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Demulsification of Water in Iraqi Crude Oil Emulsion

Zenah Hani Maddah
College of Engineering – University of Baghdad
Student
Baghdad, Iraq
z_1991_h@yahoo.com

Tariq Mohammed Naife
College of Engineering – University of Baghdad
Lecture
Baghdad, Iraq
tariqaltaee@yahoo.com

ABSTRACT

Formation of emulsions during oil production is a costly problem, and decreased water content in emulsions leads to increases productivity and reduces the potential for pipeline corrosion and equipment used. The chemical demulsification process of crude oil emulsions is one of the methods used for reducing water content. The demulsifier presence causes the film layer between water droplets and the crude oil emulsion that to become unstable, leading to the accelerated of water coalescence. This research was performed to study the performance of a chemical demulsifier Chimec2439 (commercial) a blend of non-ionic oil-soluble surfactants. The crude oils used in these experiments were Basrah and Kirkuk Iraqi crude oil. These experimental work were done using different water to oil ratio. The study investigated the factors that have a role in demulsification processes such as the concentration of demulsifier, water content, salinity, pH, and asphaltene content. The results showed in measuring the droplet size distribution, in *Basrah* crude oil, that the average water droplet size was between (5.5–7.5) µm in the water content 25% while was between (3.3-4) µm in the water content 7%. The average water droplet size depends on the water content, and droplet size reduced when the water content of emulsion was less than 25%. In Kirkuk crude oil, in water content of 7%, it was between (4.5-6) µm, while in 20%, it was between (4-8) µm, and in 25% it was between (5-8.8) µm. It was found that the rate of separation increases with increasing concentration of demulsifier. For Basrah crude oil at 400ppm the separation was 83%, and for Kirkuk, crude oil was 88%. The separation of water efficiency was increased with increased water content and salt content. In Basrah crude oil, the separation rate was 84% at a dose of salt of 3% (30000) ppm and at zero% of salt, the separation was70.7%. In Kirkuk crude oil, the separation rate was equal 86.2% at a dose of salt equal 3% (30000) ppm, and at zero% of salt, the separation 80%.

Keywords: Crude oil, Demulsification, Demulsifiers, Water-in-oil emulsion.

كسر استحلاب المياه في مستحلب النفط الخام العراقي

الخلاصة

ان تشكيل المستحلبات خلال إنتاج النفط هو مشكلة مكلفة، ويؤدي انخفاض محتوى الماء في مستحلبات الزيت الخام إلى زيادة الإنتاجية وتقليل احتمال تآكل خطوط الأنابيب والمعدات المستخدمة. يعتبر كسر الاستحلاب الكيميائي لمستحلبات النفط الخام إحدى طرق لتقليل المحتوى المائي. وجود المستحلب يسبب طبقة رقيقة بين مستحلب النفط الخام وقطرات الماء لتصبح غير مستقرة مما يؤدي إلى تسارع اندماج قطرات الماء. تم إجراء هذا البحث لدراسة أداء المستحلب الكيميائي Chimec2439

*Corresponding author
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(تجاري) وهو مزيج من مواد سطحية قابلة للذوبان وغير أيونية. كانت عينتا النفط الخام العراقية المستخدمة في هذه التجارب هي نفط خام البصرة وكركوك. وقد تمت هذه التجارب باستخدام نسب مختلفة من المياه إلى النفط. تناولت الدراسة العوامل التي لها دور على عملية الاستحلاب مثل تركيز الكاسر ودرجة الحموضة والملوحة ومحتوى الماء ومحتوى الأسفلت. أظهرت النتائج في قياس حجم القطيرات في نفط خام البصرة، أن متوسط حجم قطيرات الماء كان بين (5.5 - 7.5) ميكروميتر في محتوى الماء 25٪، بينما كان بين (3.3-4) ميكروميتر في محتوى الماء 7٪. انخفض متوسط حجم قطرة الماء بشكل ملحوظ عندما كان محتوى الماء للمستحلب أقل من 25 ٪. في مستحلب نفط خام كركوك عندما كان في محتوى الماء 7٪ كان بين (4.5-6) ميكرومتر، وفي 20٪ كان بين (4-8) ميكرون، وفي 25٪ كان بين (5-8.8) ميكرون. وقد وجد أن معدل الفصل يزداد بزيادة تركيز المستحلب، في نفط خام البصرة عند تركيز 400 جزء في المليون كان الفصل 83٪، وفي نفط خام كركوك كان اعلى فصل 88٪. وأيضا زاد فصل المياه مع زيادة محتوى الماء ومحتوى الملح، في نفط البصرة كان معدل الفصل 84٪ عند جرعة من الملح يعادل 3٪ (30000) جزء في المليون، وعند صفر٪ من الملح كان الفصل 70.7٪، في نفط كركوك الخام كان معدل الفصل 86.2٪ عند جرعة الملح يساوي 3 ٪ (30000) جزء في المليون، عند صفر ٪ من الملح كان الفصل 80 ٪.
الكلمات الرئيسية:النفط الخام، كسر الاستحلاب، كواسر الاستحلاب، مستحلب المياه في النفط.

1. INTRODUCTION

Crude oil emulsion is one of the important challenges in the petroleum industry because of its harmful damages in all production stages, which need additional costs to repair, **Al-Sharrah, et al., 2010**. Emulsions are naturally formed through the production of crude oil and the presence of these emulsions may have an impact on the production of crude oil and facilities during the drilling, transportation, production, and processing crude oils and in many locations, such as, hydrocarbon reservoirs, facilities, refineries and transportation systems, **Fakhru'l-Razi, et al., 2009**. In general, those emulsions form from flowing through valves, chokes, or pumps and are stable due to the presence of natural surfactants existing in the crude oil phase. In each case, the presence and nature of emulsion can determine both the economic and technical success of industrial process concerned, **Baker, 2018**. Knowledge of petroleum emulsions and their compounds and characteristics is necessary to control processes and improve them at all stages of oil production. The emulsion is a heterogeneous system, containing immiscible liquid intimately dispersed in another form of droplets, generally ranging between (0.1 - 20) microns, and it is stabilized by an emulsifying agent, asphaltenes and resins. The dispersed droplets are called the internal phase, and the liquid surrounding the dispersed droplets are known as the continuous phase or the external. The emulsifying agent separates the dispersed droplets from the external phase, **Kenneth, 1988.** It is known that the viscosity of water in oil emulsions (W/O) can be increased strongly by increasing the volume of water fraction and by decreasing the temperature. Effective separation of water from crude oil is necessary to ensure separation of water at the lowest cost. Because of the technical problems of water-in-oil emulsion, the emulsion breaking process which is known demulsification becomes very crucial and important to get oil with high quality and with minimum cost in all production and refinery stages **Majeed, 2016**. The water content must be less than 1%, and typically 0.3% - 0.5% because increasing water content in oil leads to rising transportation costs, **Sjöblom, et al., 2003**.

When the emulsion (W/O) is formed it stabilizes during the production. The emulsion stability is ranging from many minutes to years, depending on the nature and properties of the crude oil, **Bhardwaj** and **Hartland, 1998**. Where water-in-crude-oil emulsion formation treatments are required breaking the emulsion and accelerate the separation of the water. In addition to heating, chemical treatment with demulsifiers (surface active agents) is the most current process used for breaking emulsions, **Mohammed, et al., 1994.** Many separation techniques were used during past decades like mechanical, heating, electrical, and chemical demulsification. Every method has merits and defects. Until now, no method could reach complete destabilization without a combination with another one. However, the chemical demulsification is a crucial method for W/O emulsion treating, **Kim et al., 1996**.

A chemical method for dissolving crude oil emulsions depends on the addition of surfactants (demulsifiers) which breakdown the film of hydrophobic emulsifying agents, and allow to the coalescence of the water droplets. There are cationic, anionic, and nonionic surfactants that have used as demulsifier(surfactant), **Selvarajan, et al., 2001**. The performance of the chemical demulsifying is dependent on the suitable concentration of a properly chosen chemical to be added to the water in oil emulsion, by mixing of the demulsifier with the emulsion, **Staiss et al., 1991.**

Therefore, the main aims of the present work study the effect of water content, salt content, asphaltene content, and the dose of demulsifier, of different crude oils for Iraqi oil fields.

2. EXPERIMENTAL WORK

2.1 Materials

Materials used in this work can be divided into different groups as listed below:

2.2.1 Crude oil

The present work was carried out on selected two types of crude oil (Basrah, Kirkuk). They were provided from Al-Dura refinery in Baghdad. The physical properties of crude oil are sgown in **Table 1**. The physical properties were conducted in Daura refinery.

Table 1. Physical properties of crude oils.

Property	Basrah Crude Oil	Kirkuk Crude Oil
Sp. Gr. At 15.6°C	0.8681	0.8509
Density at 15.6˚C	0.8676	0.8504
API	26	31
Salt content (%wt.)	.0015	0.0009
Asphaltene (%wt.)	2.1	1.29
Water and Sediment content (%vol.)	0.05	Traces
Kin.Viscosity (Cst) at 15° C	21.7	11.6
Sulfur content % wt	3.33	2.33

2.2-2 Chemical Demulsifier

Chemical demulsifier Chimec2439 (commercial), which is a blend of non-ionic oil-soluble surfactants and the physical properties given from (CHIMEC S.P.A, Italy) Company, are given in **Table 2**.

Table 2. Physical properties of Chimec2439 (CHIMEC S.P. Company, Italy).

Appearance	Brown liquid
Sp.Gr.at 20 ºC	0.94±0.02
Viscosity at 20 ºC (cp)	<50
Pour point ºC	<-30 ºC
Flash Point ºC	>62 ºC

3. Experimental Procedure

3.1 Emulsion Preparation

100ml of crude oil (Basrah, Kirkuk) was weighed, then different initial water ratio (7%, 20%, 25%), with (3% wt. NaCl) were added to the different types of crude oil at room temperature. And finally, emulsification was performed using a mixer at 2000 rpm for 90 minutes to obtain a stable W/O emulsion.

The result of emulsions prepared in this way was stable for months without separation.

3.2 Demulsification Process

The surfactant (Chimec2439) with different concentrations (200,300,400) ppm was added to the emulsion at different W/O and then it was put in a separation funnel and shaken for three minutes until the surfactant spread equally to surround each water's drops and then to perform on breaking the film that surrounds water's drop. After twelve minutes, water's drops started to separate from the oil. The step that follows was calculating the water's amount separated from the oil each half an hour. Finally, the water separation percentage was calculated to study some factors affecting the process of demulsification.

The total water removal percentage (W %) was calculated according to Eq. 1:

$$Separated\ Water(\%) = \frac{Separated\ water\ volume}{Initial\ water\ volume} x\ 100 \qquad \textbf{(1)}$$

Measurements

Stability of Prepared Emulsion

The stability of the emulsions prepared was measured in two ways. The first test was the aging test, and the second test was droplets size distribution (DSD) measurement of droplets using a microscope.

Effect of Demulsifier Dose on Water Separation Efficiency

In these experiments, the effect of adding Chimec2439 on water separation efficiency with periods for the two crude oil emulsions was studied.

Effect of water content

Study the effect of different water content ratio (7%, 20%, and 25%) for the two crude oil (Basrah, Kirkuk) was performed.

Effect of Salt Content on Water Separation

The different salt contents (0%, 1%, 2%, and 3%) were examined to study their effect on water separation efficiency.

4. RESULTS AND DISCUSSION

4.1 Stability of Prepared Emulsion

Fig. 1 shows examples of microscopic images of emulsion for the different ratio of water used for the droplet size distribution (DSD) measurements for two types of crude oil Iraqi.

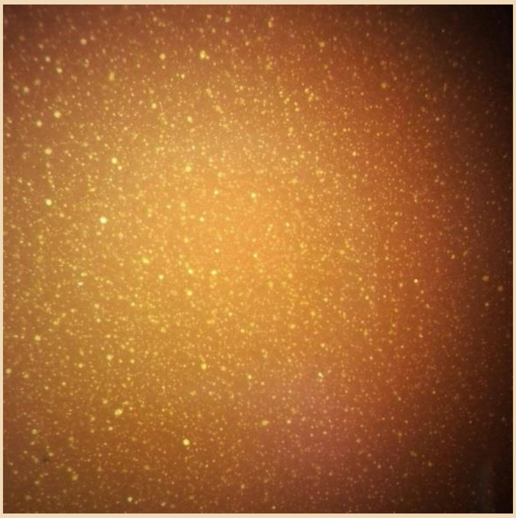
On the other hand**, Table 3.** shows the mean water droplet size or diameter in µm versus water content% of the emulsion. The results pointed to that the drop size distribution is dependent on the water content in the emulsion، and the average water droplet size reduced from 7 µm at the water content of 25% to a diameter of 3.3 µm at the water content of 7%. It was noted that when the water content of emulsion was less than 25%, the average water droplet size decreased significantly.

Table 3. Drop size distribution of emulsions droplets.

Type of Crude oil	7% emulsion droplet size (micron)	20% emulsion droplet size (micron)	25% emulsion droplet size (micron)
Basrah	3.3 - 4	4 -7.2	5.5 – 7.5
Kirkuk	4.5 - 6	4 - 8	5 - 8.8

[A]Basrah crude oil

[B]W/O Emulsion 7%vol water content



[C]W/O Emulsion 20%vol water content

[D]W/O Emulsion 25%vol water content

Figure 1. Droplets size distribution (DSD) of Basrah crude oil emulsions
[A]Basrah crude oil. **[B]**W/O Emulsion 7%vol water content.
[C]W/O Emulsion 20%vol water content. **[D]**W/O Emulsion 25%vol water content.

Figure 2. shows a typical droplet sizes distributions for water-in-oil emulsion7, droplet sizes distribution is normally represented by a histogram or by a distribution function of some sort.

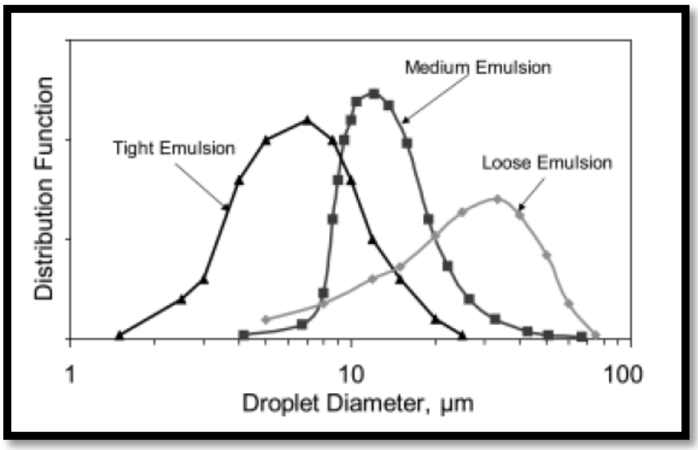
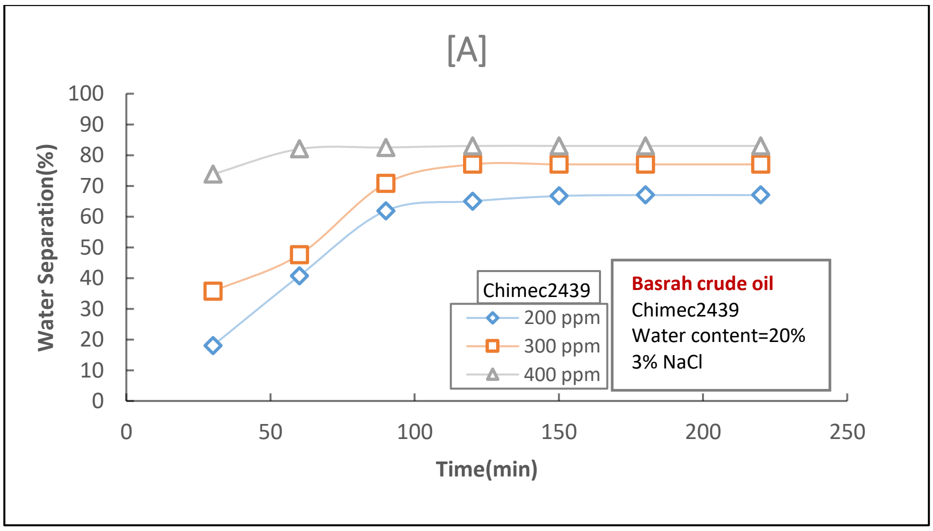


Figure 2. Emulsion Stability vs. drop size.

4.2 Effect of Demulsifier Dose on Water Separation Efficiency

The effects of water separation using different concentration of Chimec2439 (200, 300, and 400) ppm for water content 20% for Basarh crude oil is shown in **Figure 3[A].** From this figure, it was noted that the separation of water was 67%, 77%, and 83% respectively. In **Figure 3[B],** the result is also close to the crude oil Kirkuk. Using the highest concentration of Chimec2439(400 ppm) gave the highest percentage of separation of 88%. The demulsifier molecules perform a complete coverage of the water/oil interface dragging the asphaltenes away from the interface. As a result, the protecting film present around the dispersed water droplets thins, then it ruptures, and coalescence eventuates.



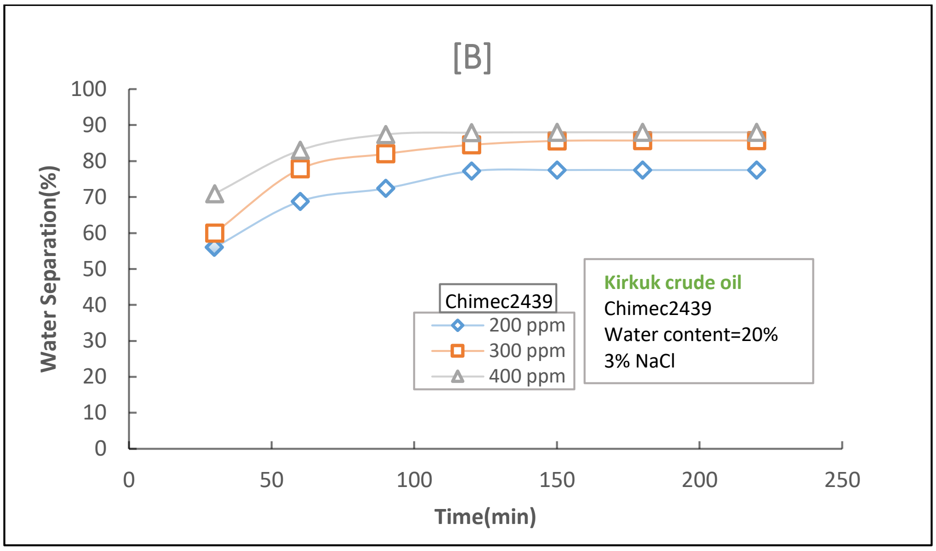
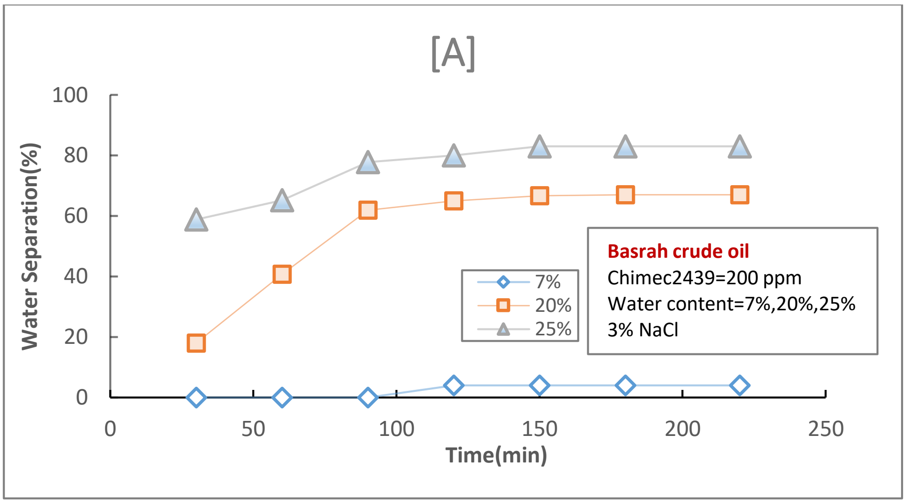


Figure 3. Effect of demulsifier dose(Chimec2439) for 20% water content on separation efficiency for **[A]:** Basrah crude oil. **[B]:** Kirkuk crude oil.

4.3 Effect of water content

Figure 4 [A] and **[B]** show the results of water content. Increasing water content increased the water separation with time for the two types of crude oil. In Basrah crude oil, when the demulsifier Chimec2439 was 200 ppm, the results showed that the highest water separation rate of 83% was at water content equal 25%, then 67% when 20% and the lowest water separation rate at water content 7%.

In the emulsion containing a larger amount of water affects the efficiency of the coalescence during the demulsification process, reducing the distance between droplets in the sample, this distance can be severely reduced with increasing water content in the emulsion, increasing the probability of collisions between droplets.



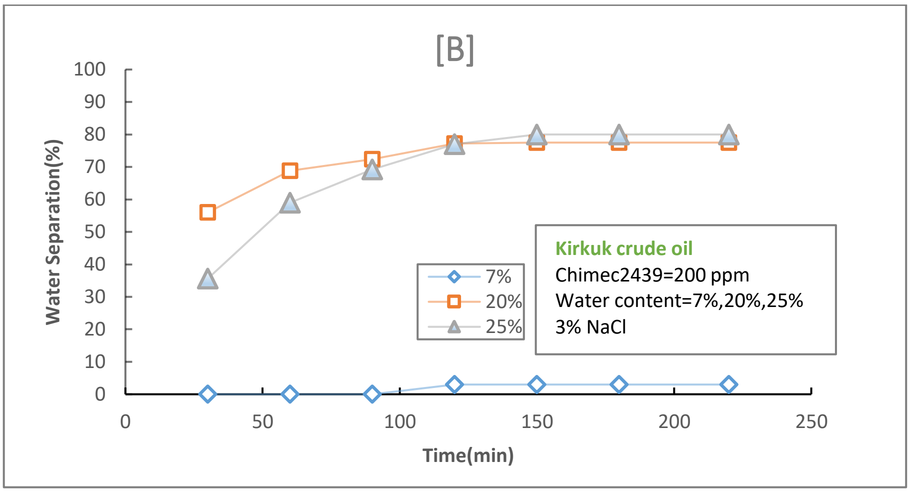
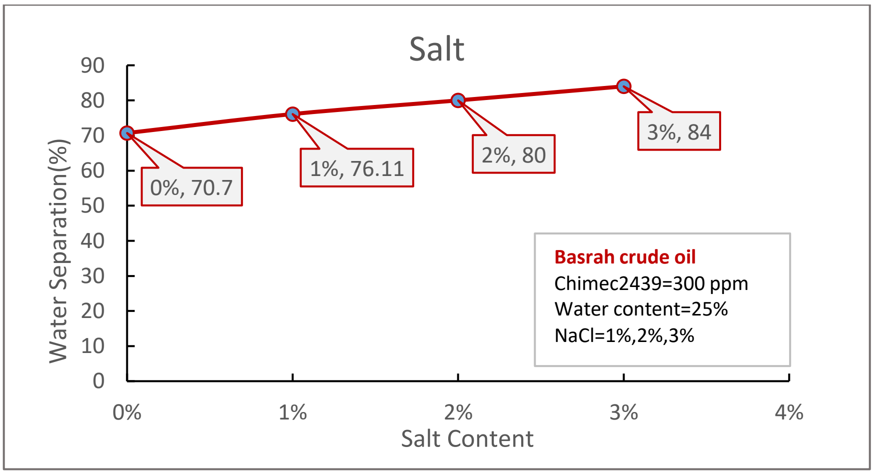


Figure 4. Effect of water content on separation efficiency when Chimec2439=200 ppm For**[A]** Basrah crude oil; **[B]** Kirkuk crude oil.

4.4 Effect of Salt Content on Water Separation

Four samples of different emulsions of salt contents (3%, 2%, 1%, zero) were prepared from crude oil. The samples have an equal concentration of (300) ppm of Chimec2439 as a surfactant. **Figure 5**. shows the addition of NaCl (sodium chloride) to the water-in-oil emulsion that was prepared. The presence of inorganic cations affects the stability of the emulsion; thus, leads to the better water separation at the highest concentration of sodium chloride, which was achieved at 3% (separated 84% of the total water) compared with the empty with no sodium chloride (70.7% of total water separation). The phenomenon can be illustrated through the clear variation in behavior of the interfacial film, **Binks,1993**.

This indicated that as the brine concentration increases, the W/O emulsion droplets would be larger due to the higher rate of aggregation and coalescence, and the emulsion stability decreases. Particle-stabilized emulsions usually have high coalescence stability, likely what might occur will be destabilization by agglomeration. This is shown in **Fig. (6)**.



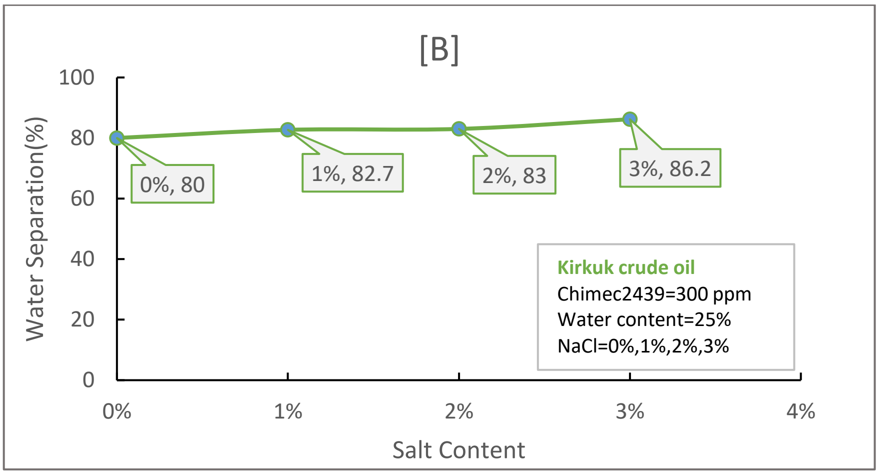


Figure 5. Effects of salt content on water separation using various concentrations of NaCl. **[A]** Basrah crude oil, **[B]** Kirkuk crude oil.

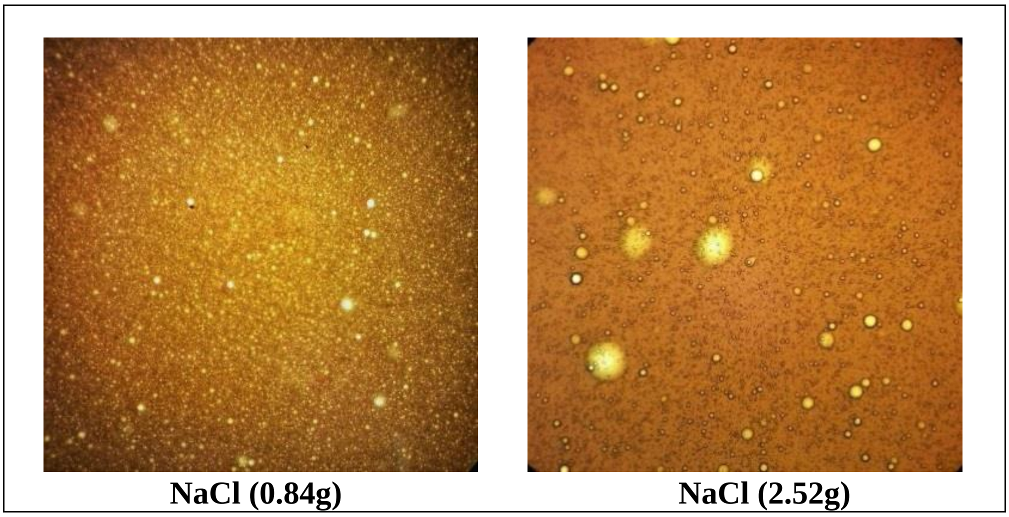


Figure 6. Droplets size distribution W/O Emulsion stability at different brine salinities.

CONCLUSIONS

The results confirm that the droplets size distribution is dependent on the water content in the water-in-oil emulsion. In this tests, for samples of different water content, the average water droplet size reduced in diameter from 7 µm at the W.C. of 25% to a diameter equal 3.3 µm at the W.C. of 7%.

Water separation efficiency increases with increasing dose of demulsifiers.

It is shown from results that increasing water content increases the water separation with up to 220 min two types of crude oil.

It can be observed that water separation efficiency increases with increasing salt content, which could be due to the destroying of the double charge layers by the NaCl.

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