**THE EFFECT OF WATER CONTENT, pH, SALINITY
AND TEMPERATURE ON THE STABILITY AND SURFACE
TENSION OF RUSSIAN URALS CRUDE OIL EMULSION**

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Abstract: The effect of pH, salinity and temperature on stability and surface tension of Russian Urals crude oil-water emulsions were investigated. Emulsions were prepared by mixing distilled water and Russian crude oil (1/3) volume ratio with three different buffered solutions of pH 2.00, 4.00 and 7.00. The stability of the emulsions and their surface tension were measured. Five aqueous solutions of NaCl (concentrations 0.570, 1.407, 1.711, 3.080 and 4.106 mol/l, respectively) were mixed with the crude oil and volume fraction 1/4 (water/oil) to make emulsions, another five aqueous solutions for the crude oil (1.50g, 2.50g, 3.50g, 4.50g and 5.50g of NaCl) were prepared. Surface tension of the emulsions and that of the crude oil and stability of emulsions were measured. In order to avoid distillation of the light components from our close measuring vessel, temperatures 20.01, 25.05, 29.01, 31.50 and 35.05 °C were applied. Surface tension of crude oil and that of an emulsion of 3/1 (oil/water) volume fraction were measured. Surface tensions of crude oil, and emulsion decrease as the temperature increases, but the surface tension of crude oil and emulsion increased as the salinity (concentration NaCl) as well as the pH value in the range (from 2.00 to 7.00) increases. On the other hand, the results of emulsions stability show that the stability of emulsions decreases both with increasing temperature and (NaCl) salt concentration, also, as the water fraction increases, the emulsion stability decreases. For pH, it was found that there is unstable emulsion formed at pH=7.00 and a very stable emulsion formed at pH = 2.00.

1. Introduction

Nowadays, separation of water-in-crude oil emulsions is a great challenge and considered as one of the important studies which, have long been of interest not only for engineers but for scientists as well [1, 2]. Many problems associated with lifting and crude oil production are due to the presence of water-in-crude oil (W/O) emulsion, which usually causes severe problems like the corrosion of equipment systems (reactors, columns, mixer, balloon, ...), decreasing the activity of the catalyst and other

environmental problems [3 – 6]. During the last sixteen years, many investigations have been under-taken to improve the resolution of these emulsions through, the combination of thermal and chemical treatments in order to provide high efficiency during the processing [5].

The formation of water-oil emulsion occurs during the refining stage of oil production [5]. Thus, it becomes necessary to separate water from crude oils due to economic and operation condition reasons [5, 6]. Water/crude oil emulsions have to be broken down in order to reduce the highest amount of water content in crude oils (demulsified) [6].

Therefore, it is necessary to determine and know the characteristics of the crude oil emulsion for a better understanding of the mechanisms responsible for the stabilization of these emulsions and to achieve high performance for the phase separation process of these emulsions [5 – 7]. Much attention is devoted to the stabilization mechanism and the factors that affect this process [6, 8].

It is believed that, the presence of surface active species which exist naturally in crude oils might be one of the main reasons for the stability of water-in-crude oil emulsions. Among these surface active species can be cited resins, asphaltenes and fatty acids [5, 8]. These substances can form an interfacial film, surrounding water droplets. The accumulation of these substances at the water-oil interface could inhibit the coalescing of the droplets and hinder the separation of the two phases [4, 5, 9]. It is common sense that asphaltenes are one of the major surfactants which stabilize the emulsion and most of the time the resins and fatty acids, could not produce high stable emulsions alone [8, 10]. Therefore, in many cases and in the presence of the asphaltene, they may connect to the asphaltene molecules which would affect emulsion stability [10]. Basically, the formation of the film depends on the concentration of resin, aromatic rings and the polar groups present in crude oil [11] as well as the inorganic solids which improve emulsion stability, due to their abilities to constitute films around the droplets and prevent them from touching each other [12, 13]. It is known that, the asphaltenes are the most polar fraction of the crude oils due to their structure which allows them to act as natural emulsifiers [8, 14, 15] through, the aggregation of many other molecules [16].

Usually, the interfacial film created between the two phases is not monomolecular but it is formed as a result of asphaltene droplets accumulation [8]. For that reason, removing the asphaltenes on flocculation level of the crude oil might improve the stability of water-in-oil emulsion [17]. The interfacial films have a resistance against deformation and compression which hinder droplets to touch each other and prevent coalescence [5, 18].

Based on knowledge of the interfacial film, there are many factors that can affect the emulsion stability; including, water-pH, temperature, droplet size and other chemical additives [8, 19 – 21]. Several authors point out the fact that, as the crude oil origin change, a multitude of the factors affecting the stability of crude oil/water emulsions effects show different behaviors [16, 22 – 24]. For example, the study which was conducted at Venezuelan crude oil/water interface shows that the pH has great influence on the asphaltenes interfacial properties and that at high or low pH [25]. The last study which was about the effects of water content, pH, temperature and salinity on the stability of crude oil emulsions under microwave method discovered that the emulsions which contain high water contents, achieved a high-performance rate of demulsification process but, this does not occur at high salt and pH contents simultaneously [8, 21].

During oil production, demulsification is considered as an important process in which the crude oil emulsion is broken down into oil and water phases. Generally, the demulsification process occurs in three steps that would affect the rate of breakdown processes in emulsions. These are flocculation, coalescence, and phase separation respectively [8, 26, 27]. The flocculation of water droplets of the internal phase

flocculate in order to form large groups of clusters, but these droplets still do not achieve coalescence. Next step is coalescence in which two or more clusters fuse together to form very large droplets where the interface is ruptured. During phase separation, large drops sink due to the gravity which leads to the breakdown of the emulsion [8, 27, 28].

Several methods are used to determine the emulsion stability. The standard method of water content measurement is Karl Fischer titration [5]. Other methods like bottle test [8, 33] distillation, microwave radiation, chemicals additives, centrifugation [29, 30, 37] and even optical microscopy [8, 28, 31, 34] are used. Not mentioning that the accuracy of distillation and optical microscopy is dubious; all these methods give a value separated from the rest of the variables while surface tension varies continuously with them. For that reason, a bottle and surface tension methods have been used for this work. The bottle test is the simplest and most common method used for lab-scale where varying amounts of chemical compounds are added to several tubes that have the same amounts of emulsion system [32]. A lot of studies have been taken recently regarding the use of bottle tests, in particular, where electrorheology and bottle tests show a similar result with optical microscopy when the effect of salinity on water-in-crude-oil emulsion was studied. They all detect that emulsion is much more stable at the lower ionic force of the aqueous phase [33, 34].

The aim of this work conducted is to investigate the effect of water content, pH, salinity and temperature on water-in-oil emulsion stability and its surface tension.

2. Experimental

2.1. Materials.

The Russian Urals crude oil was used in this study. Urals oil is a mix of high-sulfur crude oil from Urals-Volga region and light sweet crudes from West Siberia. The general characterizations of Russian Urals oil are summarized in Table 1 as determined by the laboratory of the refinery company. All the chemical substances used in this study were produced by Sigma Company with purity percentage (> 98 %). OriginPro software was used to analyze and convert the data into graphs in addition to the Microsoft Excel for the calculation of the averages and standard deviation.

2.2. Preparation of the emulsion.

Russian Urals crude oil and demineralized distilled water were mixed together to make emulsions with a known volume fraction. Emulsions were made by mechanical agitation: an electric mixer (Ultra Turrax T 25 basic, IKAWerke) with 2000 rpm at room temperature. During the mixing, a cylindrical metal vessel (diameter 55 mm, height 135 mm) was used in order to hold the samples. Water or an aqueous solution of given salinity or buffered pH and crude oil were mixed thoroughly for 15 minutes. Emulsions were separated with the aid of a separating funnel.

Table 1

General characteristics of Russian Urals crude oil

Characteristics	Value
Density (20°C gm/cm ³)	0.870
Salt content (NaCl) mg/l	17.3
Total acid number (mg KOH/1g)	0.39
Water content, %	0.1
Paraffin content, %	6

2.2.1. Effect of water content.

Water content in w/o emulsion has great influence on the emulsion stability. Asphaltene and resin are of the factors that affect the stability of crude oil emulsions, but the water content makes the emulsion system much more complicated. It is important to understand that, the external pressure of the oil phase exceeds the internal pressure of water droplets when an extremely small amount of water content is remaining in the system [35 – 37]. This would enhance the emulsion stability [36]. In order to investigate the effect of water content, five samples 55/45, 65/35, 75/25, 85/15 and 90/10 oil/water volume fractions were mixed and stability was investigated. Three parallel measurements of stability test were performed for each sample.

2.2.2. Effect of pH.

Emulsions (3/1 v/v) (oil-water) were made with three different buffered solutions of pH 2.00, 4.00 and 7.00(± 0.01 at 25 $^{\circ}\text{C}$). pH meter – Model IN-112 device was used to check and control the pH values. Stability of the emulsions and their surface tensions were measured. For the surface tension, six parallel measurements were required in order to increase the resolution of the results and decrease the standard deviation of the measurements. On the other hand, three parallel measurements of stability test were carried out for each pH sample.

2.2.3. Effect of salt concentration.

Balance type sartorius balance Cubis was used to measure the exact masses of sodium chloride (0.50g, 1.00g, 1.50g, 2.70g and 3.60g) and then five aqueous solutions of NaCl (concentrations 0.570, 1.407, 1.711, 3.080 and 4.106 mol/l, respectively) were mixed with Russian Urals crude oil with volume fraction 15 ml /45 ml (water/oil) to make emulsions. Another five aqueous solutions of the crude oil (1.50g, 2.50g, 3.50g, 4.50g and 5.50g) were prepared. Surface tension of the emulsions, that of the crude oil and stability of emulsions were measured.

2.2.4. Effect of temperature.

One of the difficulties of this measurement is the control of the temperature. For that reason, thermostat machine type; Huber GmbH. MPC 1O4 was used to heat up the samples and control temperatures simultaneously. In order to avoid distillation of the light components from our close measuring vessel, temperatures 20.01, 25.05, 29.01, 31.50 and 35.05 $^{\circ}\text{C}$ were respectively applied. Surface tension of crude oil and that of an emulsion of 45/15 (oil/water) volume fraction were measured.

2.3. Determination of interfacial tension.

Du Noüy ring and Wilhelmy plate are the most commonly used methods for the determination of interfacial tension. Contrary to the study [6] which used Du Noüy ring test, the surface tension of solution was measured according to ASTM standard method with Wilhelmy balance made by Bioforce. A thoroughly cleaned platinum plate of known weight (19.80 $\times$ 9.81 $\times$ 0.19 mm) is touched to the surface of the liquid, and due to surface tension, its apparent weight changes. The balance which is an electromagnetic one; needs a warming up period of one hour and calibration with two wires of known weight, and, in addition, a calibrating measurement with clean water is needed. Six parallel measurements were performed for each sample and then the average was calculated.

2.4. Determination of stability.

Emulsion stability was characterized by separation time in a tube where the volume of the oil phase (normalized to the oil volume applied in emulsion making) could be measured as time proceeded which occurs due to the gravity (bottle test) [8, 37]. In a regular, W/O emulsion, unstable emulsion or low stable emulsion occurs at a large amount of water separated from the system [8] that, typically might take place at high water content [37]. Three parallel measurements were carried out in the same manner for each sample and then the average was taken.

3. Results and discussion

3.1. Effect of water content.

It is clear from the measurement results which can be seen in fig 1 that, as the water fraction increases, the emulsion stability decreases. The emulsion sample that contains a lower amount of water content has achieved the highest stability rate, where it is noted at the sample (90/10; oil/water) volume fractions. On the other hand, according to the sample (45/55; oil/water) volume fractions, the lowest emulsion stability or the unstable emulsion occurred at a high amount of the water content in the system. These results contribute to the studies [31, 35, 36] that found in cases of low water content, the internal pressure of water droplets was lesser than the external pressure of the oil phase which would improve the stability of the emulsion due to the mechanical properties of the film (Stiffness of the interfacial film). On the other hand, as the water fraction increases, the internal pressure becomes higher and higher than the external pressure of the water, which leads indirectly to the extension of water droplets [37]. Basically, damage of the interface films occurs at a certain point of the energy level repulsion which depends on the internal and external pressure of both phases (water and oil) simultaneously. Increase the water fraction of the emulsion system leads in increasing of water droplets coalescence rate [37].

Figure 1 shows another strong relationship that, the emulsion stability rate does not increase by double when the water content fraction gets double charged in the emulsion system. During 80 minutes, the rate separation of the oil phase for the water-oil emulsion sample (10ml/90ml; v/v) reached 49 %, while it achieved only 56 % at the water-oil emulsion sample (25ml/75ml; v/v). This behavior of the emulsion probably occurs due to the limit stability of Urals Russian crude oils.

3.2. Effect of pH.

The results presented in Figs 2 and 3, obviously indicate that the pH has great influence on the emulsion stability which increases with decreasing pH of aqueous phase between the range (pH = 2 – 7). During 50 minutes, the separated volume fraction for emulsion sample pH = 7 reached 90 %. Whilst during same time, the emulsion sample with pH = 4 had achieved 64 % as a rate separation of the oil phase. On the other hand, the most stable emulsion occurred at the sample with pH = 2 which showed a high stability even after more than eight weeks (see Fig. 2). Hence, Figs 2 and 3 show that, there is unstable emulsion formed at pH = 7.00 and a very stable emulsion formed at pH = 2.00. These results seem identical to those obtained by [8], who found that the lower stable Algerian crude oil emulsion formed at the weakly acid medium, while this result specifies the pH values where the very stable emulsion formed at the highly acid medium.

Fig. 1. Effects of the water fraction on kinetic (W/O) emulsion stability

Fig. 2. Effect of different pH on the kinetic (W/O) emulsion stability

Fig. 3. Emulsion samples with different pH (pH = 7, 04 and 02) after 20 minutes, 90 minutes and more than eight weeks respectively (from left to the right)

Behavior of the interfacial film occurs due to repulsive forces [8, 16]. This result has been confirmed indirectly by the ones shown in Fig. 4 where the surface tension of emulsion increased as the pH value in the range (2.00 – 7.00) increased.

Fig. 4. Effect of water pH on the surface tension of (W/O) emulsion, at room temperature

3.3. Effect of salt concentration.

It can be pointed out from Fig. 5 that the stability of emulsions decreases with increasing (NaCl) salt concentration. During 80 minutes, the sample with 0.570 mol/l concentration of NaCl formed relatively a high stable emulsion with 54 % as separation rate of the oil phase, whilst the lowest stable emulsion occurs at the sample that contains the highest amount of salt concentration 4.106 mol/l when separated volume fraction achieved 98 %. Basically, emulsions can be stabilized through the repulsive charges on the surfaces of the discontinuous phase [22] and based on the theory of ions diffusion, increasing the salt concentration of the water-in-oil emulsion leads to increases of internal ionic force [38, 39] and might reduce the thickness of the interfacial layer of the emulsion system [39].

In order to confirm the previous results, it was necessary to evaluate the surface tension of emulsion and from experimental results, it was found that surface tension of emulsion increased as the salinity (concentration NaCl) increased, as shown in Fig 6. The emulsion samples with the lowest salt concentrations 0 and 0.570 mol/l respectively indicated the lowest surface tensions 28.49 mNm^{-1} and 28.97 mNm^{-1} . Furthermore, the highest surface tension 37.53 mNm^{-1} were measured at the emulsion sample which contains the highest salt concentration of NaCl 4.106 mol/l.

Fig. 5. Effect different salt concentrations on (W/O) emulsion stability

Fig. 6. Effect of salt concentrations on the surface tension of (W/O) emulsion, at room temperature

It is interesting to mention that, our finding is similar to [5]. Generally, increasing salt concentration leads to enhanced mechanical properties of the interfacial film that may hinder droplets to coalesce due to its relative resistance against deformation [5]. Also, high salt concentration may attribute to increasing intermolecular attractions which might lead to a decrease in the probability of molecules colliding with each other.

3.4. Effect of temperature.

Experimental results in Figs 7 and 8 show that surface tension of the emulsion and crude oil decrease as the temperature increases. In this regard, lowest emulsion surface tension 23.73 mNm^{-1} were measured at the temperature 35.5°C which considered the highest temperature for the evaluation in order to avoid distillation of the light components from emulsion system, whilst the highest interfacial tension 29.62 mNm^{-1} was found at the lowest temperature of 21.01°C . This behavior occurs because of increasing temperature which results in increased kinetic energy of the molecules and decreases cohesive forces.

According to Figs 7 and 8 and based on the complicated correlation between emulsion stability, surface tension and temperature as well as previous results published in the literature [37, 39], it can be concluded out that the stability of the emulsion decreases as temperature increases due to the low stability of interfacial tension at high temperature.

Fig. 7. Effect of temperature on the surface tension of (W/O) emulsion

Fig. 8. Effect of temperature on the surface tension of Russian Urals crude oil

Conclusion

The results were found according to the graphs. Surface tension of crude oil, and emulsion decrease as the temperature increases, but the surface tension of crude oil and emulsion increased as the salinity (concentration NaCl) as well as the pH value in the range (from 2.00 to 7.00) increase. It is interesting that surface tension of the emulsion in two cases (temperature and salt concentration) was relatively higher than the surface tension of the Russian Urals crude oil itself.

The results of emulsions stability show that the stability of emulsions decreases both with increasing temperature and (NaCl) salt concentration, also, as the water fraction increases the emulsion stability decreases.

For the pH, it was found that there is unstable emulsion formed at pH = 7.00 and a very stable emulsion formed at pH = 2.00. These observations can strongly enhance the efficiency of emulsification process for the production of Russian Urals crude oils.

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Влияние содержания воды, pH, солености и температуры на стабильность и поверхностное натяжение российской нефти марки Urals

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Ключевые слова: сырая нефть; эмульсия; стабильность; пленка; испытательная бутылка; капля воды.

Аннотация: Исследовано влияние уровня pH, солености и температуры на стабильность и поверхностное натяжение нефтяных и водонефтяных эмульсий, полученных с использованием российской нефти марки Urals. Эмульсии получены путем смешивания дистиллированной воды и российской сырой нефти в объемном соотношении 1/3 с тремя различными забуферированными растворами с уровнем pH 2,00, 4,00 и 7,00, соответственно. Проведены измерения стабильности эмульсий и их поверхностного натяжения. Для получения эмульсий пять водных растворов хлорида натрия (с концентрациями 0,570, 1,407, 1,711, 3,080 и 4,106 моль/л, соответственно) смешивали с сырой нефтью в соотношении 1/4 (вода/нефть); также получены пять водных растворов для сырой нефти (содержащие 1,50 г, 2,50 г, 3,50 г, 4,50 г и 5,50 г натрия хлорида, соответственно). Проведены измерения поверхностного натяжения эмульсий и сырой нефти, а также ста-

бильности эмульсий. Чтобы избежать отгонки легких компонентов из нашего близкого измерительного сосуда, применялись температуры 20,01, 25,05, 29,01, 31,50 и 35,05 ° С. Измерено поверхностное натяжение сырой нефти и эмульсии с объемной долей 3/1 (масло/вода). Наблюдалось поверхностное натяжение сырой нефти и эмульсии с увеличением температуры, но при этом поверхностное натяжение сырой нефти и эмульсии также увеличивалось по мере увеличения солёности (концентрации хлорида натрия), увеличивались значения pH в диапазоне 2,00...7,00. С другой стороны, результаты испытаний стабильности эмульсий показали, что она уменьшается как с увеличением температуры, так и концентрации соли (хлорид натрия), при этом, с увеличением доли воды, стабильность эмульсии уменьшается. Обнаружено, что существует нестабильная эмульсия, образованная при pH = 7,00, и очень стабильная – при pH = 2,00.

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Einfluss von Wassergehalt, pH-Wert, Salzgehalt und Temperatur auf Stabilität und Oberflächenspannung der russischen Erdöl Marke Ural

Zusammenfassung: In der Arbeit ist der Einfluss von pH-Wert, Salzgehalt und Temperatur auf die Stabilität und Oberflächenspannung von Öl- und Öl-Wasser-Emulsionen untersucht, die unter Verwendung des russischen Erdöls Marke Ural erhalten sind. Emulsionen wurden durch Mischen von destilliertem Wasser und russischem Rohöl in einem Volumenverhältnis von 1/3 mit drei verschiedenen gepufferten Lösungen mit einem pH von 2,00, 4,00 bzw. 7,00 erhalten. Die Stabilität der Emulsionen und ihre Oberflächenspannung sind gemessen worden. Um Emulsionen zu erhalten, wurden fünf wässrige Lösungen von Natriumchlorid (mit Konzentrationen von 0,570, 1,407, 1,711, 3,080 bzw. 4,106 mol/l) mit Rohöl in einem Verhältnis von 1/4 (Wasser / Öl) gemischt. Es wurden auch fünf wässrige Lösungen für Rohöl erhalten (die 1,50 g, 2,50 g, 3,50 g, 4,50 g bzw. 5,50 g Natriumchlorid enthielten). Die Oberflächenspannung der Emulsionen, des Rohöls, sowie der Emulsionsstabilität wurden gemessen. Um das Ablösen von leichten Bestandteilen aus dem nahen Messgefäß zu vermeiden, wurden die Temperaturen von 20,01, 25,05, 29,01, 31,50 und 35,05 ° C verwendet. Es wurde die Oberflächenspannung des Rohöls und der Emulsion mit einem Volumenanteil 3/1 (Öl / Wasser) gemessen. Es wurde die Oberflächenspannung des Rohöls und der Emulsion mit zunehmender Temperatur beobachtet, aber die Oberflächenspannung des Rohöls und der Emulsion stieg auch mit zunehmendem Salzgehalt (Natriumchlorid-Konzentration) und es gab einen Anstieg der pH-Werte im Bereich (von 2,00 bis 7,00). Andererseits zeigten die Ergebnisse von Emulsionsstabilitätstests, dass die Stabilität von Emulsionen sowohl mit zunehmender Temperatur als auch bei Salzkonzentration (Natriumchlorid) abnimmt, während mit zunehmendem Wassergehalt die Stabilität der Emulsion abnimmt. Bezüglich des pH-Werts wurde festgestellt, dass bei pH = 7,00 eine instabile Emulsion und bei pH = 2,00 eine sehr stabile Emulsion gebildet wird.

Influence de la teneur en eau, pH, de la salinité et de la température sur la stabilité et la tension superficielle du pétrole de la marque russe Urals

Résumé: Les effets du pH, de la salinité et de la température sur la stabilité et la tension superficielle des émulsions eau-huile brutes de l'Oural russe ont été étudiés. Les émulsions ont été obtenues en mélangeant de l'eau distillée et du pétrole brut russe dans un rapport volumétrique 1/3 avec trois solutions différentes avec des niveaux de pH de 2,00, 4,00 et 7,00, respectivement. Sont prises des mesures de la stabilité des émulsions et leur état superficiel. Pour recevoir des émulsions, cinq solutions aqueuses de chlorure de sodium (avec des concentrations de 0,570, 1,407, 1,711, 3,080 et 4,106 mol/l, respectivement) ont été mélangées avec du pétrole brut dans un rapport de 1/4 (eau/pétrole); sont obtenues cinq solutions aqueuses de pétrole brut (contenant 1,50 g, 2,50 g, 3,50 g, 4,50 g et 5,50 g de chlorure de sodium, respectivement). Est mesurée la tension supérieure des émulsions et du pétrole brut, ainsi que de la stabilité des émulsions. A été observée la tension superficielle du pétrole brut et de l'émulsion avec une augmentation de la température, mais la tension superficielle du pétrole brut et de l'émulsion a également augmenté avec l'augmentation de la salinité (concentration de chlorure de sodium) et une augmentation des valeurs de pH dans la gamme (de 2,00 à 7,00). D'autre part, les résultats des essais de stabilité des émulsions ont montré que la stabilité des émulsions diminuait à la fois avec l'augmentation de la température et de la concentration de sel (chlorure de sodium), tandis que, avec l'augmentation de fraction d'eau, la stabilité de l'émulsification diminuait. En ce qui concerne pH, a été constaté qu'il existe une émulsion instable formée avec pH = 7,00 et une émulsion très stable formée avec pH = 2,00.

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