solution as described
29   in Figure 1. Whereas, there was not much difference in final water separation volume as the residence
30   time extended to 30 min, implying extending settlement time is one potential method to minimize the
31   stabilization effect of polymer. To be noted, the final separation volume (i.e., at 30 min) with the presence
32   of polymer was slightly higher than that of the emulsion without polymer. It is because of the massive oil
33   droplets in the separated water, which could affect the measurement of separated water volume.
34
35   **The effect of polymer on separated water quality.** The effect of polymer on the separated water quality
36   after 24 hours is displayed in **Figure 4**. In general, the polymer had a negative effect on the separated
37   water quality, and the OIW significantly increased with increasing polymer concentration. That is because
38   adding polymer could generate more stable o/w emulsion in the separated water phase (Liu et al. 2015).
39   When the OIW at tested polymer concentrations is compared, the oil content at 50% WC is nearly double
40   than at 20% WC, which implies that the water treatment would be much more challenging at higher WC.
41   That is because, at higher water cut, the distance between oil droplets becomes larger which makes it
42   harder to collide and coalesce.
43
44   **The effect of polymer on the volume fraction of phases.** It is worth mentioning that the addition of
45   polymer resulted in a concentrated o/w emulsion layer sandwiched between the top oil layer (w/o
46   emulsion) and the bottom separated water layer during the oil-water separation process, as shown in
47   **Figure 5**. According to our observation, the interfaces between this intermediate layer and the top layer
48   or bottom layer became clearer with prolonged settling time. After 24 hours, this intermediate emulsion
49   layer still existed, and the intermediate layer at 20% WC was thicker than that at 50% WC. At the same

water cut, the more the separated water, the thicker the intermediate layer, which was more difficult to eliminate. The thickness change of this layer with respect to time was also related to the water cut. The intermediate layer became thinner with time at 20% WC but slightly thicker at 50% WC. The formation of the middle emulsion layer may result from the higher viscosity of the aqueous phase generating concentrated stable o/w emulsion.



(a) At 20% WC  (b) At 50% WC
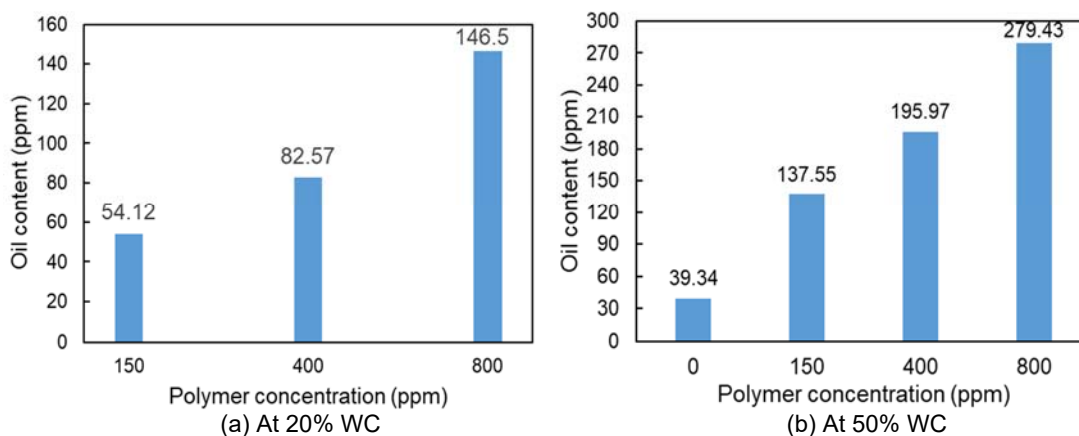
Figure 4–The effect of polymer on water quality



(a) At 20% WC  (b) At 50% WC
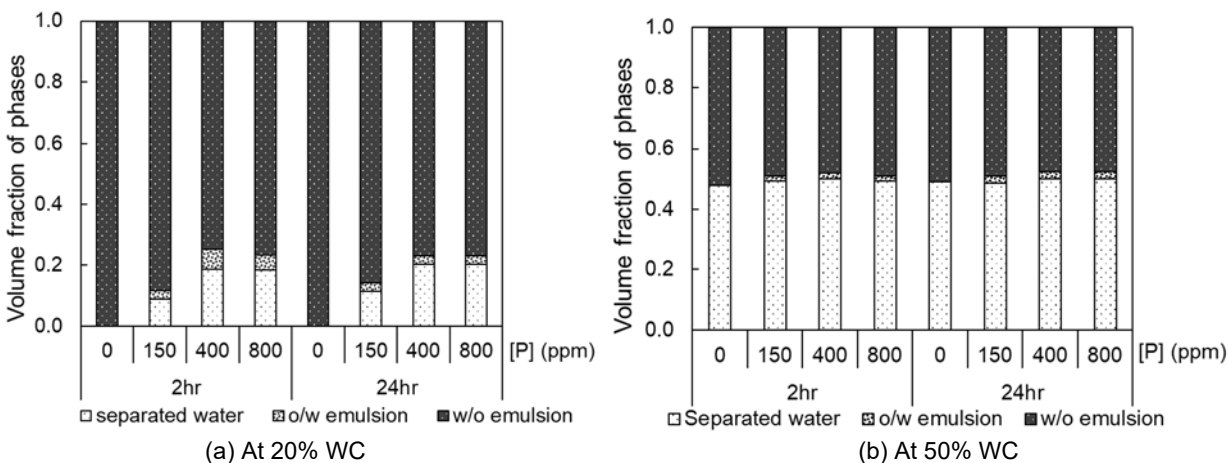
Figure 5–The effect of polymer on the volume fraction of phases

The positive effect of polymer for w/o emulsion by promoting phase separation acting as emulsion breaker has been reported by Lin et al. (2008) and Argillier et al. (2013). Different from their findings, the negative effect of polymer on the separated water quality and the formation of intermediate o/w emulsion layer were observed in our study. Those phenomena which were not reported earlier may be due to the use of solvent-diluted heavy oil or synthetic water rather than the actual crude oil or produced water. It has been reported that the addition of solvent could improve the quality of the separated oil and water (Opawale 2009).

**Chemical demulsification without polymer**

In most oilfields, the typical requirement for the total separation process is to produce dry oil and clean water. Dry oil should contain no more than 0.3% water by volume and clean water should have an oil content of less than 100 ppm, preferably 50 ppm (Hirasaki et al. 2010). The separation process on ANS consists of a slug catcher (130 $^{o}$F), a heater and a separator (170 $^{o}$F). In our experiment, we mimicked the first stage separation in the slug catcher, the demulsification efficiency of over 90% and oil content of less than 100 ppm would be acceptable (Hilcorp, personal communication, July 05, 2019).

1  **The performance of individual demulsifiers. Figure 6** shows the performance of four types of
2  demulsifiers with a dosage of 100 ppm at 20% WC. As can be seen, three oil-soluble demulsifiers,
3  E12085A, E18276A, and R01319, promoted oil-water separation, and clear separated water was obtained
4  with an oil content less than 20 ppm. The demulsification efficiency of the three oil-soluble demulsifiers
5  at 12 hours in decreasing order was E18276A, E12085A, and R01319. It also can be seen that, as for
6  E18276A, water separated rapidly in the first 3 hours and then slowly until it reached the plateau after 6
7  hours. However, as for E12085A and R01319, the time needed to reach the plateau was 10 hours,
8  indicating a slower separation rate. In terms of OIW shown in Figure 6(b), E18276A yielded the lowest
9  value. Therefore, among the four evaluated demulsifiers, E18276A is the most effective emulsion breaker
10 from the perspective of demulsification efficiency, separation rate, and OIW. Whereas, in the case of
11 water-soluble demulsifier, N1691, no water separation was observed, since N1691 can be rarely soluble
12 in the continuous oil phase, causing the barriers to the diffusion and adsorption process of N1691
13 molecules on the oil-water interface (Kang et al. 2018). Note that even though E18276A had the most
14 efficient performance, it did not render complete separation of the water phase in the measured time scale.
15



(a) Separation kinetics                    (b) Oil content in the separated water
Figure 6–The performance of demulsifiers on oil-water separation at 20% WC
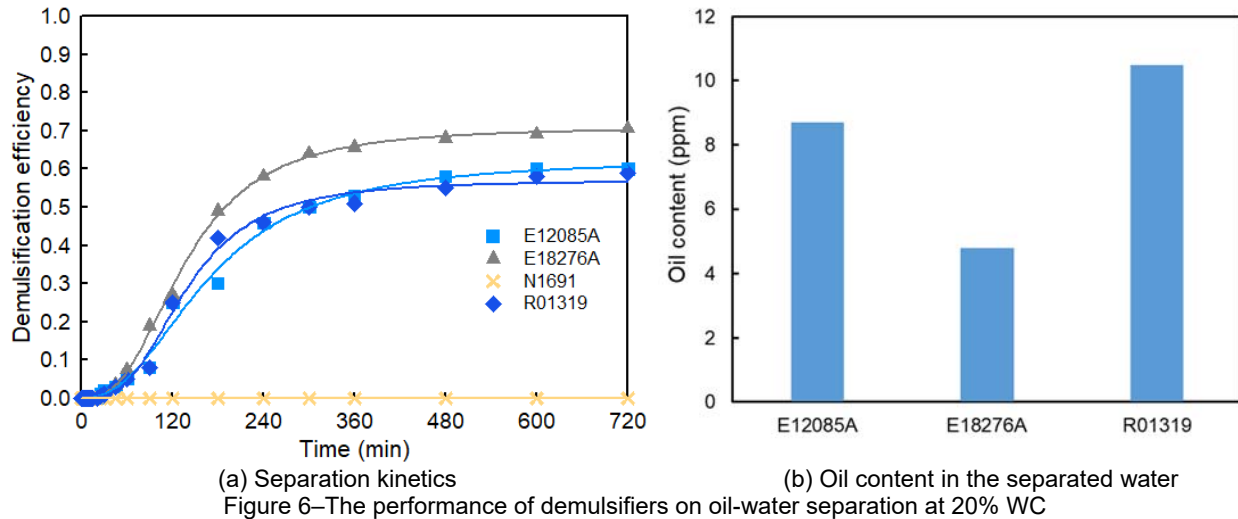
20  The performance of the four demulsifiers at a dosage of 100 ppm for emulsion generated at 50% WC
21 is shown in Figure 7. As can be seen from Figure 3(b), the water separation efficiency of the blank sample
22 could achieve 90% within 5 min, and eventually could reach about 93% at 30 min. However, as seen from
23 **Figure 7(a)**, with the addition of four emulsion breakers, all the water separation efficiencies of the four
24 tested samples were lower than 85% at 30 min. Thus, the addition of four emulsion breakers seemed to
25 impede the separation. By comparing **Figure 4(b)** (i.e., the oil content at 0 ppm polymer concentration)
26 and **Figure 7(b)**, it can be found that  the addition of the four demulsifiers could help to reduce OIW.
27 However, N1691 had an advantage over the other three oil-soluble demulsifiers in terms of separation
28 speed, resulting in higher separation efficiency within 60 min, since the unstable w/o/w emulsion was
29 converted to stable w/o emulsion after the addition of three oil-soluble demulsifiers as shown in **Figure
30 8**. Thus, the slower separation occurred due to the high viscosity of the continuous heavy oil phase. This
31 conversion might be attributed to the strong lipophilicity of the oil-soluble demulsifiers (Lv et al. 2014).
32 However, the lack of knowledge of the properties of the tested demulsifiers does not allow us to pinpoint
33 the precise underlying reasons. Comparing Figure 6(a) and Figure 7(a), it can be seen that although
34 R01319 was not as efficient as E18276A for emulsion generated at 20% WC, R01319 had a higher
35 separation speed than E18276A at 50% WC, implying R01319 has poor diffusivity in oil but could disrupt
36 the interfacial film effectively. Note that if the settlement time was 4 hours, E12085A performed better
37 than N1691 and R01319 with the highest efficiency and lowest oil content in water. Generally, no
38 emulsion breaker can perform well for emulsion at 50% WC from the standpoint of the three criteria.
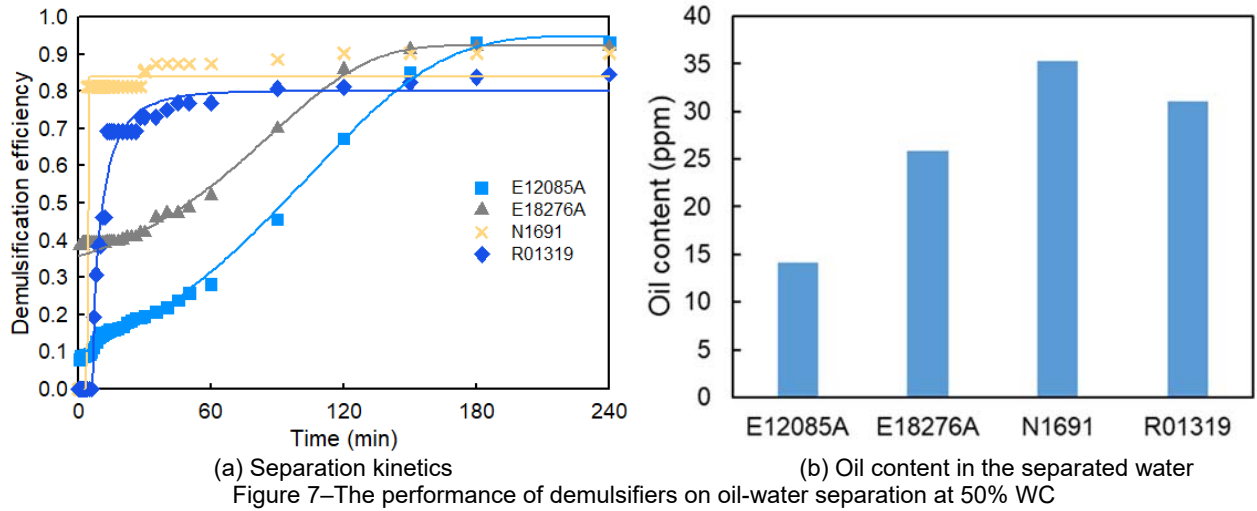
(a) Separation kinetics

(b) Oil content in the separated water

Figure 7–The performance of demulsifiers on oil-water separation at 50% WC



(a) without demulsifier

(b) with E12085A
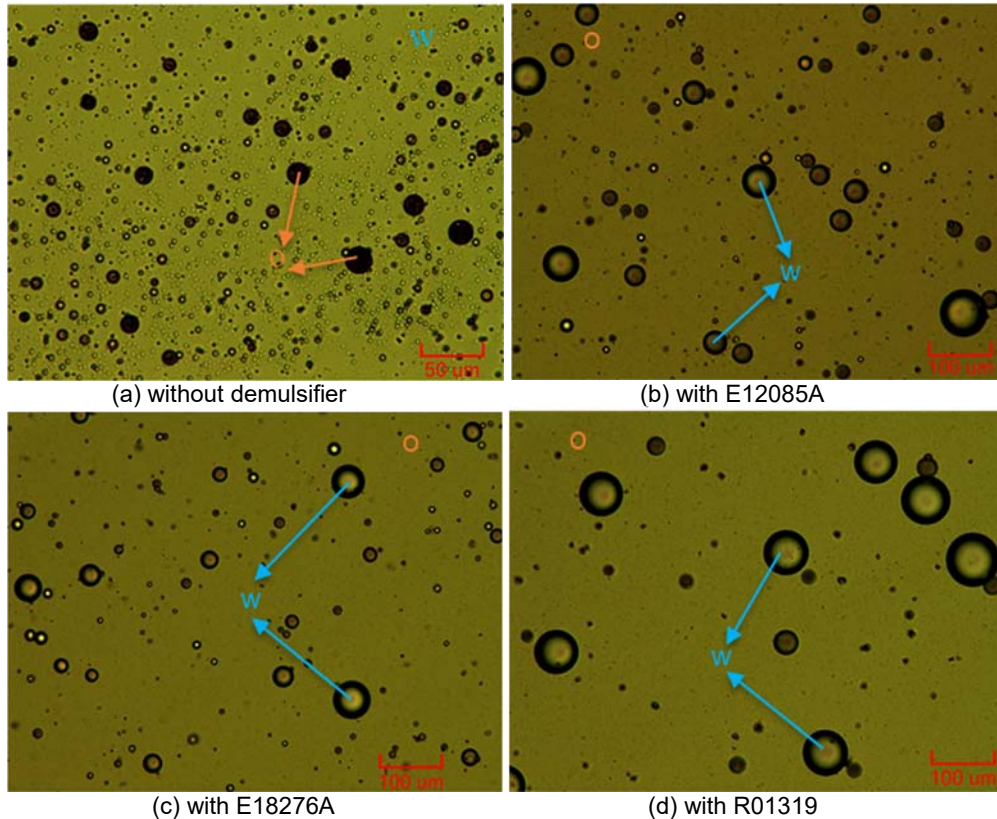
(c) with E18276A

(d) with R01319

Figure 8–Microscopic images of emulsions (a) without demulsifier (b) with E12085A (c) with E18276A (d) with R01319

**The effect of demulsifier dosage.** Demulsifier dosage is one important factor affecting the demulsification performance and thus in determining the overall cost of demulsification in the application. Besides, overdosage of demulsifiers may lead to counterproductive effects, such as resulting in more stable w/o emulsion and producing stable reverse o/w emulsion (Manning and Richard, 1995). As shown in Figure 6, the most efficient demulsifier, E18276A, did not yield a separation efficiency of over 90% at the dosage of 100 ppm. Therefore, the influence of the demulsifier dosage of E18276A on oil-water separation was investigated for which the results are shown in **Figure 9**. Although increased dosage enhanced the demulsification efficiency, it was offset by higher OIW.

(a) Separation kinetics           (b) Oil content in the separated water
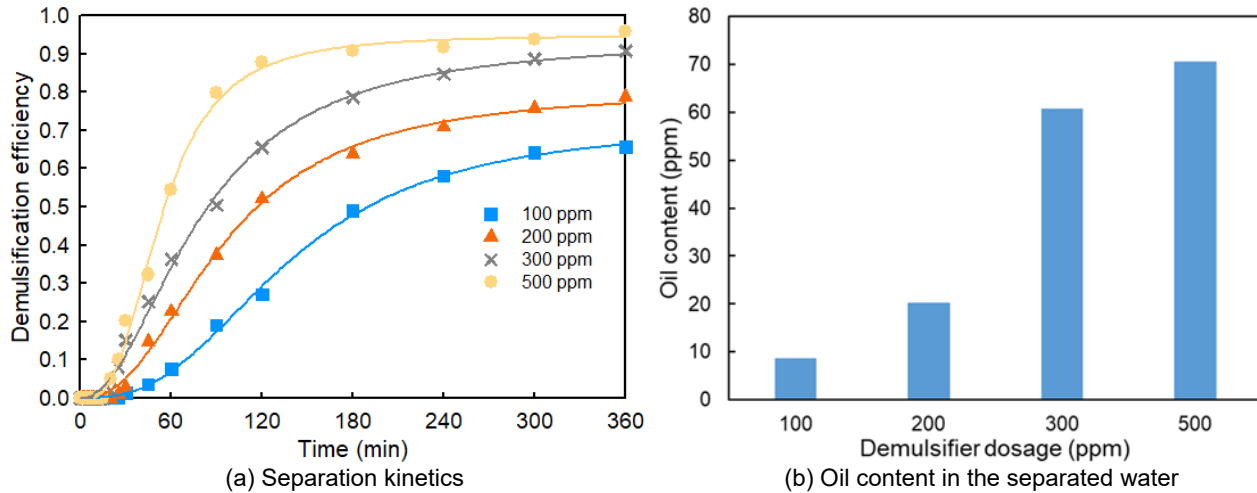
Figure 9–The effect of dosage on the performance of E18276A for emulsions at 20% WC

**The performance of the compound demulsifiers.** Multiple compound emulsion breakers were also proposed and evaluated to find the most efficient combination which can make use of the advantage of individual emulsion breaker to a maximum extent. Based on the analysis for each emulsion breaker performance in previous tests, E12085A produced the best water quality and the highest separation efficiency if the residence time was long enough; E18276A had the optimum performance for w/o emulsion; N1691 was capable of breaking the emulsion at 50% WC in a short residence time at low dosage; R01319 had better ability to disrupt the interfacial film. Thus, the performance of compound emulsion breakers, E12+N16, E12+R13 and E12+E18, were investigated at 100 ppm, as shown in **Figure 10**. E12+E18 is the most promising compound emulsion breaker which achieved a faster and more efficient separation than either E12085A or E18276A at the same dosage. E12+N16 increased the separation efficiency from 65% to 80% at 2 hours compared with E12085A itself and yielded better water quality than either E12085A (Figure 10 (b)) or N1691 (Figure 7(b)). Moreover, the separation efficiency of compound demulsifiers, both E12+E18 and E12+N16, achieved 90% at the end of the tests. However, the separation efficiency of the compound demulsifier of E12+R13 was about 80% at the end of the test. Thus, it is concluded that the demulsification performance of E12+R13 was not as efficient as that of E12+E18 and E12+N16.

In order to provide a comprehensive analysis, the performances of the qualified emulsion breakers for emulsion at 50% WC without polymer are compared in the radar chart (**Figure 11**) in terms of demulsification efficiency, water clarity, separation speed and dosage. These four parameters are defined as the dimensionless number in the following equations:

$$Efficiency = \frac{V_s}{V_t} \tag{2}$$

$$Water\ clarity = \frac{C_a - C_m}{C_a} \tag{3}$$

$$Separation\ speed = \frac{T_m - T_e}{T_m} \tag{4}$$

$$Dosage = \frac{C_{max} - C}{C_{max}} \tag{5}$$

where, $V_s$ is the separated water volume at 4 hours;

      $V_t$ is the total water volume;

      $C_a$ is the allowed oil content in water, typically less than 100 ppm;

      $C_m$ is the measured oil content in water after 24 h;

      $T_m$ is the measurement time for separation which is 4 h;

$T_e$ is the time required to reach the separation equilibrium;

$C_{max}$ is the maximum dosage of emulsion breaker used in the experiment;

According to the definition, the larger the enclosed area in the radar chart, the better the performance of the corresponding emulsion breaker. It is obviously seen from Figure 11, E12+E18, E12+N16 and N1691 are the better performing demulsifiers. E12+E18 is the most efficient emulsion breaker in terms of dosage and separation efficiency; E12+N16 is the most efficient emulsion breaker in terms of water clarity; N1691 is the most efficient emulsion breaker in terms of dosage and separation speed.
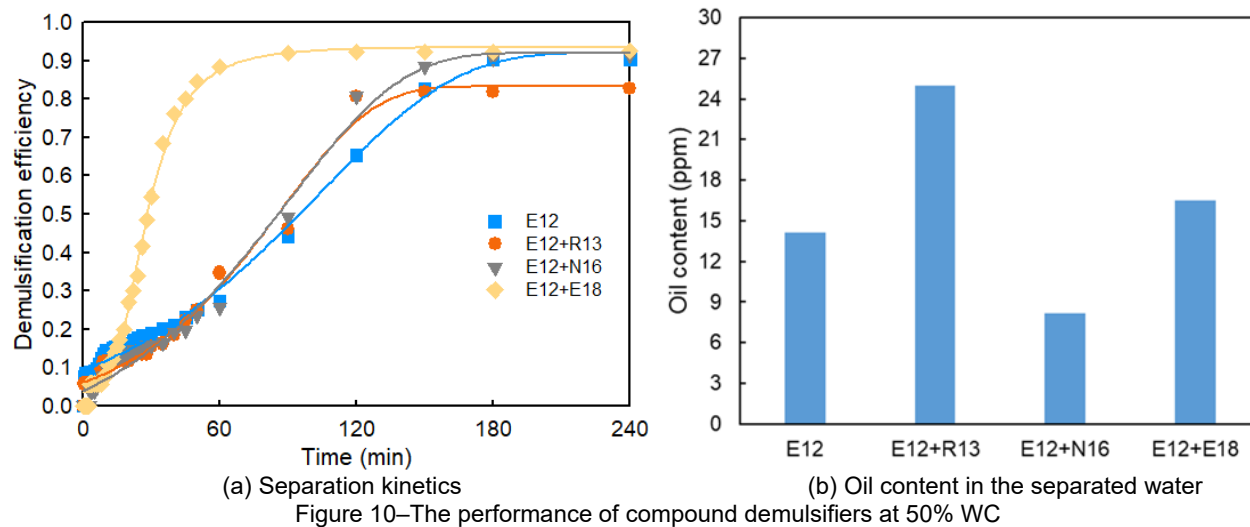


(a) Separation kinetics
(b) Oil content in the separated water
Figure 10–The performance of compound demulsifiers at 50% WC
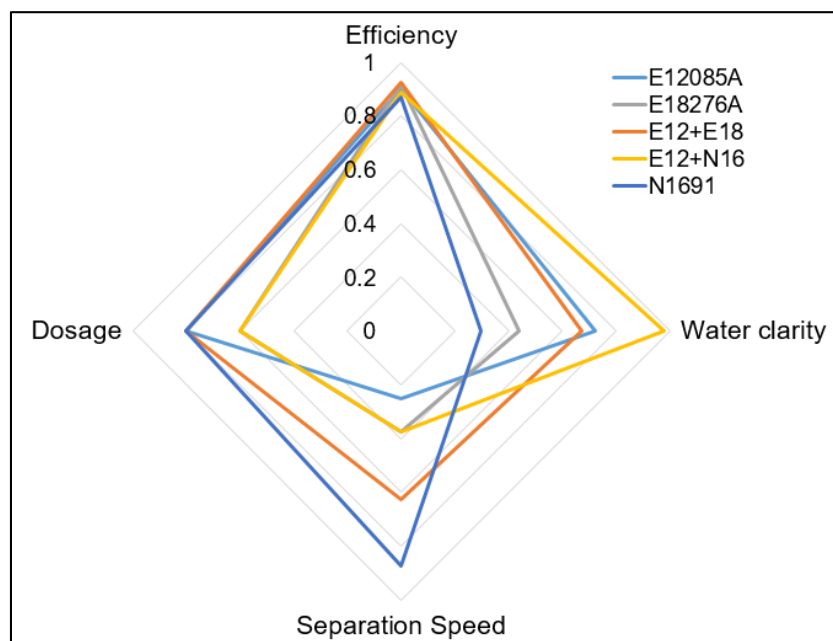


Figure 11–Radar chart for the performance of demulsifiers at 50% WC

**Chemical demulsification in the presence of polymer**

In the presence of polymer, the performance of the four individual emulsion breakers and the aforementioned compound emulsion breakers were evaluated and the emulsion breaker with the optimum performance was proposed. The effect of polymer concentration on the proposed emulsion breaker was also investigated.

**The performance of individual demulsifiers.** The performance of the four demulsifiers with the dosage of 100 ppm was evaluated for the emulsion with 150 ppm polymer at 20% WC. **Figure 12 (a)** shows that

all three oil-soluble demulsifiers performed better than the water-soluble demulsifier. According to the observation during the separation process, the three oil-soluble demulsifiers could effectively eliminate the intermediate layer described in Figure 5 and obtain a clear water phase. As can be seen from **Figure 12**, E18276A had the most efficient performance in terms of separation efficiency, separation speed and OIW; however, the dosage appeared to be insufficient to achieve a separation efficiency above 90%.
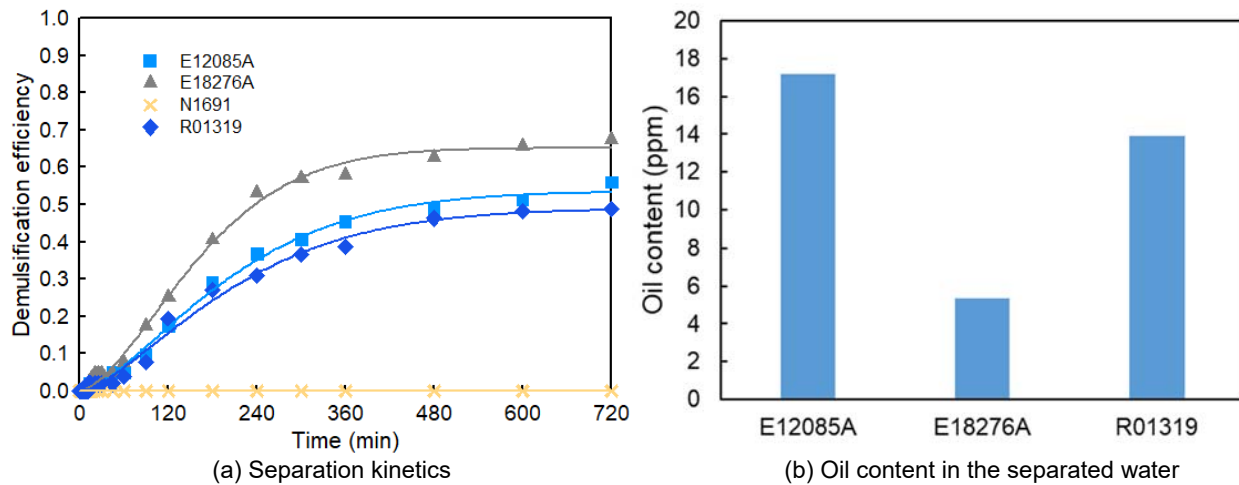


(a) Separation kinetics                          (b) Oil content in the separated water
Figure 12–The performance of demulsifiers for emulsion with 150 ppm polymer at 20% WC

The performance of the emulsion breakers with the dosage of 50 ppm for the emulsion with 800 ppm polymer at 50% WC is shown in **Figure 13**. All the four emulsion breakers achieved a separation efficiency of over 90% in less than 15 min, and the three oil-soluble emulsion breakers achieved an OIW lower than 50 ppm. However, the water-soluble emulsion breaker, N1691, yielded an unsatisfactory OIW of 160 ppm. Therefore, the application of N1691 after polymer breakthrough may be limited due to its poor performance. E12085A and R01319 are highly competent for emulsions in the presence of polymer at 50% WC.
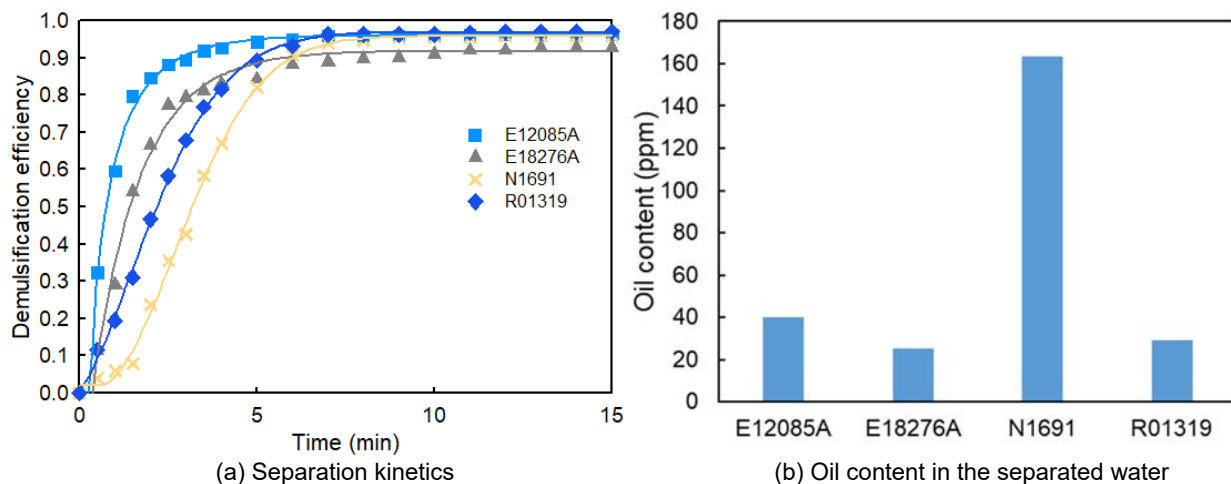


(a) Separation kinetics                          (b) Oil content in the separated water
Figure 13–The performance of demulsifiers for emulsion with 800 ppm polymer at 50% WC

**The performance of the compound demulsifier.** The compound emulsion breakers, E12+E18 and E12+N16, were also evaluated for emulsion with 150 ppm polymer at 20% WC. The performance of the compound emulsion breakers is shown in **Figure 14**. Since there was no water separation for E12+N16, Figure 14 only shows the performances of E12+E18 in comparison with E18276A. At a dosage of 100 ppm, the separation efficiency of E12+E18 was slightly lower than that of E18276A. However, when the dosage was above 100 ppm, E12+E18 yielded a similar separation efficiency and lower OIW.
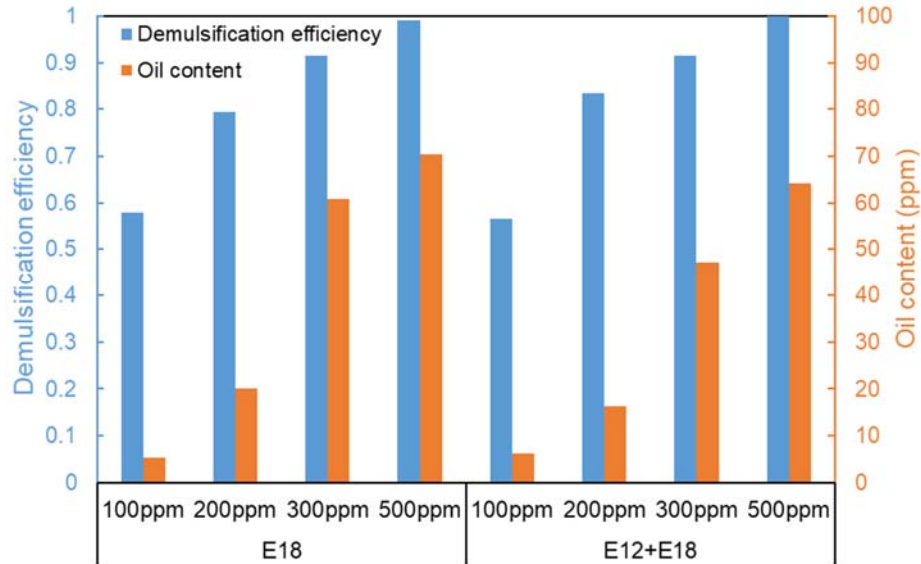
Figure 14–The performance of compound demulsifiers for emulsion with 150 ppm polymer at 20% WC

As mentioned in the previous analysis (Figure 13), two individual emulsion breakers E12085A and R01319 are most applicable to treat emulsion with 800 ppm polymer at 50% WC. The performances of compound emulsion breakers, E12+E18 and E12+N16, are compared with those of E12085A and R01319 by radar chart in **Figure 15**. It can be seen that E12+E18 exhibited the optimum performance.
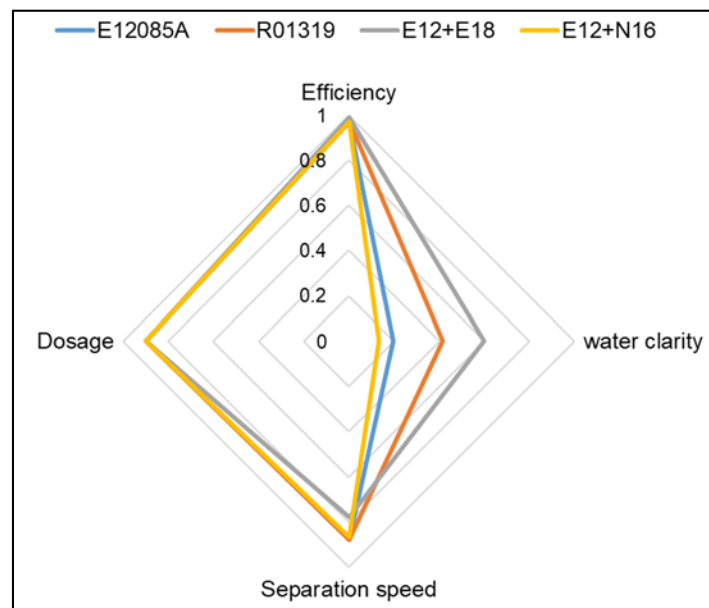


Figure 15–The performance of demulsifiers for emulsion with 800 ppm polymer at 50% WC

**The effect of polymer concentration.** Based on the above analysis, compound emulsion breaker, E12+E18, has the potential to be used for emulsions generated at both 20% WC and 50% WC. Since the varying water cut and polymer concentration after breakthrough can change the demulsifier demand, the influence of polymer concentration on the performance of demulsification was also investigated at the two water cuts. The effect of polymer concentration on the demulsification performance of E12+E18 for emulsion at 20% WC is shown in **Figure 16**. In this case, polymer concentration had no obvious effect on the demulsification performance. E12+E18 with a dosage of 500 ppm could help to achieve the separation requirements at varying polymer concentration. It may be expected that the required emulsion breaker

dosage might be increased or a new demulsifier might be needed when the polymer concentration is above 800 ppm due to the decrease of demulsification efficiency and increase of OIW.

For emulsion generated at 50% WC, the effect of polymer concentration on the demulsification performance of E12+E18 is shown in **Figure 17**. It is obvious that at the same dosage of 50 ppm, the demulsification efficiency was higher in the presence of polymer. In other words, a higher demulsifier dosage would be required in the case of no polymer.
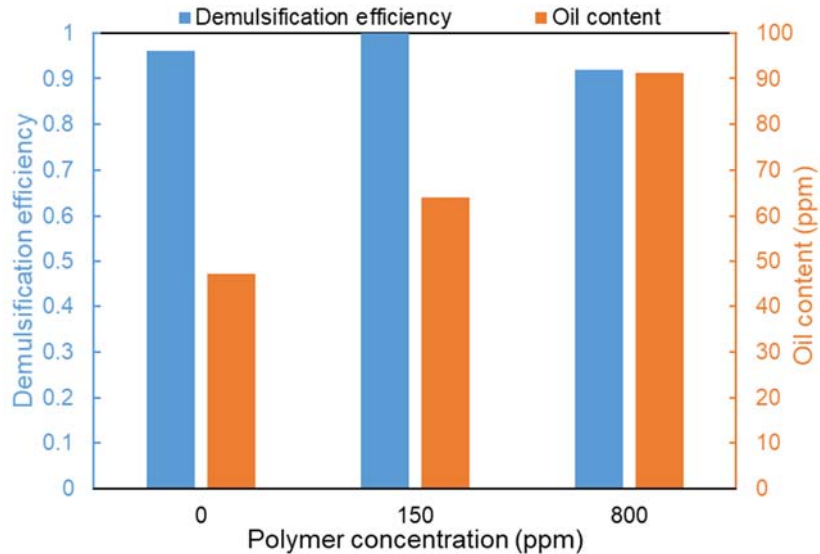


Figure 16–The effect of polymer concentration on demulsification for emulsion at 20% WC
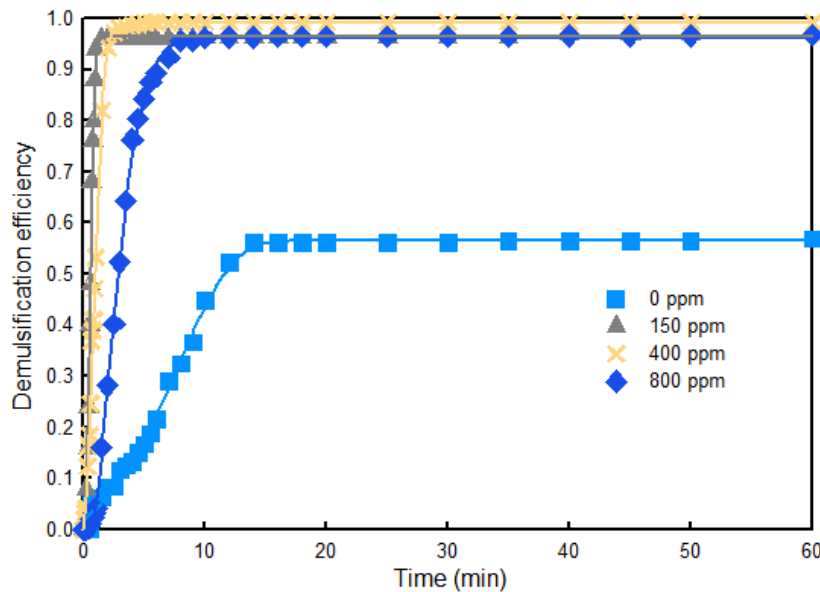


Figure 17–The effect of polymer concentration on demulsification for emulsion at 50% WC

## Conclusions

In the framework of this study, the gravitational and chemical separation behavior of heavy oil emulsion prepared with actual heavy oil and produced water from the ANS polymer flooding pilot site was investigated by the bottle test method against various influence factors. The main conclusions are as follows:

For the gravitational separation, polymer generally favored the oil-water separation for emulsion at 20% WC but in a complex manner. The maximum water volume was separated when the polymer concentration

reached 400 ppm, but further increasing polymer concentration reduced the water separation. For emulsion at 50% WC, the emulsion became more stable with increasing polymer concentration which resulted from the increased viscosity of polymer solution. It is also observed that polymer resulted in poor water quality and contributed to the formation of a stable intermediate o/w emulsion layer regardless of water cut which was also attributed to the increased viscosity of the aqueous phase.

For the chemical demulsification, oil-soluble demulsifiers exhibited better performance than water-soluble demulsifier for emulsions both with and without polymer at 20% WC. E18276A was found to be the most effective emulsion breaker at the dosage of 500 ppm in terms of separation efficiency, separation speed and water clarity. As for emulsion at 50% WC, no individual emulsion breaker could perform well from the standpoint of all three criteria. In this case, water-soluble demulsifier N1691 exhibited the fastest separation in the absence of polymer; whereas the presence of polymer reduced the separation speed of N1691 and resulted in higher OIW by preventing the coalescence of oil droplets. E12085A yielded better performance in terms of separation efficiency and water quality for emulsion at 50% WC, irrespective of the polymer; while the disadvantage of E12085A lied in the slowest separation when the polymer was absent.

In spite of the complicated interactions involved in the system of heavy oil, produced water, polymer, and demulsifier, the compound emulsion breaker, E12+E18, was found to be the most effective demulsifier which could be potentially applied to the ANS polymer flooding pilot. Implicitly, we consider the satisfactory demulsification performance at intricate operational conditions as one of the key supporting contributors to the primary objective of improving heavy oil recovery by polymer flooding.

As a novelty in this study, the radar chart, which is composed of demulsification efficiency, separation speed, water clarity, and optimized dosage, has been proposed to evaluate the performance of different types of demulsifiers in an intuitive but comprehensive way. This evaluation method establishes an excellent example for future similar studies. More importantly, the findings of this study have implications for the treatment of produced fluid from the first ever polymer flooding pilot on ANS.

## Acknowledgments

## Nomenclature

$C_a$ = the allowed oil content in water, ppm [µg/g]
$C_m$ = the measured oil content in water after 24 h, ppm [µg/g]
$C_{max}$ = the maximum dosage of emulsion breaker used in the experiment, ppm [µg/g]
$d$ = the diameter of the dispersed droplets, m
$g$ = acceleration of gravity, m/s$^2$
OIW = oil content in water, ppm [µg/g]

ppm = parts per million, [mg/L] or [μg/g]

$V_s$ = the separated water volume at 4 h, mL

$V_t$ = the total water volume, mL

WC = water cut in percentage

TDS = total dissolved solid, ppm [μg/g]

$T_m$ = the measurement time for separation, h

$T_e$ = the time required to reach the separation equilibrium, h

$\eta$ = the viscosity of the continuous phase, Pa· s [kg/(m·s)]

$v$ = the sedimentation or creaming rate, m/s

$\Delta\rho$ = the density difference between oil and water, kg/m$^3$

# References

Al Kalbani, H., et al. "Impact on crude dehydration due to back production of polymer." *SPE EOR* Conference at Oil and Gas West Asia. Society of Petroleum Engineers, 2014.

Al-Kayiem, Hussain H., and Javed A. Khan. "Evaluation of Alkali/Surfactant/Polymer Flooding on Separation and Stabilization of Water/Oil Emulsion by Statistical Modeling." *Energy & Fuels* 31.9 (2017): 9290-9301.

Argillier, J. Francois, et al. "Methodological Approach for Analyzing the Impact of Chemical EOR on Surface Processes." *SPE International Symposium on Oilfield Chemistry*. Society of Petroleum Engineers, 2013.

Argillier, J-F., et al. "Influence of chemical EOR on topside produced water management." *SPE Improved Oil Recovery Symposium*. Society of Petroleum Engineers, 2014.

Chen, Hua-xing, et al. "Oil–water separation property of polymer-contained wastewater from polymer-flooding oilfields in Bohai Bay, China." *Environmental technology* 36.11 (2015): 1373-1380.

Chen, Hua-xing, et al. "Effect of partially hydrolyzed polyacrylamide on emulsification stability of wastewater produced from polymer flooding." *Journal of Petroleum Science and Engineering* 133 (2015): 431-439.

Dalmazzone, Christine, Christine Noïk, and Jean-François Argillier. "Impact of chemical enhanced oil recovery on the separation of diluted heavy oil emulsions." *Energy & Fuels* 26.6 (2012): 3462-3469.

Deng, Shubo, et al. "Produced water from polymer flooding process in crude oil extraction: characterization and treatment by a novel crossflow oil–water separator." *Separation and Purification Technology* 29.3 (2002): 207-216.

Duan, Ming, et al. "Treatment of wastewater produced from polymer flooding using polyoxyalkylated polyethyleneimine." *Separation and Purification Technology* 133 (2014): 160-167.

Fang, Shenwen, et al. "Treatment of produced liquid from polymer flooding by using cationic surfactant." *Separation Science and Technology* 49.3 (2014): 432-437.

Feng, Jiachao, Zhao Jiansen, and Chan Shaobing. "Water/Oil Separation Characteristics of Daqing Oilfield Polymer Flooding Production Fluid." *SPE Annual Technical Conference and Exhibition*. Society of Petroleum Engineers, 1994.

Gao, Changhong. "Viscosity of partially hydrolyzed polyacrylamide under shearing and heat." *Journal of Petroleum Exploration and Production Technology* 3.3 (2013): 203-206.

Hirasaki, George J., et al. "Separation of produced emulsions from surfactant enhanced oil recovery processes." Energy & fuels 25.2 (2010): 555-561.

Kang, Wanli, et al. "Stability mechanism of W/O crude oil emulsion stabilized by polymer and surfactant." *Colloids and surfaces A: Physicochemical and engineering aspects* 384.1-3 (2011): 555-560.

Kang, Wanli, et al. " Demulsification performance, behavior and mechanism of different demulsifiers on the light crude oil emulsions." Colloids and Surfaces A: Physicochemical and Engineering Aspects 545 (2018): 197-204.

Li, Feng, et al. "Effect of laponite particles on the emulsion stability of produced water from polymer flooding." *Journal of Petroleum Science and Engineering* 124 (2014): 155-160.

Li, Zhongwei, et al. "Synthesis and properties of novel branched polyether as demulsifiers for polymer flooding." *Colloid and Polymer Science* 294.12 (2016): 1943-195818.

Lin, Meiqin, et al. "Influence of polymers on the stability of Gudao crude oil emulsions." *Petroleum Science* 5.2 (2008): 159-162.

Liu, He, et al. "Successful Practices and Development of Polymer Flooding in Daqing Oilfield." *Asia Pacific Oil and Gas Conference & Exhibition*. Society of Petroleum Engineers, 2009.

Liu, S., Zhao, X., Dong, X., Miao, B., & Du, W. (2007). Experimental research on treatment of produced water from a polymer-flooding process using a double-cone air-sparged hydrocyclone. *SPE Projects, Facilities & Construction*, 2(03), 1-5. doi:10.2118/95343-PA

Liu, Yang, et al. "ASP flooding produced water management: evaluation, disposal and reuse." *SPE Middle East Health, Safety, Environment & Sustainable Development Conference and Exhibition*. Society of Petroleum

Engineers, 2014.

Liu, Yang, et al. "Study on emulsification behavior and optimized separation technology of high concentration polymer flooding produced liquid in Daqing Oilfield." *SPE Middle East Oil & Gas Show and Conference*. Society of Petroleum Engineers, 2015.

Lv, G., Wang, F., Cai, W., & Zhang, X. (2014). Characterization of the addition of lipophilic Span 80 to the hydrophilic Tween 80-stabilized emulsions. *Colloids and Surfaces A: Physicochemical and Engineering Aspects, 447*, 8-13.

Manning, Francis S., and Richard E. Thompson. *Oilfield processing of petroleum: Crude oil*. Vol. 2. PennWell books, 1995.

Nguyen, Duy Thai, and Nick Sadeghi. "Selection of the right demulsifier for chemical enhanced oil recovery." SPE International Symposium on Oilfield Chemistry. Society of Petroleum Engineers, 2011.

Opawale, A. O. 'Oilfield Emulsion Control: A major issue during; A major issue during heavy crude oil production. Society of Petroleum Engineers. doi:10.2118/128352-MS

Preziosi, Valentina, et al. "Phase inversion emulsification." *CHEMICAL ENGINEERING* 32 (2013).

Sjöblom, Johan, et al. "Influence of HPAM on W/O emulsion separation properties." *Journal of Dispersion Science and Technology* 38.2 (2017): 206-215.

Targac, G. W., et al. "Unlocking the value in West Sak heavy oil." *SPE International Thermal Operations and Heavy Oil Symposium*. Society of Petroleum Engineers, 2005.

Wang, Dongmei, et al. "Review of practical experience by polymer flooding at Daqing." *SPE Reservoir Evaluation & Engineering* 12.03 (2009): 470-476. doi:10.2118/114342-PA

Wang, Yan, et al. "Effects of Na–montmorillonite particles on the emulsification stability of polymer flooding produced water." *Colloids and Surfaces A: Physicochemical and Engineering Aspects* 410 (2012): 125-129.

Wu, Di, et al. "Rheology and stability of IOR produced liquid in Daqing oilfield." *SPE Asia Pacific Improved Oil Recovery Conference*. Society of Petroleum Engineers, 1999.

Wylde, Jonathan James, Jubal Lincoln Slayer, and Victor Barbu. "Polymeric and Alkali-Surfactant Polymer Enhanced oil recovery chemical treatment: chemistry and strategies required after breakthrough into the process." *SPE International Symposium on Oilfield Chemistry*. Society of Petroleum Engineers, 2013.

Zhang, Jian, et al. "Synthesis and performances for treating oily wastewater produced from polymer flooding of new demulsifiers based on polyoxyalkylated N, N-dimethylethanolamine." *Polymers for Advanced Technologies* 26.2 (2015): 190-197.

Zheng, F. F., P. Quiroga, and G. Sams. "Challenges in Processing Produced Emulsion from Chemical Enhanced Oil Recovery-Polymer Flood Using Polyacrylamide. Paper SPE 144322 presented at the SPE Enhanced Oil Recovery Conference, Kuala Lumpur, 19–21 July." (2011).