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Demulisification of Water in Oil Emulsion by Using Fatty Alcohol as Demulisifier Combined with Thermal Method

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Abstract

Emulsified water is generally present in crude oil as a result of the mixing occurring during production operation. The formation of emulsions conducts problems in production as well as in transportation. Therefore, they need to demulsify through demulsification process. In the present work, the chemical demulsification combined with thermal heating is used to treat Iraqi crude oil (Basrah oil) for separating the water from water in oil emulsions.

Many variables were studied to indicate their influence on water separation. They have been included chemical demulsifier concentration were (3- 8%), temperature (50 – 70°C), the water content of the emulsion (10 – 30%) and salt concentration (1-3%). All experiments were carried out on an emulsion prepared by mixing speed of (500 rpm) for (15 min). Also, viscosity and density were measured for samples before and after demulsification.

From the experimental results, there were noticed that the percentage water separation increased with increasing demulsifier concentration, temperature, water content and salt concentration. The best separation efficiency reached 66.7 % of initial water content present in the oil. Also, it was being seen the viscosity and density of emulsion decreased after treating by demulsification process.

Keywords: demulsification; demulsifies; crude oil; water in oil emulsion.

1. Introduction

Water naturally is existed in the crude oil and attributed as an oil field emulsion. This emulsion can happen at different stages include during drilling, producing, transporting and processing of crude oil [1].

An emulsion resulted when combined two immiscible liquids together. There are two main kinds of emulsion namely oil-in-water (o/w) and water-in-oil (w/o). While, in some cases, complex emulsions like oil-in-water-in-oil (o/w/o) and water-in-oil-water (w/o/w) emulsions can be existing. There are three major criteria that represent substantial role during the emulsification process [2]. First, the formation of an emulsion entails the availability of two immiscible liquids. Secondly, the emulsion is formed by stratifying mechanical energy to generate droplets. This is the most significant step in emulsification process. The third criterion is the existence of an agent handling fractional solubility in both phases which known as emulsifier [3].

Normal substances such as; resins, asphaltenes, carboxylic acids, and solids such as; waxes and clay stabilize these emulsions. The emulsions have stability, extending from slight minutes to a few years, relying on the type of the crude oil and the quantity of water [4].

The problems of formation water with crude oil including: the corrosion of pipe work, pumps, production equipment and downstream overhead distillation columns, cost for pumping or transferring water through pipeline or tankers, the poisoning of downstream refinery catalysts and the problems related to increasing viscosity of oil as a result of tiny dispersed water within crude oil. Therefore, there are a number of commercial and operating purposes of removing the emulsified water from the crude oil [5]. For economic and working purposes, it must separate total water from the crude oil emulsion before refining and transport. So as to apart the water content of the produced crude oils, the emulsions have to be broken through demulsification method [6].

Demulsification is known as a process of breaking emulsions with the purpose to remove water from oil [7]. The methods that are ready for demulsification can be categorized as electrical, microwave, thermal and chemical demulsification. The most wide methods used for treating emulsions include using chemical additives combined with heat to conform separation processes of the emulsion. These chemical additives are commonly known as demulsifiers [5]. These demulsifiers are surface-active agents and achieve a high surface area at the crude water-oil interfaces. This makes in the variation of firm films of normal crude oil substances by a film that is helpful to water droplets to coalescence [8-9]. Demulsification of crude oil emulsions can happen by the destruction the central emulsion layer using consecutive additions of a demulsifying agent to the layer while heating and mixing with sequent settling [10].

The aim of the present work is to evaluate 2-ethylhexanol fatty alcohol (waste alcohol from butanol production) as demulisifer for breaking Iraqi crude oil emulsion. Demulisifier concentration, the water content of emulsion and salt concentration were studied. Also, the effect of temperature on demulsification performance and properties after demulsification were investigated.

2. Experimental work

2.1. Materials

In this study Basrah crude oil in Iraq was supplied by Al-Daura refinery with density and viscosity of being 0.911 g/cm^3 and 76.8 cP respectively while the API was 24. Fatty alcohol (2-Ethylhexanol) used as demulsifier and supplied from India. Fresh water used throughout the experiments and sodium chloride used to adjust the salinity of aqueous phase before added to the crude oil.

3. Method

3.1. Emulsion preparation

Water-in-oil emulsions were prepared by mixing crude oil and brine solution to obtain 30% (v/v) water content. In 500 mL beaker, the crude-oil was stirred at 25°C using mechanical stirrer at a rate of 500 rpm for 15 minutes to get a stable emulsion. This speed approach to that used by Al-Sabagh [11]. Emulsions were leaving two weeks to make sure that no separation took place, before the treatment.

3.2. Demulsification process

Fig. 1. Crude oil after separation process

The bottle test was used to evaluate the efficiency of the demulsifier to separate water-in-oil emulsions. The demulsifier was added to (200 mL) water-in-crude oil emulsion at a concentration (8%). The mixture was stirred for 3 minutes and placed in a (250 mL) graduated cylinder. Then, the cylinder was placed in a thermostatic water bath at 70°C. Water separation (in mL) was noticed periodically to record the amount of settled water as shown in Fig. 1. The water separation percentage has been calculated as illustrated in Eq.1 [12].

$$\text{Water separation\%} = \frac{volume\ of\ water\ seperated}{original\ volume\ of\ water} * 100 \quad (1)$$

The emulsion was poured into separation funnel as shown in Fig. 2 to withdraw water to measure the density and viscosity of the remaining solution to compare with that of original emulsion and with crude oil. Viscosity was measured using Fungilab viscometer as shown in Fig. 3 while density measured by using pyknometer. The process is repeated for different water content, salt concentration, demulsifier concentration and temperature.

Fig. 2. Separation funnel for separate water and crude oil

Fig. 3. Viscometer Fungilab

4. Results and discussion

4.1. Effect of the demulsifier concentration

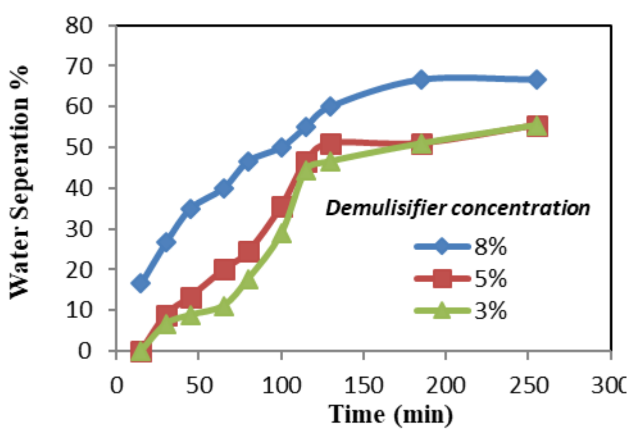

Fig. 4 Effect of the demulsifier concentration at constant temperature 70°C, water content 30% and salt content 3%

One of the most remarkable parameters prevailing the adsorption of demulsifiers at the interface is the demulsifier concentration that is shown in Fig. 4 at constant water content 30%, salt content 3%, and temperature 70°C. From this figure, it can be seen the separation efficiency, increased from 55% to 67% after 4h treatment as breaking agent increased from 3% to 8%. The increase of the demulsifier concentration led to an increase in the adsorption of the demulsifier molecules on the W/O interface, which displace the natural emulsifiers (asphaltene). This reduced the mechanical fixedness of the interfacial film, and this fixedness keeps to decrease until being thinner, and then breakdown completely with more adsorption of the demulsifier agent on the interface [13].

4.2. Effect of the water content

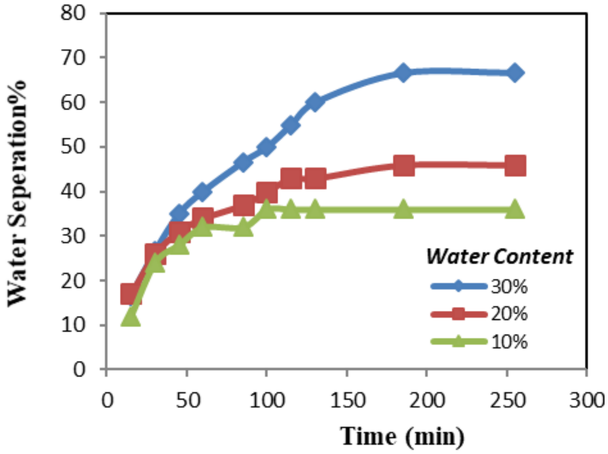

Fig. 5. Effect of water content at constant demulsifier concentration 8%, temperature 70°C and salt content 3%

The effect of the initial water content of emulsion on demulsification efficiency illustrated in Fig. 5. It can be observed the separated water increase from 36% to 67% as water content increasing from (10%-30%). This because the hardness of water/oil films reduced with increasing water content in the bulk till the interior pressure be greater than the exterior pressure at that moment, fast rupture of the water/oil interface happened, and the coherence of water droplets increased. The higher water content, the fewer interval between a drop and a drop becomes small, leading to the rapid combination [14].

4.3. Effect of salt content

In the petroleum industry, there is a wide difference in the salt content of the crude oils depending on most on the origin and may be, on the production wells or area within a field. The quantity of inorganic salts differs with the geologic formation.

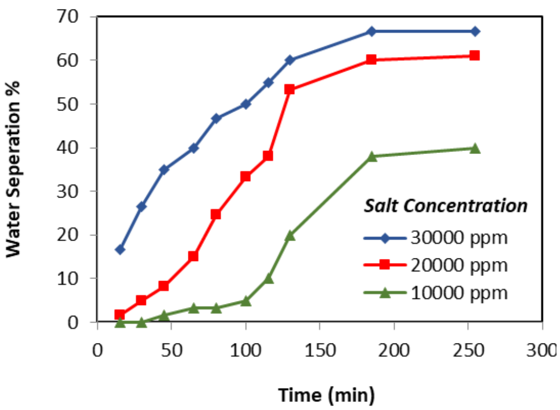

Fig. 6. Effect of salt content at constant demulsifier concentration 8%, temperature70°C and water content 30%

It can be observed from Fig. 6 that water separation efficiency increases with increasing salt content. The addition of sodium chloride (inorganic salt) to the crude oil emulsion leads to an inverse action on emulsion stability; so that, the preferable separation of water was obtained for the sample governing the highest concentration of 3% NaCl (67% separation of total water) comparison to the lower concentration of NaCl (38% separation of total water) at time 3 hr. This phenomenon could be explicated by the pronounced variation in interfacial film behaviour. The salt ions result in an increase in relaxation of the forming film [15]. These results are in coincidence with those attained by Hajivand and Vaziri [16].

From the theory of diffuse ion, it is well known that for the same water content, when the salt concentration increases, this lead to increase the internal energy of the system [17]. Thus, the emulsions are not thermodynamically stable, and water droplets combine with each other to produce bigger droplets and increase the rate of coalescence.

4.4. Effect of the temperature

In the present study, the activity of temperature on the demulsification efficiency was investigated. The results showed in Fig. 7 and that by raising the temperature from 50°C to 70°C, this gave rise to better demulsification efficiency to reach 67% at higher temperatures while for low temperature (50°C) the separation was 39% at time 3h. The stability of emulsion can be decreased by conditions that reduced the film forming capacity of the crude oil. These films can be contracted by increasing the temperature through two ways [18].

The first, by enhancement the rate of coalescence by implying sufficient energy for the revel of two droplets occurring previous to coalescence. The second, by giving rise to a reduction in the viscosity of continuous phase; which assisted the kinetic motion of the dispersed water droplets, hence increasing increased revel leading to film relaxation, rupture of film and coalescence [19]. In other words, increasing the temperature results in decreasing the viscosity of the oil (continuous phase) and increase the occurrence of collision between the emulsified droplets "water." As a result, the difference in density between the oil and aqueous phase increases and hence makes water droplets to separate. Higher temperature, perhaps increases the solubility of emulsifiers, from the interface, into the oil phase, causing weaker film and a greater amount of water droplet coalescence and separation [11].

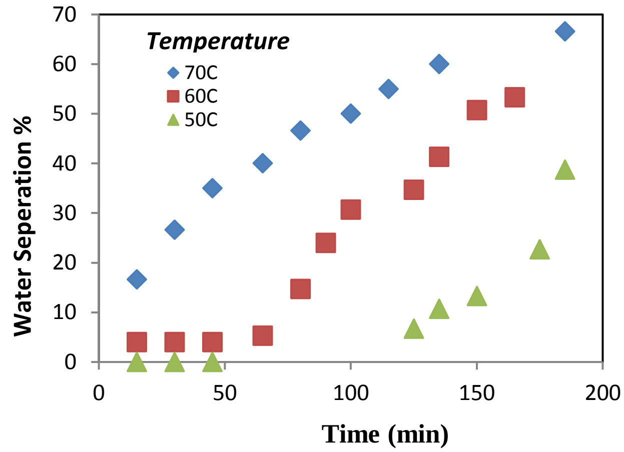

Fig. 7. Effect of temperature at constant water content 30%, salt content 3% and demulsifier concentration 8%

4.5. Viscosity and density of emulsion

4.5.1. Effect of the water content on viscosity and density

Fig. 8 illustrates the effect of water content on the viscosity of the emulsion at salt content 30000ppm and using demulsifier concentration 8%.

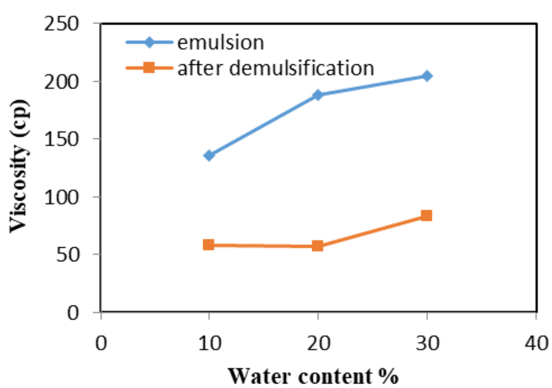

Fig. 8. Effect of water content on viscosity at salt concentration 3%, demulisifier concentration 8% and temperature 70°C

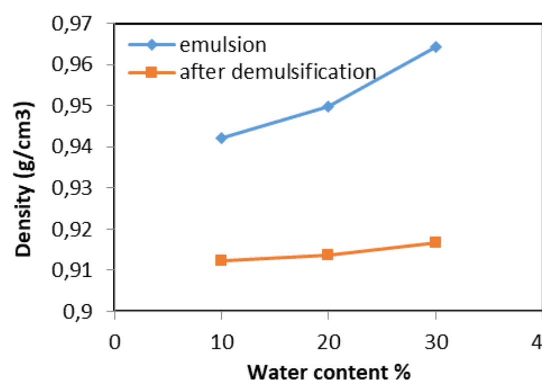

Fig. 9. Effect of water content on density at salt concentration 3%, demulisifier concentration 8% and temperature 70°C

From this figure two behaviors were shown, the first was that as water content increased from 10% to 30% the viscosity increased from 136 to 205cP (blue color) compared with the viscosity of oil alone was 76.8cp this because emulsions show non-Newtonian behavior. The second behavior was that the viscosity decreased after demulsification process as shown in the same figure to reach 87cp (red color) for water content 30%. The addition of demulsifier and implementation of heat will decrease the viscosity. As the results, the accumulation of water droplets and mobility of water are increased causing collisions, coherence and then increase the rate of separation [20]. The same behavior was shown for density and illustrated in Fig. 9. It decreases from 0.9643 g/cm^3 as an emulsion to reach 0.9167 g/cm^3 after treating at water content 30%. Heat applied to emulsion will reduce the density of oil at a greater rate than that of water and therefore allows more settling of water. This is because the variety in densities of the two liquid phases may be increased [20].

4.5.2. Effect of salt content on viscosity and density

The same as the water content effect on emulsion, the salt content also effect on viscosity and density of emulsion as shown in Figs. 10 and 11. Fig. 10 illustrates the effect of salt content on the viscosity of the emulsion at constant temperature 70°C, demulsifier concentration 8% and water content 30%. From this figure, it was seen that viscosity decreased from 287 to 204cp as salt increased from 10000 to 30000ppm (blue color) but after demulsification, it decreased for all amounts. While the density increased from 0.948 to 0.962g/cm^3 as the amount of salt increased from 10000ppm to 30000ppm as indicated in Fig. 11.

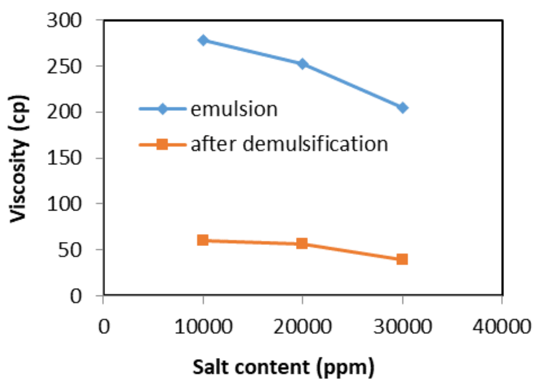

Fig. 10 Effect of salt content on viscosity at water content 30%, demulisifier concentration 8% and temperature 70°C

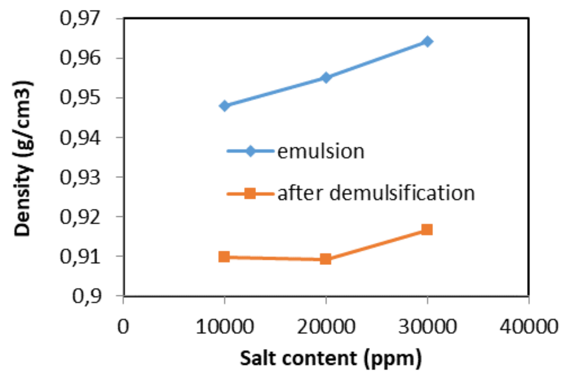

Fig. 11. Effect of salt content on density at water content 30%, demulsifier concentration 8% and temperature 70°C

5. Conclusions

1) Separation efficiency increases with increasing chemical demulsifier and temperature because the increase of the demulsifier concentration led to an increase in the adsorption of the demulsifier molecules on the W/O interface and the higher temperature might increase the solubility of emulsifiers.
2) Separation efficiency increases with increasing water content of emulsion.
3) Separation efficiency increases with increasing salt content of emulsions; this could be due to the destroying of the double charge layers by NaCl that delay the coalescence of water droplets.
4) The best demulsification efficiency was 67% that obtained at water content 30%, salt concentration 3%, demulsifier concentration 8% and temperature of 70°C.

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