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ORIGINAL ARTICLE

Tweens demulsification effects on heavy crude oil/water emulsion

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Abstract The demulsification role of Tweens (nonionic polymers) was determined in the separation of water from heavy crude oil emulsion. According to the previous researches, these nonionic polymers, having hydrophilic and lipophilic groups, are appropriate for making oil in water emulsion. In this research their effects in certain concentrations on demulsifying of water in crude oil emulsion were proved. High molecular weight, alkenes' chains and groups of ketone and ester in these polymers can improve their performance for the demulsification of water in crude oil emulsion. Their efficiencies are improved with electronegative groups such as oxygen. They leave no corrosion effect because they are neutral and do not leave counter ions.

1. Introduction

Water and oil emulsions (suspended water droplets in crude oil) are formed during the production process of crude oil. The stability of the emulsion has a range from few minutes to years and it varies by the characteristics of the crude oil and water (Bhardwaj and Hartland, 1998). The amounts of stable or unstable emulsions in crude oil vary among different oils (Schramm, 1992; Langevin et al., 2004; Ivanov and Kralchevsky, 1997). Emulsions must be removed because the water in emulsion occupies extra space and makes more corrosions in the processing equipments and pipelines, therefore it can increase the costs. In addition, emulsification could change the characteristics and properties of the crude oil (Grace, 1992).

Polymeric surfactants are the most common demulsifiers for water in oil emulsion breakage (Zaki et al., 1996).

Nonionic surfactants have a good effect on the demulsification of crude oil because they do not leave any counter ion in the products (Bhardwaj and Hartland, 1993).

Molecules with a high number of hydrophilic groups even if they have low molecular weights showed excellent demulsifying abilities (Shetty et al., 1992). Polysorbates, called Tweens, are the polymeric surfactants and oily liquids derived from PEG-ylated sorbitan (a derivative of sorbitol) esterified with fatty acids. Tweens have a hydrophilic subunit which is a poly

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ether or polyoxyethylene and their lipophilic subunit is a polysurbate. The number that follows the Tweens polyoxyethylene part refers to the total number of oxyethylene –(CH_2CH_2O)– groups found in the molecule (Table 1) (Schramm et al., 2003).

These surfactants are illustrated as the emulsification agents for stabilizing oil in water emulsions. They are used as solubilization agents for oil-soluble vitamins, wetting agents, cosmetics and food products. Some studies have been done on the effects of Tweens for the preparation of micro emulsions to make oil in water emulsions (Martins et al., 2011).

But there is this assumption: If the surfactants can make oil in water emulsion, maybe they can remove water from water in oil emulsions. In other words, we are supposed to examine this assumption that some emulsifiers with some structural properties can have both emulsification and demulsification effects in different cases and some emulsifiers for making oil in water emulsions can demulsify water in oil emulsions.

The polymeric demulsifiers can be absorbed on the oil/water interface. Interfacial active fraction in the oil has number of functional groups that can penetrate into the oil/water interface in order to form an interfacial layer which can be broken by the demulsifiers (Fig. 1) (Zaki et al., 1996).

In the recent years, a lot of research has been done on ionic and nonionic demulsifiers. Studies have showed that the presence of more hydrophilic parts in demulsifiers cause more separation of water from oil and it has a great effect on the amount of HLB number of surfactant (Grace, 1992). Tweens have appropriate hydrophilic parts because of their high oxyethylene groups. This group allows the surfactant that can make more hydrogen bonds and have stronger hydrophilic parts.

Some researchers have showed that the high molecular weights of the demulsifier improve its performance. They showed that more concentration of the demulsifiers improves their effect but not below 500 ppm (Zaki et al., 1996). Increasing of hydroxylic agents can lead to better separation (Xinru et al., 2006) and percent of nonionic polymers increases the efficiency of demulsifiers (Peña et al., 2004). The presence of electronegative atoms and alkane chains (with 4–9 carbon atoms) in the demulsifier can improve the separation ability of oil and water (Redmond, 1988). The ketonic and esteric parts enhance the ability of separation of oil and water emulsion (Berger et al., 2008). Increasing the degree of polymerization (DP) improves the characteristics of demulsifiers (Manalastas et al., 2000).

Bancroft stated that "a hydrophilic liquid has a tenacity to make water as a dispersing phase but hydrophobic one has a tenacity to make oil as a dispersing phase" (Bancroft, 1913). Grifin stated the hydrophilic–lipophilic balance (HLB) concept to show the amphiphilicity for nonionic surfactants, Surfactant with low HLB gives water in oil emulsions, whereas high HLB ones give oil in water emulsions (Griffin, 1949). Since the Tweens have high HLB number, they probably can help the water in oil emulsion of crude oil to break well (Table 1). Researches have showed that the increasing of the amount of HLB is more effective on demulsification (Abdel-Azim et al., 1998).

In this research, the effect of nonionic Tweens on the separation of water from crude oil was investigated by "Bottle Test" method.

2. Materials and methods

In this part, the breakage ability of Tweens on oil/water emulsion in crude oil was examined. For this purpose, it was needed to simulate an oil exploitation unit in the laboratory. A schematic exploitation unit has been shown in Fig. 2. We designed these steps in the methods of experimental section.

2.1. Materials

The list of materials which were used for this research included:

Crude oil (Azadegan field of Heavy crude oil, Iran), xylene (Merck, mixture of isomers for synthesis 99%), ethanol (Merck, absolute for synthesis 99.5%), acetone (Merck, for synthesis 99%), toluene (Merck, extra pure 99%), nitric acid (Merck, extra pure 65%), silver nitrate (Merck, GR for analysis ISO, 99.8%), potassium thiocyanate (Merck, GR for analysis ACS. 99%), distilled water, Tweens: (Tween 20, Tween 40 , Tween 60, Tween 80, Tween 85, Ph Eur, NF).

2.2. Instrumentation part

Centrifuge (Sigma 2–16P, Max. rpm 7800).

2.3. Methods

2.3.1. Determination of water percentage

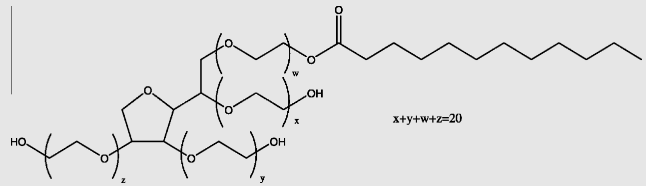
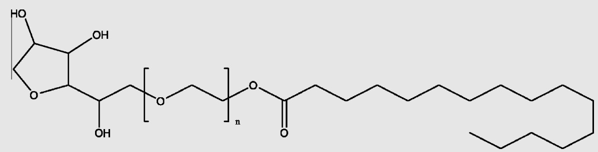
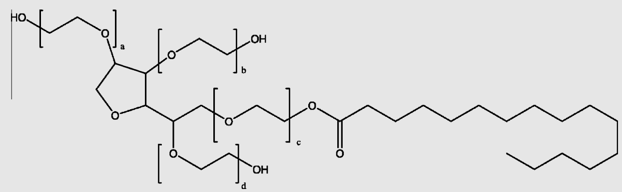
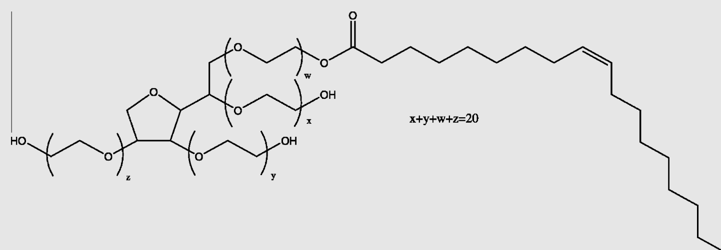
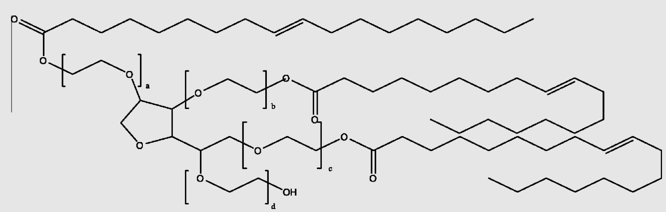
For the determination of water percentage (presented in crude oil samples), modified ASTM D4007-02 standard method was applied. A solution consisting of xylene and oil with 1:1 volume ratio was poured in two centrifuge tubes, Oil can be solved in xylene and this matter facilitates the centrifuge step. Then synthetic demulsifier was added to one of the tubes for complete demulsification of water in oil emulsion. After that both of the tubes were centrifuged at 1700 rpm for 5 min. Since the amount of primary water was under 10% of the total volume of sample, 10% water (wash water) was added to the samples (ASTM D4007-02).

2.3.2. Bottle test: Examination of water separation, desalination stage and determination of the salt amount

In this experiment, the effects of 5 kinds of Tweens were examined. 90 mL of oil and 10 mL water were poured to bottle tests. 300, 400, 500, 600, 700, 800 and 900 ppm of all of the Tweens were added into the bottle tests. Then, the bottles were shaken until a homogenous solution was obtained. After this step, the amount of water separation was measured according to the modified ASTM D1401-98 and ASTM D4006-81 standard methods (ASTM D1401-98 and ASTM D4006-81).

In the desalination stage, before putting the bottles into water bath at 70 °C, they were shaken. The thermostat was put in the blank bottle. After 15 min the amount of separated water (lower part of bottle) was measured and then it was removed of the bottle with a syringe. The amount of salt was measured before and after the bottle test by modified IP 77:72 standard test method. It is one of the common methods for crude oil salt measurement. This method includes two parts, first is the removal of all amounts of salts from oil and next part is its measurement by the titration method. Titration method follows Volhard titration because there is

Table 1 Tweens' structures with HLB number.

Row	Structure	HLB[a]
Tween 20		16.7
Tween 40		15.6
Tween 60		14.9
Tween 80		15.0
Tween 85		11.0

[a] These numbers were given from Griffin's article (Griffin, 1949).

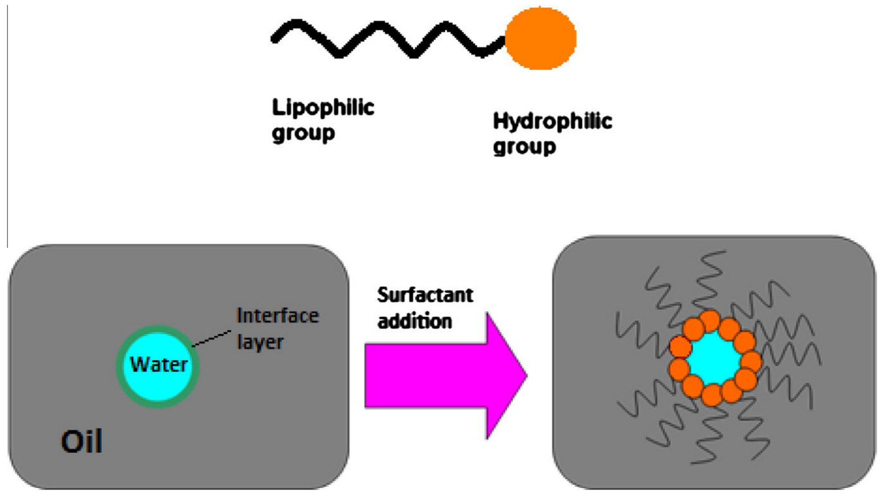


Figure 1 Schematic display of demulsifier structure and its penetration into layer around water droplet.

no necessity for providing the neutral media in this method. In this standard method samples were heated to start the reflux (the temperature was between 100 and 120 °C); warm toluene was added to the sample and stirred to complete the dissolving of sample. Heated alcohol and acetone were added to this mixture and it was allowed to stir. When the aqueous and organic phases were formed, the mixture was boiled and distilled water was added. When the materials made two phases, Bottom layer (aqueous phase) was taken and added to a beaker. Nitric acid was added to the mixture and then the beaker was heated to boiling point of mixture. For the determination of the presence of hydrogen sulfide, its vapors were checked by a lead acetate paper. Then the solution was boiled again. Excess silver nitrate was added in order to convert all chloride into silver chloride and remained silver nitrate was titrated by thiocyanate. Ferric alum was used as indicator and Volhard titration was followed. Also a blank titration was performed with toluene as sample (IP 77:72).

2.3.3. Measurement of basic sediments and water (BS&W)

The separated water was removed and the container of oil was shaken until it got a homogeneous form. Xylene and bottle test oil were poured in a centrifuge tube; the tube was shaken and centrifuged. Three phases were formed: water, emulsion and oil. The amount of water, emulsion and oil were measured. Then the synthetic demulsifier was added and the previous steps were repeated. In this section

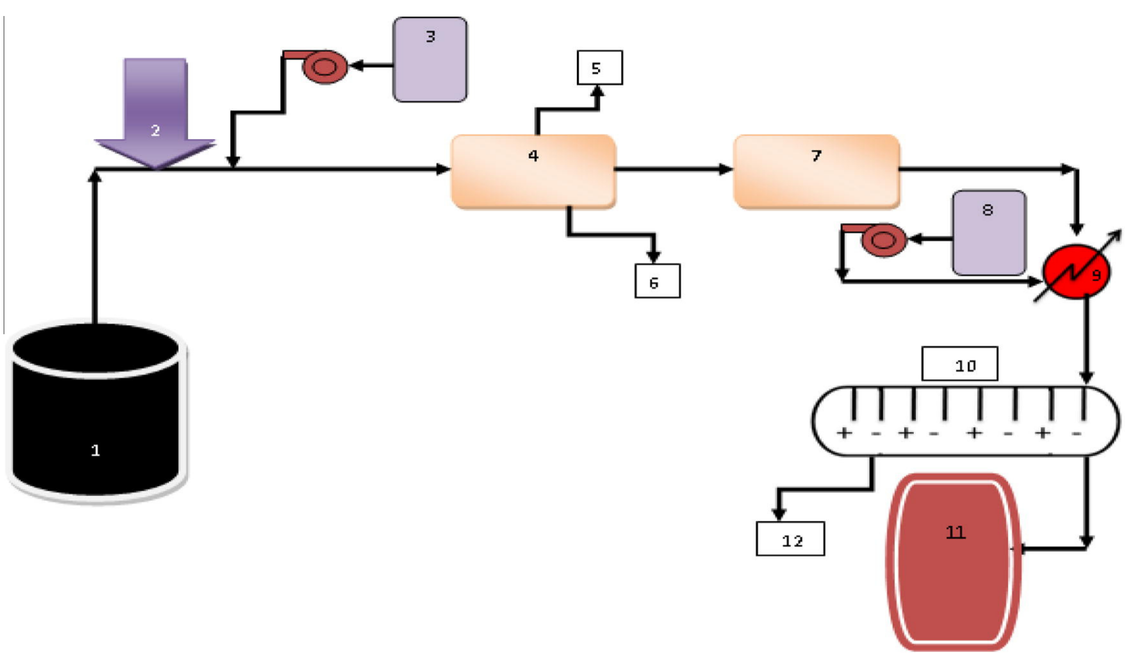


Figure 2 Exploitation unit: (1) oil well (reservoir), (2) demulsifier injecting place, (3) wash water injecting place, (4) first separator, (5) gas exiting place, (6) water exiting place, (7) second separator, (8) water for salt washing, (9) heat transducer, (10) desalination unit, (11) refinery unit, (12) removal of wash water.

there are two phases: water and oil. The amount of oil and water were measured.

3. Results and discussion

The line plots show the demulsification effect of each Tween (Fig. 3A and B).

All the samples had a better separation of water and salt than that of the blank sample. The best dosage of Tween 20 was 400 ppm, that it left the minimum amount of salt and showed good separation of water. No change in the aqueous phase color was observed. The optimum dosage of Tween 40 was obtained in 600 ppm, with a sharp interface. Water phase showed a good quality (without any cloudy phase) but it had little droplets of oil. Tween 60 had the best water separation in 300 ppm dosage but desalination in comparison with the blank sample was not enough. Tween 80 had the best performance in 600 ppm but separated water had a light yellow color. Tween 85 had the best effect in 600 ppm dosage and the salt separation was exactly perfect. In 300 and 400 ppm, the Tweens ability of water separation was similar but the ability of desalination was different. In 300 ppm the best performance was belonged to Tween 40 and in 400 ppm it was belonged to Tween 20. The best results in 500 ppm were obtained by Tween 60. Tween 85 in 600 ppm had the best result for desalination. This dosage is the critical dose, because the higher dosage showed a bad performance in desalination and water separation. The best results were obtained when the amount of emulsion was low. The dosage that left low emulsion was obtained with BS&W method and it showed that the lowest amount of remained emulsion belongs to Tween 20; it refers to its higher HLB. It has been proved in researches High HLB makes water in oil emulsion unstable. The high amounts of hydrophilic groups and shorter length of lipophilic groups of Tween 20 in comparison with other Tweens makes it demulsify more effectively. With oxyethylene groups it can make the hydrogen bonds and be attracted to the droplets and force them to join together. And it is obvious that Tween 20 showed a reasonable amount of separated water and remained water in dosage that it showed the lowest amount of remained emulsion. Furthermore, these results have proved the first assumption; they showed that in some cases if an emulsifier for oil in water emulsion has oxyethylene groups and high HLB number, it helps the emulsifier to show the demulsification effect for water in oil emulsions.

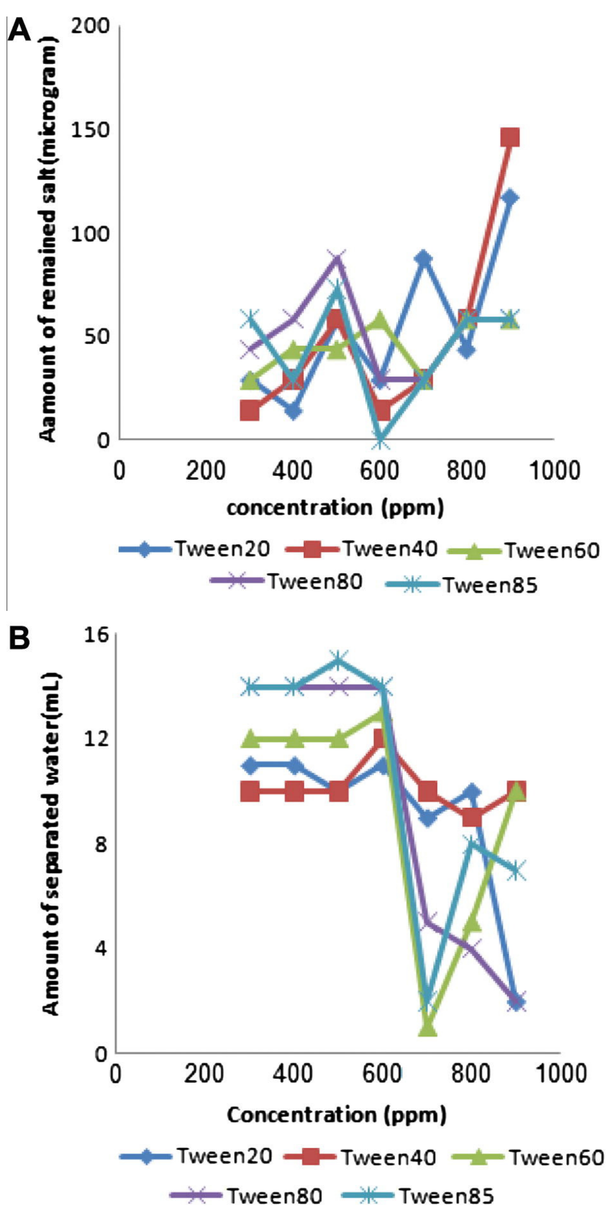


Figure 3 Line plots of salt (A) and water (B) separation versus dosage of demulsifiers (ppm).

4. Conclusion

According to the results, Tweens below 700 ppm concentrations, with their hydrophilic and lipophilic groups, have shown demulsification effects. Tweens show a better demulsification effect with increasing in HLB amount. In addition because of neutrality, they produce no counter ion; therefore there is no corrosion effect by using them. It is obvious that they have a reasonable effect in low dosage and it is not necessary to use high amount of demulsifiers. These results also show Tweens (in dosage lower than 700 ppm) as a good demulsifier for the separation of water and salt from crude oil.

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