Emulsion Stability Of Heavy Oil With Surfactants And Nanoparticles

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Abstract

The recovered crude oil is often in form of an emulsion and the recovery is cut off when water to oil ratio exceeds a certain amount. The emulsions vary from water-in-oil to oil-in-water and the step that follows is to coalesce droplets to get two continuous liquids. Difficulties arise when the oil contains emulsifiers. There are naturally occurring surfactants, or the oil recovered is by enhanced oil recovery techniques which have additives that stabilize the droplets. We have considered below a heavy oil (viscosity 650-750 mPa.s) containing one of the three surfactants: a nonionic surfactant or a cationic surfactant or an anionic surfactant. In addition, the mix can have alumina or silica nanoparticles or none. Most of the results have straightforward interpretations. There is no apparent effect due to nanoparticles. Cationic surfactants appear to give rise to a secondary haze. If the system contains nonionic surfactant then it can be destabilized by raising the temperature, except for one notable case. There are also cases of precipitation of nanoparticles. We observe that overall, phase separation happens best in presence of anionic surfactant, although complete phase separation rarely happens. This is attributed here to the very high viscosity of oil, which feature is independent of the additives.

Introduction

The first step in explaining emulsion stability comes from Derjaguin-Verwey-Overbeek (DLVO) theory which looks at the London-van der Waals attraction and the electrostatic double layer repulsion between two droplets. This is the flocculation step which brings two droplets together. At the next step or at larger droplet concentrations, the DLVO theory is no longer applicable as two neighboring droplets are always close. This feature is aggravated when the droplets are larger than usual. For one to use DLVO theory to get the rates of flocculation, the droplets have to be less than 0.1 μm. For concentrated systems of large droplet size such as our system below, the key feature that prevents coalescence is the thin film of dispersion medium intervening between two adjacent droplets. Film thinning is determined by the mobility of the interface, and can be retarded by the use of surfactants. Effects of surfactant solubility, phase, oil/water ratio appear to be known. Much of the above can found in common references (Miller and Neogi 2008).

The problem with emulsion stability involving crude oil is well known. Brine is found as water-in-oil (w/o) emulsion and has to be removed before downstream operations as it is very corrosive. With time, relatively more brine and less oil is produced, and at some point the oil recovery is stopped. The emulsion may well be oil-in-water (o/w) at that point. These emulsions can be very stable, stabilized by naturally occurring materials or in case of enhanced oil recovery (EOR) by additives used. The surfactant flood is used to generate ultralow interfacial tension which is necessary for a good oil displacement. Recipes for practically all feasible surfactants are available, where often surfactants need cosurfactants such as alcohol, to reach ultralow interfacial tension (Shah and Schechter 1977; Shah 1985). A recent review looks at alcohol-less sweeps, that

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uses the soap formed due to alkali flood and provides a list of surfactants, all with branched chains, some are partially ethoxylated but all are sulfonates or sulfates (Hirasaki et al. 2011). Petroleum sulfonates are also considered. Finally, surfactants are often introduced as foams to provide stable sweeps (Smith 1988; Li et al. 2008). In some cases, some other additive is used to break the stability. As is apparent, the range of surfactants that can be found at the production well is very high and simple ones are considered in the present work. The use of nanoparticles has not yet seen field work. One difficulty with additives, including just surfactants, is that they often degrade under field conditions. Nanoparticles, defined as < 30 nm in diameter, may not degrade. In addition, they appear to fulfill all the requirements for enhanced oil recovery: higher viscosity of the displacing medium and appropriate changes in interfacial tension and wettability (Bera and Belhaj 2016; Zhang et al. 2014; Cheringhian and Hendraningrat 2016; Ko and Huh 2019).

To study emulsion stability in the laboratory, it is important to look at how they are made. Of interest here are emulsions from heavy crude. In the first attempt, oil and a 1% solution of NaCl in water were introduced in a large measuring cylinder and emulsified using a homogenizer till the suspension turned white. It implied that the dispersions were in a range smaller than the wavelength of light and hence they scattered light. However, the process required too much heavy oil and was not used. Fine emulsions of this kind are needed to study DLVO type of flocculation, hence that approach was abandoned. The next one attempted was spontaneous emulsification. Miller (1988) provides one case and we tried a variation. Here, oil was layered into a measuring cylinder and then 1% NaCl solution in water was added to the top. As oil was less dense, it was expected to rise and form an emulsion. However, the oil chose to cling to the glass surface as it rose upwards. The experiment was redone by rinsing the measuring cylinder with silicone oil. Now, the oil rose up in the center in one or two tendrils, which did not break and kept pumping oil to the top. This method of spontaneous emulsification was hence abandoned. Finally, the oil was mixed with the 1% solution of NaCl, 1% each of a surfactant and nanoparticles. The mixture was hand shaken and stirred with a magnetic stirrer overnight. This process was thus used to make emulsions. It gave drops that were larger than the colloidal range and usually at larger concentrations. As a result, the studies below are confined to the results of film thinning of the dispersion medium that intervenes between two large drops. This is the coalescence step. If we let emulsions stand, the then lower density liquid collects at the top. The collection times can go up to an hour if unstable, as seen by Sjöblom et al. (1990) for a 50:50 by volume model oil and water system containing a nonionic surfactant. This also the method practiced industrially. Kokal (2005) presents another issue involving surfactants, namely, ethoxylated and related surfactants can be used to demulsify naturally occurring crude emulsions. This is also echoed in some of the articles in Brochardt and Yen (1989).

In the work presented below, emulsion stability of heavy oil has been explored over many emulsifiers. Although some work with heavy oils are reported, we believe that we present here the first overall view of the role of emulsifiers for a heavy oil. Because of the high oil concentration and large droplet sizes, it is the emulsifier that should control emulsion stability. It is the effectiveness of the additives in phase separation, that are being considered. Some general conclusions are expected which are of value. Mechanisms are only suggested which although reasonable, will take further work to prove that those apply.

Experiments

Crude from A-Hauser, Kansas, of API gravity 19.9º/specific gravity of 0.9340 and viscosity of 650 mPa.s, all at 23°C was used. Nanoparticles were purchased from Sigma Aldrich and used as supplied. Aluminum oxide particles were < 50 nm in diameter, and silica had a nominal diameter of 12 nm. The crude oil was A-Hauser as mentioned earlier. However, when a second sample was brought in, it showed a viscosity of 3000 mPa.s. It was assumed that as the oil had been left outside in a drum through the winter, some wax may have precipitated and was not dissolving under room condition. Consequently, the oil was placed in an oven at 80ºF for 30 minutes and on cooling reached a viscosity of 750 mPa.s and 23º API, very close to the previous sample of 650 mPa.s and 19.9º API. Water used had 1% NaCl. The surfactants were used as purchased: IGEPAL CO-530 (Stepan), cetyl ammonium bromide (CTAB) from Calbiochem and sodium dodecyl sulfate (SDS) from

Aldrich, and used as received. That is, simplest of nonionic, cationic and anionic surfactants were used. SDS does have the common sulfonate group, both SDS and CTAB have hydrocarbon chain lengths commonly encountered. The nonionic surfactant has the ethoxy group mentioned earlier. Water to crude oil volumetric ratios were taken to be 1:9, 2.5:7.5, 5:5, 7.5:2.5, 9:1. Hence the batches were:

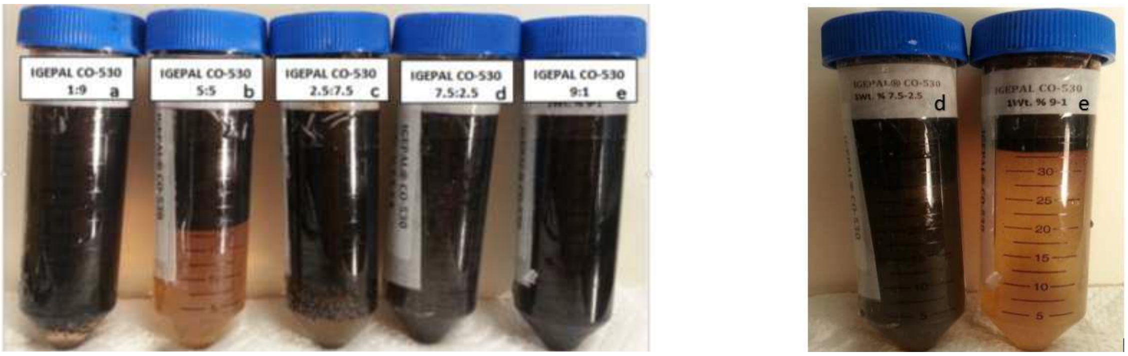
1) Water: oil 1:9, 2.5:7.5, 5:5, 7.5:2.5, 9:1 v/v, water containing 1 wt% NaCl, 1wt% IGEPAL CO-530
2) Water: oil 1:9, 2.5:7.5, 5:5, 7.5:2.5, 9:1 v/v, water containing 1 wt% NaCl, 1wt% SDS
3) Water: oil 1:9, 2.5:7.5, 5:5, 7.5:2.5, 9:1 v/v, water containing 1 wt% NaCl, 1wt% CTAB
4) Water: oil 1:9, 2.5:7.5, 5:5, 7.5:2.5, 9:1 v/v, water containing 1 wt% NaCl, 1wt% IGEPAL CO-530, 1 wt% Al_2O_3 nanoparticles
5) Water: oil 1:9, 2.5:7.5, 5:5, 7.5:2.5, 9:1 v/v, water containing 1 wt% NaCl, 1wt% IGEPAL CO-530, 1 wt% SiO_2 nanoparticles
6) Water: oil 1:9, 2.5:7.5, 5:5, 7.5:2.5, 9:1 v/v, water containing 1 wt% NaCl, 1wt% SDS, 1 wt% Al_2O_3 nanoparticles
7) Water: oil 1:9, 2.5:7.5, 5:5, 7.5:2.5, 9:1 v/v, water containing 1 wt% NaCl, 1wt% CTAB, 1 wt%, Al_2O_3 nanoparticles
8) Water: oil 1:9, 2.5:7.5, 5:5, 7.5:2.5, 9:1 v/v, water containing 1 wt% NaCl, 1wt% SDS, 1wt% SiO_2 nanoparticles
9) Water: oil 1:9, 2.5:7.5, 5:5, 7.5:2.5, 9:1 v/v, water containing 1 wt% NaCl, 1wt% CTAB, 1 wt% SiO_2 nanoparticles

Every batch was put on a tube rack and maintained in a water bath at 24°C. Phase separation took place rapidly and if phase separation did not happen in 4 hours, the temperature was raised to 40°C.

Results and Discussion

The breaking of emulsions begins with the flocculation step with small droplets colliding with each other. This step does not happen here because the concentration of the dispersed phase is large, the repulsive electrostatic forces between droplets are weak due to high NaCl concentration, and drop sizes are large. Even if we had started with fine emulsions, this step would be over very soon because of the above two reasons. In the next step, when the two droplets that have approached one another the intervening thin film drains. This drainage is retarded by surface active materials and by high viscosity in the thin films. At latter times the droplets are sufficiently large to show sedimentation or creaming, but the coalescence may not may not have completed.

With this short overview, we look at our systems. Present samples looked homogeneous. The phase separation took place almost instantaneously. The aqueous phase was often tea colored and sometimes in the oil phase two regions were seen, one black and the other dark brown but with no marked interface. All photographs shown below were taken after 24 hours with **Figure 1** as the only exception.



(a) (b)

Figure 1—(a) 1% nonionic surfactant in 1% NaCl, from left to right, low water to high water. All at 25°C. (b) The two at high water contents at 40°C. One apparently remains stable and the other fully destabilizes.

IGEPAL CO-530 is a nonionic surfactant (nonyl phenol ethoxylate C_9E_6). The ethoxy groups are polar but lose that property when the temperature is raised. Shown in Figure 1(a) are IGEPOL CO-530 with water and oil (batch 1). It is very surprising as to how small amounts of oil is able to ingest such large amounts of water. It is being assumed that one has w/o system if the emulsion appears black. On heating to 40°C, one of the samples with a high water content (7.5:2.5) did not break but the one with a higher water content (9:1) did break as shown in Figure 1(b). All others broke. Consequently, we find significant cases where oil is very active in emulsifying because heavy oil contains asphaltene reaching upto 15%. It is often suggested that asphaltene adsorb on the surface droplets making them stable (El-Sayed Abdel-Raouf 2012; Tchoukov et al. 2012). Thus, a total of a large amount of emulsifiers may explain why so much water can get ingested into the oil. In case of SDS (batch 2), no stable emulsion is found. The water is pristine as seen in **Figure 2**. In **Figure 3** no stable emulsion is formed (CTAB batch 3), but the water is not clear, tea colored at high water content and becomes very dark at low water content. This coloring is probably due to a secondary haze (Suzuki et al. 1984) which is made out of very small droplets. Now, the heavy oil is acidic, so that the oil molecules are anionic. If a cationic surfactant and an anionic surfactant are brought into contact, liquid crystals are formed. It is possible to surmise that some association of this kind happens here in presence of cationic surfactants as they form ion pairs with the oil molecules. These adsorb on the surfaces of the very small droplets making them stable. Suzuki et al. (1984) showed that the stability of the secondary haze in their case was due to small amounts of liquid crystal phase present at the interface.

Figure 2—1% SDS in 1% NaCl at 25°C, all systems are quite unstable.

Figure 3—1% CTAB in 1% NaCl at 25°C, all systems are unstable with some significant differences from SDS. The water: oil ratio in this figure has been reversed.

We discontinue referring to the batch numbers below as the figure numbers and batch numbers are the same. We find that only the nonionic surfactant can form stable emulsion which destabilizes at 40°C. It should be mentioned that at neutral pH, SiO_2 has a small negative surface charge (Sahai 2002) and Al_2O_3 has a small positive surface charge (Berg et al. 2009). Consequently, CTAB will adsorb on SiO_2, with their head groups and the outward pointed tails will make them hydrophobic, thus the cluster will be insoluble in water where they can precipitate but the ensemble can be oil soluble. Conversely, Al_2O_3 has a small positive charge and SDS head groups will adsorb on the surface. It should be mentioned that heavy oil has a significant acidity and the acid groups will be active as discussed earlier.

IGEPAL CO-530 with Al_2O_3 showed least stability at 25°C at water: oil ratio of 7.5:2.5. At 40°C all cases became unstable showing full or nearly full phase separation as shown in **Figure 4**. For IGEPAL CO-530 and SiO_2, the whole batch formed stable oil continuous emulsions. The emulsions could not be broken at 40° to even 60°C. This is shown in **Figure 5**.

In general, we expect a smooth change in emulsion stability as we go from low water to high water. However, for IGEPAL CO-530, we find a maximum or a minimum at some intermediate value of water to oil ratio suggesting a second mechanism at work due to asphaltene. In Figure 5 emulsion stability is overwhelming and there is no apparent intermediate water to oil ratio of least stability.

All the stable systems above appear black and they have been assumed to be w/o type. If oil is the continuous phase, its drainage rate will be very slow because of its very large viscosity even at 60ºC. In a model for percolation threshold of random non-overlapping distribution of spheres of same diameters, Park and MacElroy (1989) find that the continuous phase becomes segregated only at 96.5 volume percent of water, the dispersed phase. Thus, 90 percent water could be ingested into oil and still remain oil continuous, explaining why even this case is stable in Figure 5.

Figure 4—IGEPAL CO-530 with Al_2O_3 at 40°C where emulsions broke fully.

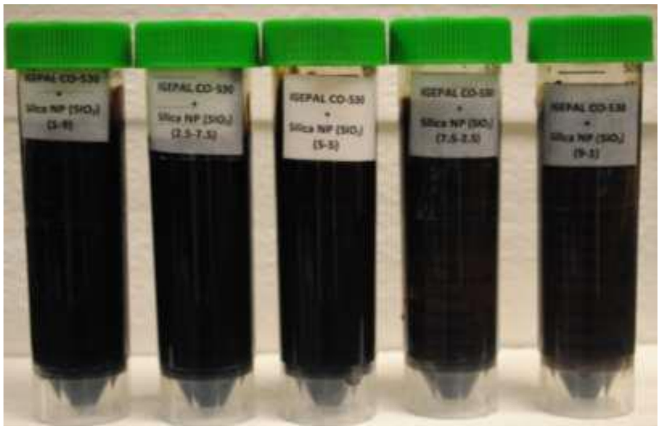


Figure 5—IGEPAL CO-530 with SiO_2 at 25°C where the emulsion did not break at 40º, 50º and 60°C.

The question arises as to why only systems with nonionics appear to be oil continuous. Ionic surfactants lie at oil-water interface with their hydrocarbon tails in the oil and charged groups in water. Because of the charged head repulsion the interface curves outwards with oil inside and water outside. That is such surfactants favor o/w. However, the nonionics show a more flexible interface and for instance do not need alcohols as cosurfactants to form microstructures of different shapes that ionic surfactants do (Miller and Neogi 2008). This could help to explain why nonions have a bias towards w/o compared to ionics.

Figures 6 and **7** show SDS and CTAB respectively with Al_2O_3. Both show unstable emulsion as observed from increasing water content. CTAB shows a brown haze (secondary haze) as noted earlier. Similarly, the cases with SDS and CTAB are shown respectively in **Figures 8** and **9**. They are unstable but both have precipitates at large water content as shown there.

Figure 6—SDS with Al_2O_3 where all systems are unstable at 25°C.

Figure7—CTAB with Al_2O_3, all unstable at 25°C.

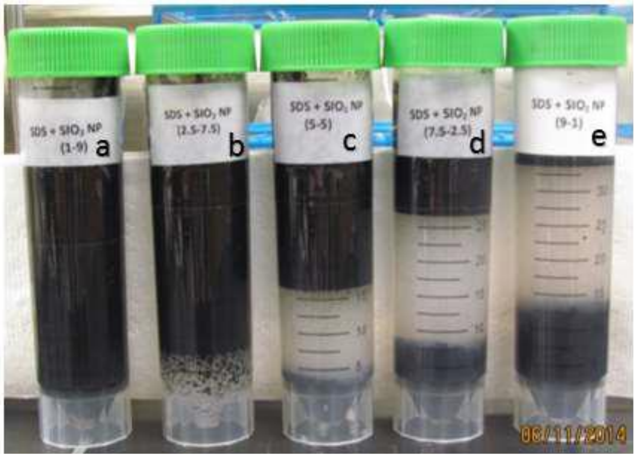


Figure 8—SDS with SiO_2 at 25°C. Notice the settled precipitate on the right.

Figure 9—CTAB with SiO_2 at 25°C. Notice the settled precipitate on the right.

As mentioned earlier, the combinations of constituents are large and we have aimed at breadth rather than depth. It looks like a more important feature as the starting point. With this cautionary remark, we make a few observations below. With the needs of an oil producer in mind, we note that CTAB produces secondary haze. These are very difficult to coalesce and leads to the conclusion that cationic surfactants should be avoided. SDS leads to unstable emulsions with no secondary haze. Hence, anionic surfactants appear to be very suitable. Emulsions with nonionic surfactants break with increasing temperatures. There are exceptions, particularly, where nanoparticles are present but their presence is not necessary. We have suggested based on available literature, that asphaltene plays a role in those cases.

Nanoparticles themselves do not seem to be very active, accept in the nonionic systems mentioned above where the range of the anomalous behavior is increased. Hydrophobic nanoparticles were not used because of their cost and that they are not commonly available.

If the heavy oil is extracted under hot conditions (such as by using steam) this is the best time to separate the two phases under sedimentations. Additives do not make much difference, except for cationic surfactants which give rise to secondary haze, or nonionic surfactants near HLB.

Conclusions

We have covered a very large area of heavy oil emulsions containing additives and found that phase separation was best in presence of the anionic surfactant. Even then the separation was not complete. The problem lies in the large viscosity of the oil. Other additives could prevent reasonable degrees of phase separation, where the mechanisms could be explained by existing literature.

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Conflicts of Interest

The author(s) declare that they have no conflicting interests.

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