



Foaming Characteristics of Vinyl Acetate-Acrylic Acid (VA-AA) Copolymer-based Surfactants

Shubham N. Borole, Gerard T. Caneba*

Department of Chemical Engineering Michigan Tech University Houghton, MI 49931 USA

*Corresponding author (Email: divankovic@andersonuniverseity.edu)

Abstract – Foaming is an important characteristic of surfactants that is proposed to be utilized for oil recovery and oil herding purposes. In this paper, comparative laboratory studies of foamability and foam stability studies of in-house vinyl acetate-acrylic acid (VA-AA) copolymer-based surfactants with commercial counterparts are made. Foam stability and foam volumes are measured using the Ross-Miles static foam-height test method, for surfactant-water systems. The same set of tests is also done with surfactant-water-oil formulations, with the aid of a double-sonication method of oil dispersion in the water-surfactant mixtures. Results indicate that in-house vinyl acetate-acrylic acid (VA-AA) copolymer-based surfactants possess the best foam stability behavior over commercial counterparts, and it has also proven to have superior foamability behavior compared to typical anionic surfactants and most nonionic surfactants.

Keywords – Vinyl Acetate-Acrylic Acid Copolymer, Surfactants, Foam Stability, Foamability, Ross-Miles Method, Double-Sonication Method

1. Introduction

Surfactants find a wide range of uses based on their unique properties, particularly their influence on interfacial surfaces. Few examples are enhanced oil recovery in petroleum industry, engine oil separations in automotive industry [1], and detergents in textile industry and as a floating agent in ore extraction processes. Because of their distinctive macromolecular structure, they are able to adhere or adsorb on interfaces, which result in lesser application of energy for separation of the phases.

Specific properties of surfactants are due to their typical molecular structure which comprises of two different and operationally opposite structures, called as lyophobic or the hydrophobic group and lyophilic or hydrophilic group. The hydrophobic group is the tail part and hydrophilic is the head part of a typical surfactant structure. In immiscible aqueous solutions, such structures successfully remain attached to both phases according to the affinity of the group structure. For example, where water is the solvent, the hydrophobic part is responsible for distortion of the water phase causing increase in free energy of the system, hence requiring less work to be done on the system for phase separation. At the same time the hydrophilic part remains attached to the water phase preventing the surfactant to be excluded from the system [1].

Hydrophobic groups in surfactant molecules are usually long chain hydrocarbons, whereas the hydrophilic part relies

on strong specific interactions, such as polar, hydrogen-bonded, and ionic groups. There are four basic classifications of surfactants based on the nature of the hydrophilic head. The following classifies commercial surfactants based on the following functional groups:

- Anionic - The hydrophilic head part is a negatively charged group.
- Cationic - The hydrophilic head part is a positively charged group.
- Nonionic - The hydrophilic part does not have any charge.
- Zwitterionic - The hydrophilic part may have both positive and negative charges [2].

Further classifications are also available based on nature of attached hydrophobic groups, and even the long-range macromolecular architecture of both hydrophilic and hydrophobic groups.

Current research focusses on comparing foaming characteristics of vinyl acetate-acrylic acid (VA-AA) based copolymer surfactants with other commercially available surfactants. Typically, the so-called B6-1 VA-AA tapered block copolymer surfactant used in this work (Figure 1) has the following CAS registry [3]:

- CAS # [903900-50-5]
- Type of polymer – a reduced regulatory requirement (RRR) polymer
- CAS Name of polymer: 2-Propenoic acid with ethenyl acetate, hydrolyzed

• Common Name: Partially hydrolyzed vinyl acetate-ammonium acrylate copolymer

• Molecular Structure:

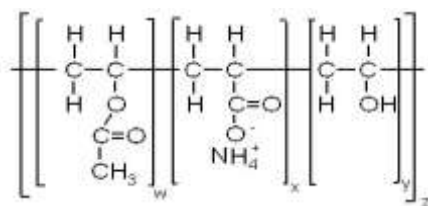


Figure 1(a). Molecular structure of the B6-1 VA/AA tapered block copolymer surfactant that was produced from the FRRPP process



Figure 1(b). Linear bead model of the Vinyl Acetate (open beads) and Acrylic Acid (filled beads) segments that make up the tapered B6-1 VA-AA block copolymer. Bead numbers are drawn to scale to approximate molecular make-up of the blocky VA-AA material with 6 wt % AA segments. Other VA-AA-based in-house copolymer surfactants used in this work have similar structure to B6-1.

Based on prior foam formation and stability work by Caneba using an atmospheric test method [3] and the Miles-Ross method [4], nonionic commercial surfactants, such as Igepals and Triton X-155, have performance characteristics that are close enough to those of in-house B6-1 VA-AA-based surfactants for applications in light crude oil. This work further makes the comparisons using exclusively the Miles-Ross method with more extensive statistical data in the presence light crude oil. It should be noted that the above-mentioned prior efforts by Caneba indicate much better foam performance characteristics of in-house B6-1 VA-AA-based surfactants compared to commercial nonionic surfactants, when done in the presence of heavy crude oil. Finally, it should be noted that nonionic surfactants are much more expensive than anionic surfactants; the in-house B6-1 VA-AA-based surfactants has recently been estimated to involve a bulk sale price of \$1.29/lb [5], which is close to bulk price range of anionic surfactants.

2. Foamability and Foam Stability

Oil spills have been a point of concern for government and industries involved in consumption of oil and petroleum products. Because of the irreplaceable uses of oil and oil products, it has been very prominent among all sectors of industry covering transportation, plastics, fertilizers and many more. All these applications involve transportation of oil using railways, roadways, ships and pipelines which sometimes makes it difficult to control accidents leading to oil spills[6]. The crude oil for most part contains hydrocarbon compounds ranging from low to high molecular weights. Some hydrocarbon groups that might be present are olefin, aromatics, saturates and polar compounds. Properties such as viscosity, density, specific gravity, solubility, flash point, pour point and vapor pressure become important in oil spill applications.

Recent oil spills that occurred are Yellow Stone River spill at Montana, Gulf Oil spill of Mexico and Enbridge in Michigan in 2011, 2010 and 2010 respectively.

One of the characteristics of surfactants is foaming which is utilized for recovering oil from oil wells or oil spills. Foams are created because of pressure applied through a gas causing the film of liquid to expand. This property of the liquid of the film is called film elasticity and is required condition for foam production. Surface Active agents or surfactants depending on their structure have different foaming characteristics. But there is no direct correlation because, distinct features such as efficiency of the surfactant, maximum foam height obtained with given concentration, and also the foam height measured at time zero and after particular amount of time. Measurement of foam heights at different times gives an idea of foam stability[7].

Surfactants are usually added to water based two phase systems with interfaces. Interface is a boundary layer between two immiscible phases and possesses interfacial energy holding the two phases. Application of surfactants to such boundaries helps in reducing the interfacial tension, thereby making easier to form foams[8].

The most widely used procedure for foam height measurement is the Ross Miles Pour Test Method, which is also approved by ASTM as a standard method[1]. The core of the procedure involves dropping of a known concentration of a surfactant solution from a particular height on to the same solution and measuring the height of the foam produced. Specially designed Ross Miles apparatus is used for this purpose. Several other methods have been formulated to measure foaming characteristics. A shaking method was suggested by C. Stiepel, which was more dependent on the shaking style of the experimenter. H. J. Christmann proposed use of air bubbling to achieve foaming, which was also followed by C. W. Foulk and J. H. Miller with a minor change[8]. Current method that has been used follows basic concept of

free falling of the liquid solution and can be correlated to actual surfactant application scene, which makes it a good choice for testing foaming ability. The Ross Miles Pour Test uses the force applied on the solution through the kinetic energy of the falling droplets of the solution. Foam stability can be described as ability of the foam formed to sustain itself against its breakdown or collapse which might be caused because of various factors like increase in bubble size, movement of accompanying fluid or gas/liquid mixture, weakening of bubble walls or rupture due to gravitational forces of overhead foams. Presence of surfactant molecules can play an important role in strengthening bubble walls against factors described above. For example, such molecules can increase bulk viscosity of the bubbles helping it to withstand additional weight and pressure caused by flow of fluids[9]. A very general method to determine foam stability is to calculate half-life of the foams. Half-life of foams can be defined as time taken by generated foam to reach half of its initial volume. The generation and calculation of foam height/volume is done by static foam tests, such as the Birkman and Ross-Miles protocols[10]. The Ross-Miles foam height test is used in further experiments of current work to calculate half-life values of foams generated by various types of surfactants.

Surfactant foams have found immense importance in oil

recovery processes. After the primary oil recovery treatment which volumetrically capitalizes only 5-20% of total oil via water flooding, secondary and tertiary treatments find scope to recover most of remaining oil to the surface[3]. Sometimes primary and secondary treatments both involve water flooding which still accumulate 35% of the total Oil-in-place[9]. Further removal is facilitated by use of chemical flooding where surfactants are injected along with the fluid for effective removal of crude oil. Different surfactants have different roles to play. Addition of surface active agents causes increase in wettability of the porous rock surfaces conducting oil displacement. Also, it causes drastic reduction in surface tension at water-oil interface leading to spontaneous emulsification. Hence the oil droplets come together easily and can be pushed easily towards production wells.

The conceptual explanation of water/chemical flooding by five-spot pattern is attempted in Figure 2 below. The outer injection wells are used to inject water/brine/chemical to push the crude oil towards the inner production well. In case of waterflooding mixture of oil and water are collected from the production well and later subjected to a simple gravity separation method. However during chemical flooding where surfactants can be used, emulsified oil is collected from the production wells. Hence demulsifying agents find applications in such case for crude oil separation.

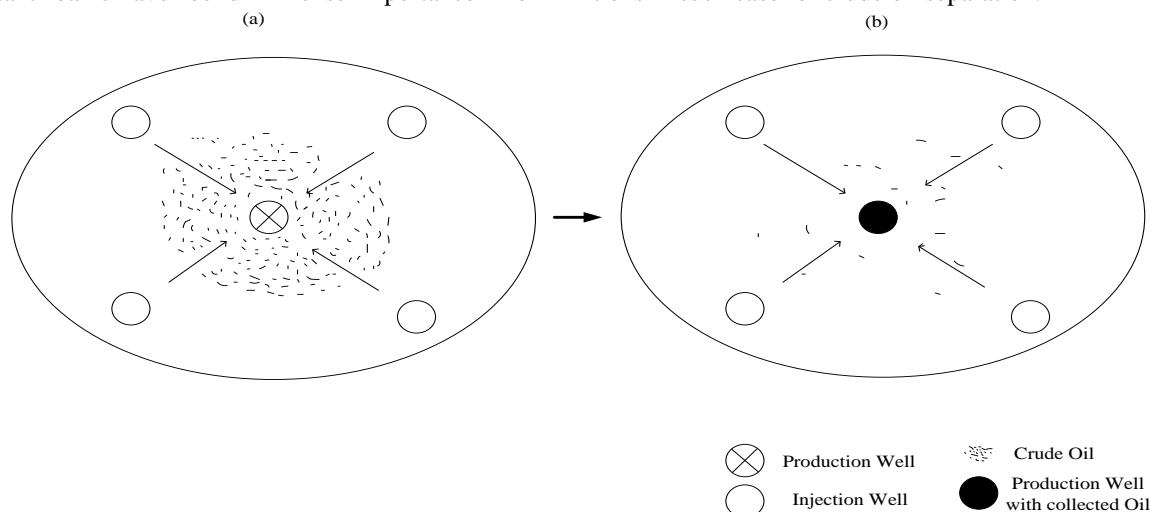


Figure 2: Description of a five-spot pattern injection and production wells for crude oil displacements in secondary/tertiary treatments.

It can be seen that at the end of treatment crude oil particles are displaced towards the production wells. Although different results are obtained during waterflooding and chemical/surfactant flooding. Use of surfactant allows formation of foams which are capable of reducing surface tension at rock pores leading to effective movement of oil. Higher stability of foams is preferred during such operations for effective displacement, because continuously-increasing injection pressure cannot be applied indefinitely. Hence, it is evident that longer lasting foams will have a very productive impact on oil recovery procedures.

Emulsification and Dispersion:

After the conduction of the foam height tests with water, foam generation in the presence of dispersed crude oil was measured. Zuidgeest and Huettel[11] used a sonication technique for crude oil dispersion to prove that dispersions facilitate penetration of oil components into saturated sands. Vikingstad and coworkers [12] used 1-5wt% of different crude oils in synthetic sea water for static foam tests. For current static foam tests using Ross-Miles apparatus in the presence of crude oil, 5wt% of crude oil was added to 1wt% of surfactant solution in water. This solution was exposed to ultrasonic waves to disperse fine oil droplets throughout the mixture.

For a large variety of immiscible solid-liquid or liquid-liquid systems, ultrasonics can be applied successfully in laboratories and industries. Other options are mechanical mixing at high rates or micro-fluidizers. However, because ultrasonic homogenizers are relatively inexpensive, easy to clean and provide similar intensities of turbulence, they appear more feasible for usage. The primary mechanism behind such treatments is cavitation. Cavitation can be basically described as expansion of newly formed or existing bubbles, and further collapse of such bubbles under high pressure [13].

Ultrasonic horns and baths can be used for these purposes. But the amount or size of the batch is limited. Also it has been suggested that ultrasonic homogenization is more appropriate for small size batches [13-15]. The reason behind this can be understood as in ultrasonic mixing, the samples have to be kept close to the transducer source whether it is a bath or a probe (horn). However, high capacity sirens and different types of electromagnetic or piezoelectric transducers are also used on industrial scale.

Emulsifier types of surfactants play an important role in formation of stable emulsions during homogenization processes. The type of emulsifier can play a role in resultant oil-in-water or water-in-oil emulsions. According to Bancroft [15-16], the molecules of the emulsifying agent will reduce the surface tension between oil and water by formation of a thin film. The interfacial tension between oil and the film compared to that of water and the film will be different. If the surface tension between oil and the film is lower, then an oil-in-water emulsion is formed, and vice-versa. As generally assumed, it is believed by many that water soluble surfactants will cause formation of oil-in-water emulsions and similarly oil soluble surfactants will help formation of water-in-oil emulsions.

Double sonication technique has been used previously for efficient dispersion of carbon nanotubes (CNTs) [17]. A similar approach was followed for emulsifying crude oil in water to prepare a homogeneous mixture. This method has proved to save significant amount of time as compared to using any one of the two given ultrasound sources. Apart from this, use of blenders or mixers also does not homogenize crude oil solutions in water. Moreover such methods tend to create unwanted foams which are undesirable. As this system proved efficient for CNT dispersions, comparatively better efficiency of double sonication system was presumed and no such readings like time taken for dispersion was noted. Nevertheless as expected, the double sonication technique was more effective and less time consumption as was observed during the experiments.

For displacement of oil in reservoirs, foams have been used prevalently by injection to water-surfactant slug. In foam displacement processes for enhanced oil recovery, the foam stability in presence of crude oil is an important factor [18]. For this purpose, different types of static tests can be performed as discussed previously to identify efficient foaming surfactant solutions. The Bikerman foam stability test and the Ross-Miles foam method are very prominent among the

techniques used to determine foam stability, especially in mining, brewing and detergent industries. This is mainly because these methods are simple to follow and the foam stability is based on foam height (easy to evaluate) instead of foam film thickness determination [19]. The Atmospheric Static foam test for foam volume against time was carried out for different surfactants in water in presence of crude oil by Caneba [3]. The test was carried out for comparative analysis of Vinyl Acetate-Acrylic Acid based copolymeric surfactant against commercially available surfactants. Mechanical shaking was done with 3ml of crude oil added to 10ml of 0.5% surfactant in water. A similar approach is followed to determine foam stability in presence of crude oil.

3. Experimental

3.1. Materials and Chemicals

Crude oil used in this work was light sweet crude from a Louisiana Gulf of Mexico oilfield. Commercial surfactants were obtained from various company sources, and vinyl acetate-acrylic acid-based copolymer surfactants were produced in-house through the FRRPP process [3], and 1 % by weight aqueous solutions were prepared for each surfactant (up to 300 ml) and stored in air tight containers.

3.2. Ross-Miles Method

For finding the foam heights for different surfactant solutions the ASTM procedure D-1173-53 (2001) entitled, "Standard Test Method for Foaming properties of Surface Active Agents" [20] was followed, which is also called as Ross and Miles test procedure. Setup and overall procedure for the use of the method with respect to surfactant-water mixtures are indicated elsewhere [4], and details include:

- The Ross-Miles foam test column that is manufactured from Pyrex 7740 or equivalent type 1 class-A borosilicate glass. It has a normal operating temperature of 230°C, and an intermittent extreme of 460°C. The manufacturing company does not specify a maximum operating pressure for this item due to varying conditions.
- The water bath system (model EX-500 from Neslab Exacal) that is operated at $50 \pm 1^\circ\text{C}$.
- The thermocouple reader that is manufactured by Omega Engineering, Inc., Type J, Model number 115JC.

For application of the Miles-Ross method with respect to surfactant-water-oil mixtures, the basic procedure is modified in following manner. The inner walls of the apparatus were rinsed with 50-ml 1 wt % surfactant, 5 wt % light crude oil, both in distilled water, to fill up the receiver. The reservoir was filled with 200 ml of 1 wt % surfactant, 5 wt % light crude oil, both in distilled water. The reservoir valve was opened and the mixture is allowed to be dropped from the top in the center of the liquid surface of the receiver mixture making sure it does not touch inner wall of the glassware. As soon as the reservoir was empty, the timer was started and foam heights were measured after every 30 seconds.

3.3. Double Sonication Method

The double sonication equipment system, shown in Figure 3 below, includes a Branson 1200 Ultrasonic Bath with dimensions of 154 mm x 140 mm x 100 mm (length x breadth x height). The bath was operated at 20 kHz frequency and 100-250 Watts power. The source of vibrations was from the

side walls of the chamber. The second ultrasonic source equipment is a Cole-Palmer ultrasound probe with dimensions of 13 mm x 53 mm (diameter x length). The instrument was operated at 20 kHz frequency and was run at 20-40% of 750W power. The sound waves are emitted from the tip of the probe.

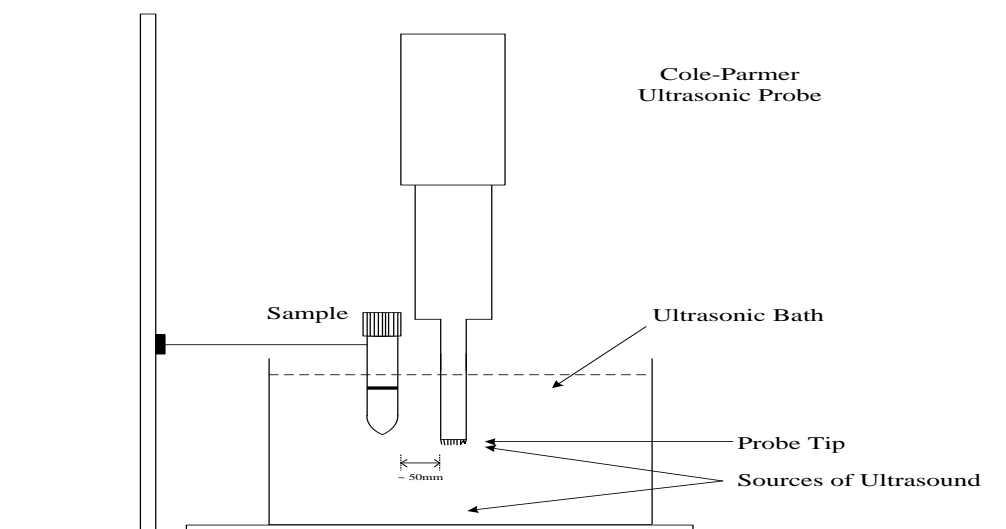


Figure 3: Double Sonication system for dispersion of crude oil in water showing best placements of ultrasonic probe and sample test tube.

From the Branson ultrasonic bath, ultrasound waves are emitted from the transducer which passes through the liquid (water) causing alternating high and low pressures in the liquid medium[21]. This suggests that the waves are longitudinal. Similarly, there is a piezoelectric transducer attached on

top of the Cole-Palmer ultrasonic probe. Vibrations are emitted through the titanium probe tip which propagates throughout the liquid medium from which the tip is immersed (Figure 4).

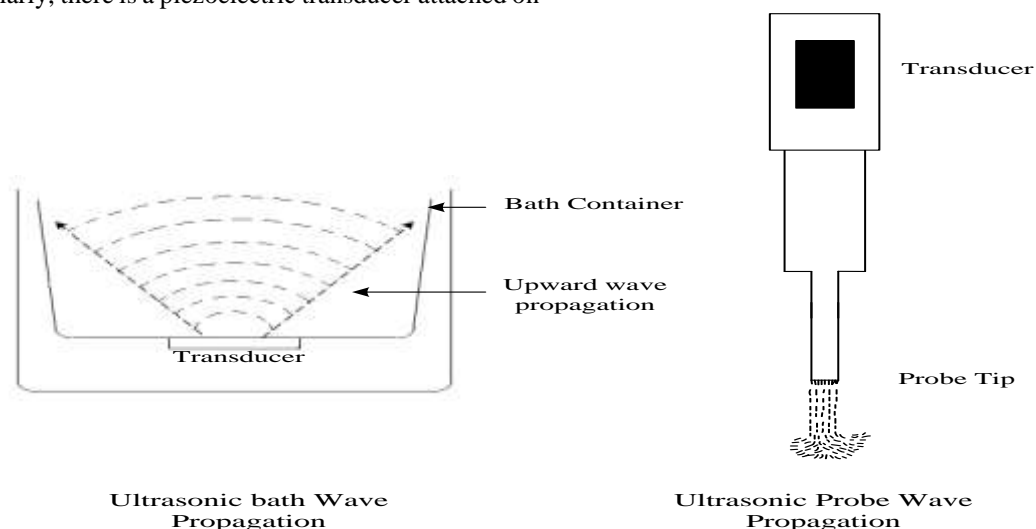


Figure 4. Wave propagations from the two ultrasonic sources in the double sonication system.

The ultrasonic bath is filled with 1500 ml of distilled water and the probe is immersed approximately one inch above the bottom surface of the bath chamber. Since the main aim of the apparatus is to homogenize the mixture, horizontal or vertical movement/adjustment of the probe is carried out as

required to get more effective ultrasonic cavitations in the sample. The sample is exposed to the probe via indirect method. In the indirect method, the sample is enclosed inside a beaker or a tube and then immersed in the bath. Additionally, the ultrasonic probe is immersed into the bath, not inside the

sample. But in case of direct method, the probe is immersed right inside the sample container or the sample can be directly poured in the bath.

The total sample size containing surfactant (1wt %) and crude oil (5wt %) in water is 300-400 ml. Based on the size of ultrasonic bath and frequency of the probe sonicator, the samples are dispersed in smaller quantities or sample sizes of 15-30 ml as per dispersibility of the surfactant added. Small batches of 15-30ml solutions are prepared. The sample test tube is shaken and immersed in the bath such that the surface level of the solution inside the tube matched the level of water in the ultrasonic bath, but not is below the water level of the bath. At the same time it is placed at a distance of approximately 50mm with respect to the ultrasonic probe. The ultrasonic bath was started by pressing the ON button on the sonicator. Furthermore, the ultrasonic probe is switched on and required frequency power (40%) is set. Safety ear muffs are worn mandatorily before switching on both systems. The system is sonicated constantly in batches for 30 min at power of 40%. Subsequent batches are started after providing minimum of 30 min to cool down the system. After every 4 hours of operation the distilled water inside the bath is replaced.

Because of the fact that the ultrasonic bath can be run overnight because of its low power levels, after double sonication is done the sample test tube is kept under ultrasonic bath only for emulsification. The position of the sample test tubes were required to be readjusted for getting better dispersion. Each sample test tube is homogenized and collected in separate containers as per the surfactant solutions. Final solutions are taken further to perform Ross-Miles foam height test.

4. Results and Discussion

4.1. Foamability and Foam Stability of Surfactant-Water Mixtures

Using the Miles-Ross method, foam heights vs time were obtained for different surfactant-water mixtures as shown in the Figures 5 and 6. Figure 5 is the plot of average foam height values out of a triplicate of readings (Foam Height vs time runs). In Figure 6, foam height readings for each of the surfactants are shown, with error bars corresponding to the highest and lowest foam height values vs time.

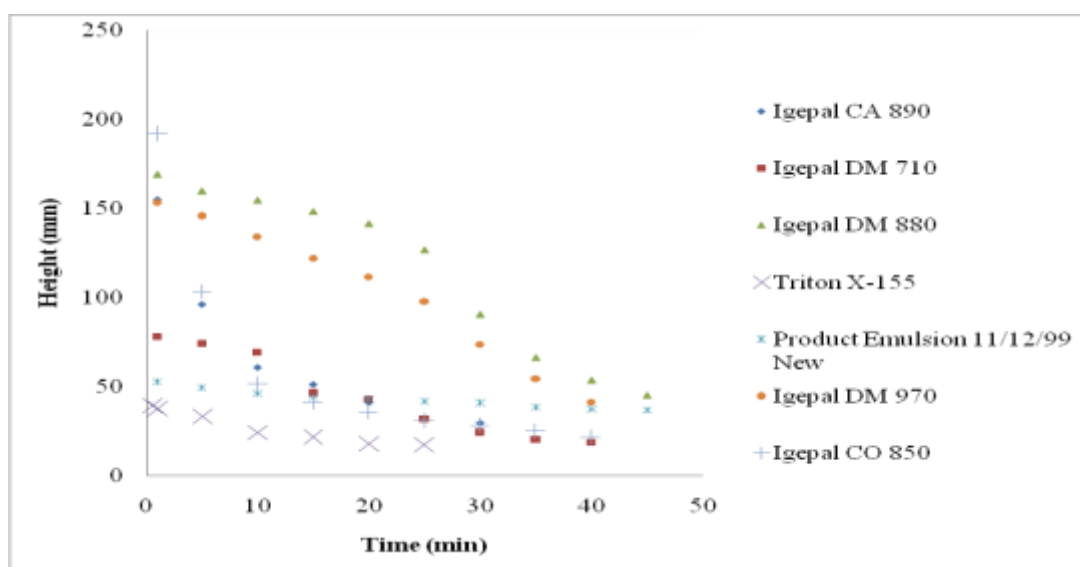


Figure 5. Average foam height from the Miles-Ross Method vs time for various surfactant-water mixtures.

Here we are considering two factors namely the volume of foam produced which is directly proportional to the height of the foam produced and the amount of time the foam is able to sustain successfully. As shown in Figures 5 and 6, Igepal CO 850, Igepal DM 880, Igepal DM 970 and Igepal CA 890 have good initial foam heights but they lack stability. Such surfactants can be considered for on field applications, but if the foam generated is not present for longer time the recovery becomes more difficult due to foam collapse. Additionally, a large proportion of the amount of applied surfactant can be unusable, because of adsorption onto rock surfaces in oilfield

injection or dilution in oil spill control applications. The only highly stable surfactant is the in-house VA-AA-based “Product Emulsion 11/12/99 New”, which can be visualized to stay for a longer time and utilized efficiently for subterranean oil recovery processes. Its lower foam volume can be compensated by its relatively lower cost per dry product weight. Also, in field applications involve use of spraying techniques at higher velocities, more stable foam formation is very important especially in oil-herding operations.

Surfactants Igepal DM 880 and Igepal DM 970 show very good foam heights for initial 25-30 minutes can be considered

good foaming agents. Although at longer times, foam volume levels are close to those of the in-house Product Emulsion 11/12/99 New surfactant, the drop in foam volumes of these commercial surfactants between the 0-35 minute and 35+ minute periods indicate less foam stability that can be detri-

mental to oilfield and oil-herding operations. Again, the relatively lower cost of the in-house VA-AA-based “Product Emulsion 11/12/99 New” surfactant can compensate for lower initial foam volumes.

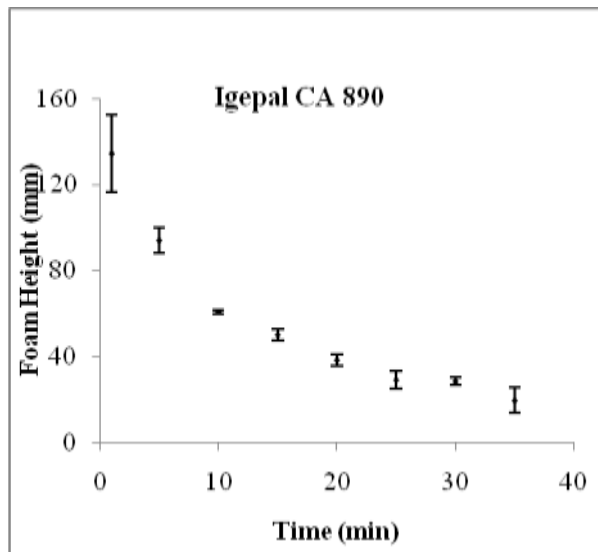


Figure 6(a). Foam height vs time for Igepal CA 890-water system using the Miles-Ross method at 50°C. The initial foam height is high but it decreases faster with time, showing less stability and relatively good repeatability after 10 minutes.

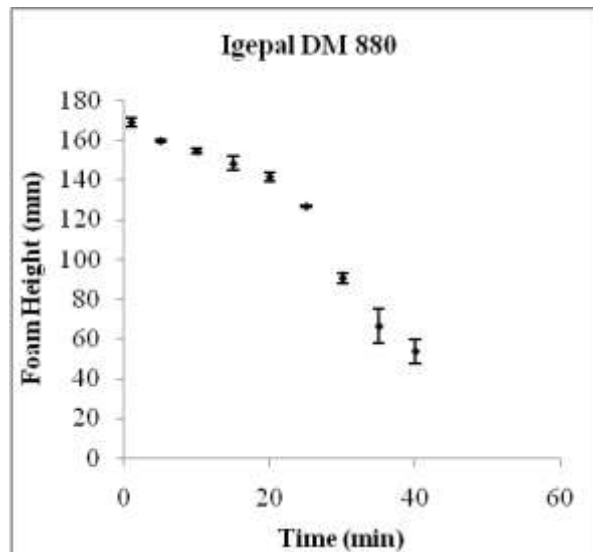


Figure 6(c). Foam height vs time for Igepal DM 880-water system using the Miles-Ross method at 50°C. The initial foam height and height is very good up to 25 minutes followed by a sharp drop, although foam heights are still maintained at good levels. Also, results show consistency in foam heights up to 30 minutes.

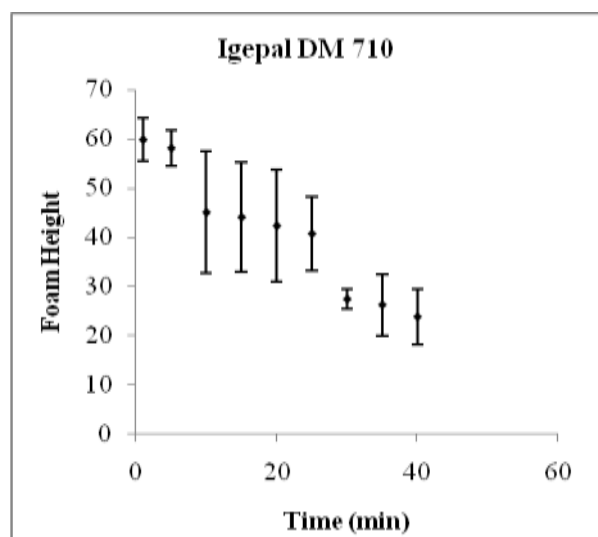


Figure 6(b). Foam height vs time for Igepal DM 710-water system using the Miles-Ross method at 50°C. Results below show poor foam stability, poor repeatability and relatively low foam heights after 30 minutes.

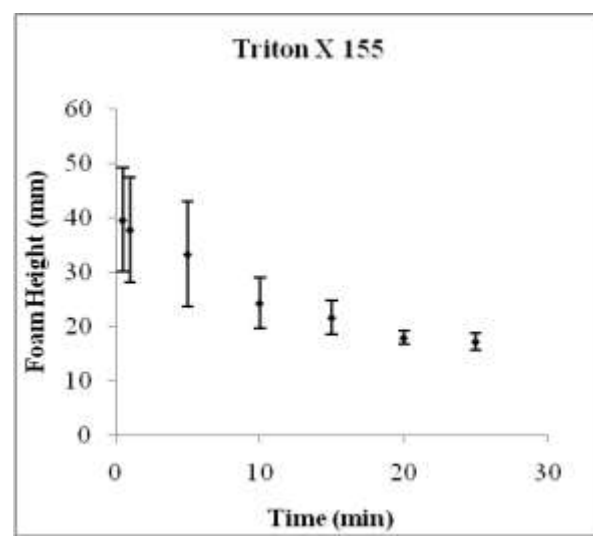


Figure 6(d). Foam height vs time for Triton X 155-water system using the Miles-Ross method at 50°C. The results below show relatively poor foam heights and foam steadiness at early times.

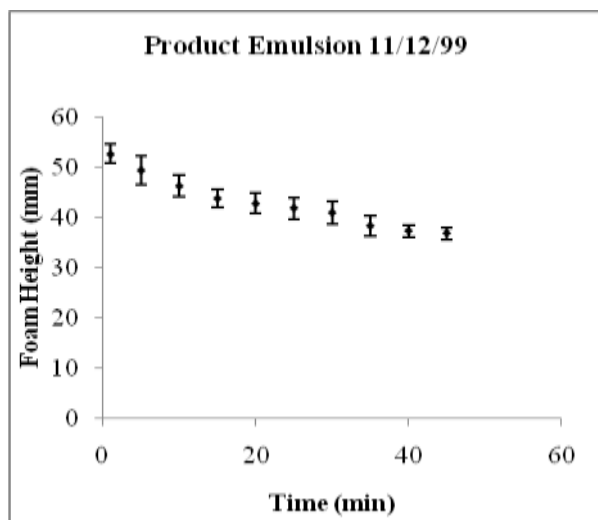


Figure 6(e). Foam height vs time for “Product Emulsion 11/12/99 New”-water system using the Miles-Ross method at 50°C. The initial foam height is average, but the surfactant shows consistently high stability even at longer times.

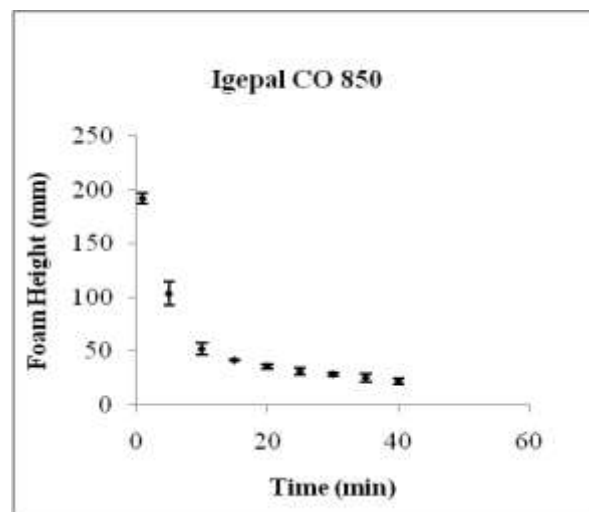


Figure 6(g). Foam height vs time for Igepal CO 850-water system using the Miles-Ross method at 50°C. The initial foam height is relatively high, but the surfactant shows poor stability as there is a sharp slope reduction after 10 minutes.

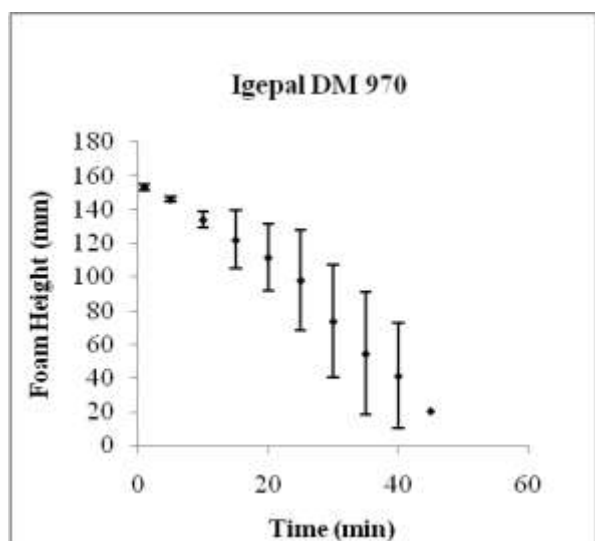


Figure 6(f). Foam height vs time for Igepal DM 970-water system using the Miles-Ross method at 50°C. The results show very good initial foam heights and repeatability, but relatively poor foam stability and repeatability after 10 minutes.

In order to determine stability of foams produced during the tests, half- life values based on previously of foam heights vs time were also calculated using two approaches.

Half Life Definition: The time at which the height was equal to half of the initial foam height is termed as half-life of the foam.

Plotting H/H_o vs $\ln(t)$ vst. The $\log t$ value at $H/H_o = 0.5$ was found as $\ln(t_{1/2})$ and $t_{1/2}$ was found by taking the inverse natural logarithm [7].

Sample calculations for Igepal CA 890 are shown below.

First, averageFoam Height vs time was plotted (Figures 5 or 6(a)), and $t_{1/2}$ was found at $H/H_o = 0.5$.

$t_{1/2}$ = Time at which Height = $155.133/2 = 77.6$ mm in Figure 6(a).

Thus, $t_{1/2} = 7.64$ min

Secondly, the data was nondimensionalized and graph of H/H_o vs $\ln(t)$ was plotted. A fairly straight line will be obtained based on which $\ln(t)$ will be found at $H/H_o = 0.5$; thus,

$\ln(t_{1/2}) = 0.8832$, and $t_{1/2} = 7.64$ min

Similarly $t_{1/2}$ values of all remaining surfactants were calculated from the graph or based on equation of trend line.

Table 1. Half-life values calculated for different surfactant solutions.

Surfactant	$t_{1/2}(\text{min})$		Average	Standard Deviation
	Approach 1	Approach 2		
Product Emulsion11/12/99 New	758.1	757.9	758.0	0.15
Igepal DM 880	32.8	31.6	31.6	0.83
Igepal DM 970	30.2	30.2	30.2	0.016
Igepal DM 710	23.7	21.8	21.8	1.3
Triton X 155	16.7	17.8	17.8	0.76
Igepal CA 890	7.64	7.64	7.64	0
Igepal CO 850	3.81	4.42	4.42	0.43

The above table can be displayed in form of chart as shown below for better comparisons of half-life values.

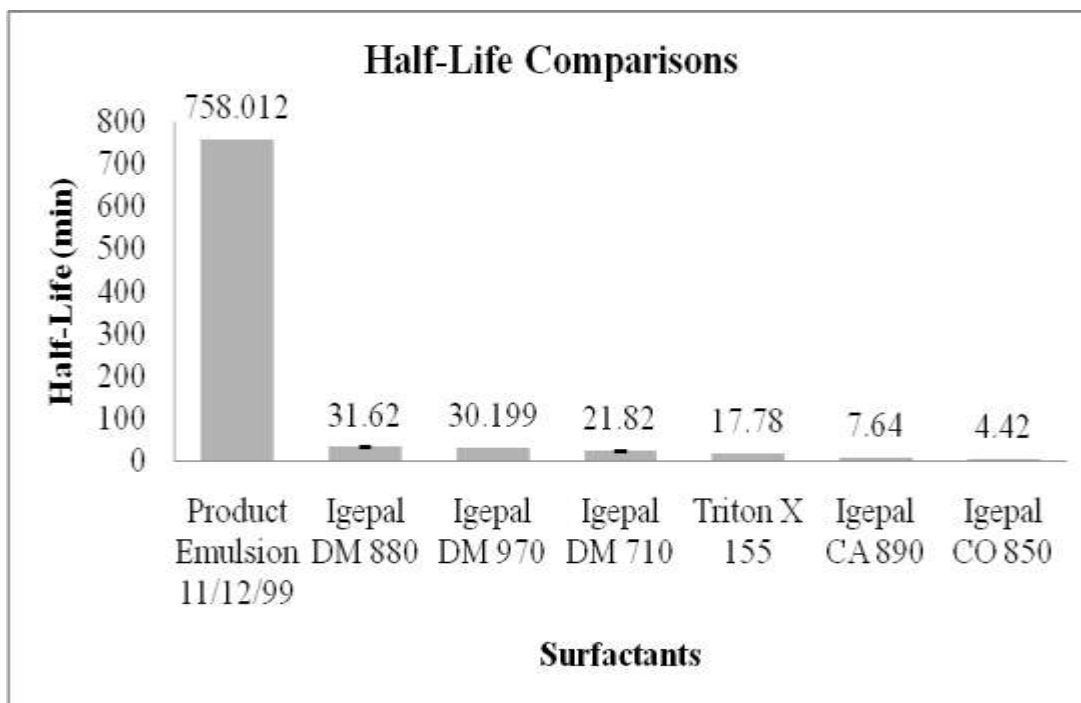


Figure 6. Half-life comparisons of various surfactants at given concentration in water as foaming agents.

Half-life values for Product Emulsion 11/12/99 New is relatively higher compared to any other surfactant solution for given concentrations suggesting very stable foams. This is an additional quantitative affirmation of the above-mentioned arguments from results of Figures 5 and 6.

4.2. Foamability and Foam Stability of Surfactant-Water-Oil Mixtures

After noting the foam heights for various surfactant solutions in presence of crude oil, the following data were obtained (Table 2). It can be seen that the foam volumes have significantly decreased after addition of crude oil in the solution. The above data can be shown graphically in Figure 7 below.

Table 2. Declining Foam Heights vs Time for different surfactants at given times with crude oil.

Time (min)	Avg. Foam Height (mm)				
	Igepal DM 710	Igepal DM 880	Triton X 155	Product Emulsion 11/12/99	Igepal DM 970
0.5	16.34	22.01	20.92	18.45	20.19
1	15.44	17.82	13.16	17.15	16.62
1.5	14.71	16.23	11.62	15.59	16.007
2	13.94	15.08	10.47	13.94	14.73
2.5	13.05	13.98	9.80	13.10	14.13
3	11.83	13.26	9.41	12.80	12.97
3.5	11.38	11.84	8.64	12.56	11.64
4	11.05	11.10	7.93	12.09	10.70
4.5	10.36	10.72	7.42	11.65	10.40
5	10.08	10.2	7.15	11	9.74
10	9.28	8.74	6.59	10.42	8.59

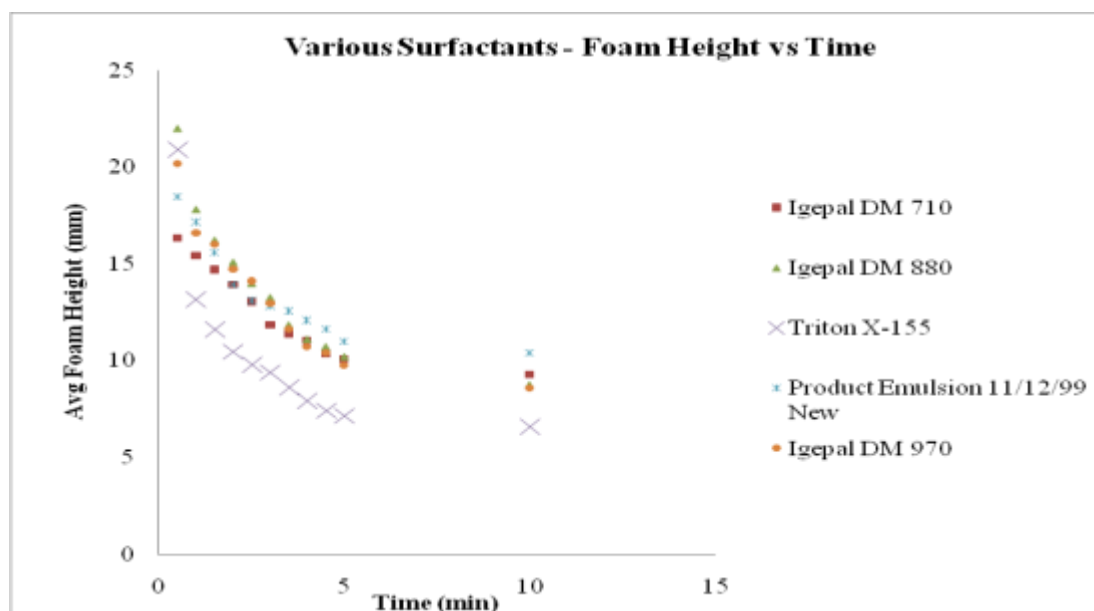


Figure 1. Combined chart showing changes in foam height vs time measurements using the Miles-Ross method for various surfactant-water-oil mixtures.

All surfactant-water-oil mixtures show a similar dropping trend in foam volume with time. Although the amount of foam generated is relatively less than those with surfactant-water mixtures (Figures 5 and 6), foam volumes with the in-house Product Emulsion 11/12/99 New surfactant mixtures are higher than those of other commercial surfactants tested.

Again Half-Life values were calculated to determine most stable foaming agent. Half-life values ($t_{1/2}$) were calculated from the time at which $H=H_0/2$, and results are shown in Table 3 and Figure 8 below.

Table 3: Average Half-Life values for tested surfactants with crude oil.

Surfactant	T-Half (min)
Product Emulsion 11/12/99	14.32
Igepal DM 710	12.416
Igepal DM 880	11.46
Igepal DM 970	11.29
Triton X 155	2.156

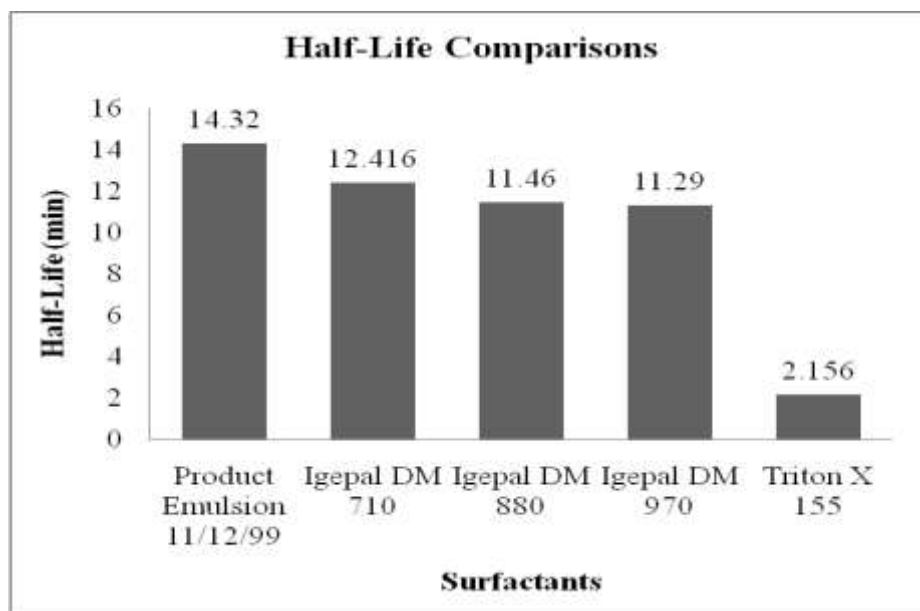


Figure 2. Half-Life comparisons for various surfactants with crude oil.

From above data and chart, “Product Emulsion 11/12/99 New” shows highest half-life value, but other foaming agents

also have very close half-lives, except for the Triton X 155. It can also be noted from the graph (Figure 8) that after 10 min

all the foam volumes become fairly stable, considering the foaming capability has been reduced considerably after addition of crude oil.

At the end of the report, we can see different set of experiments and procedures involved regarding surfactant interactions with oil and characteristic study of properties for oil recovery purposes. Firstly foam tests were conducted to primarily determine foam stability and also assessment of foamability. Better performances of lab-synthesized surfactants were observed after this step. Secondly, it was important to determine behavior of surfactants in presence of oil and again assess their performance in terms of foam stability. The static foam test used here was the widely used Ross-Miles test which includes dropping of 200ml of sample solution on 50ml of the same sample solution to produce foams. The immiscibility of crude oil in water makes it practically difficult to carry out this test. Since there has to be 200ml of crude oil-water mixture in presence of surfactant, crude oil being less dense stays on the top and effect of total crude oil cannot be counted. Hence, the samples were dispersed in surfactant-water mixtures using the double-sonication method. Furthermore, foam height tests were again conducted after making dispersed mixtures using double sonication technique. Oil acts as a defoaming agent in presence of foams and as expected the quantities of foam generated were reduced. Again, in-house B6-1 vA-AA-based surfactants were better performers in terms of half-life values.

5. Conclusions

After following the different set of experiments, it is clear that a comparative study has been made concerning various surfactants which can be classified into two main groups i.e. Commercial and in-house B6-1 VA-AA-based surfactants. In-house surfactants perform better in most experiments. However, the commercial surfactants were better in terms of the amount of foam produced or foamability, especially at early times. Foamability shortcomings can be compensated by the relatively low projected selling price of in-house VA-AA-based surfactants compared to more expensive non-ionic commercial surfactants.

Acknowledgements

The authors wish to acknowledge the MTU Center for Environmentally Benign Functional Materials (CEBFM) and Department of Chemical Engineering for underwriting the expenses associated with this project.

References

- [1] Rosen, M.J., & Solash, J., Factors affecting initial foam height in the Ross-Miles foam test. *Journal of the American Oil Chemists' Society*, **46**(8), 399-402 (1969).
- [2] Myers, D., *Surfactant Science and Technology*. John Wiley & Sons, New York (2006).
- [3] Caneba, G.T., Free-radical retrograde-precipitation polymerization (FRRPP): Novel concept, processes, materials, and energy aspects. Springer-Verlag, Heidelberg, ISBN 978-3-642-03024-6 (2010).
- [4] Caneba, G.T., & Dar, Y.L., Emulsion free-radical retrograde-precipitation polymerization (EFRPP) and related topics. Springer-Verlag, Heidelberg, ISBN 978-3-642-19871-7 (2011).
- [5] Tanghetti-Abrams, Z., personal communication as a result a chemical engineering senior design project at Michigan Tech University (2013).
- [6] Fingas, M.F., *The basics of oil spill cleanup*. 3rd ed., Taylor and Francis, Boca Raton, FL (2012).
- [7] Iglesias, E., Anderez, E., J. Forgiarini, A., & Salager, J.L., A new method to estimate the stability of short-life foams. *Colloids and Surfaces a-Physicochemical and Engineering Aspects*, **98**(1-2), 167-174 (1995).
- [8] Rosen, M.J., *Surfactants and interfacial phenomena*. 2nd ed., Wiley Interscience publication, New York (1989).
- [9] Schramm, L.L., *Emulsions, foams, and suspensions fundamentals and applications*. Wiley-VCH Imprint, John Wiley & Sons, Hoboken, NJ (2005).
- [10] Tyrode, E., Pizzino, A., & Rojas, O.J., Foamability and foam stability at high pressures and temperatures. I. Instrument validation. *Review of Scientific Instruments*, **74**(5), 2925-2932 (2003).
- [11] Zuidgeest, A., & Huettel, M., Dispersants as used in response to the MC252-spill lead to higher mobility of polycyclic aromatic hydrocarbons in oil-contaminated gulf of Mexico sand. *PLoS One*, **7**(11), (2012).
- [12] Vikingstad, A.K., Skauge, A. Høiland, H., & Aarra, M., Foam-oil interactions analyzed by static foam tests. *Colloids and Surfaces A: Physicochemical and Engineering Aspects*, **260**(1-3), 189-198 (2005).
- [13] Leong, T.S., Wooster, T.J. Kentish, S.E., & Ashokkumar, M., Minimising oil droplet size using ultrasonic emulsification. *Ultrasonic Sonochemistry*, **16**(6), 721-7 (2009).
- [14] Karbstein, H., & Schubert, H., Developments in the continuous mechanical production of oil-in-water macro-emulsions. *Chemical Engineering and Processing*, **34**(3), 205-211 (1995).
- [15] Sadurni, N., Solans, C., Azemar, N., & Garcia-Celma, M.J., Studies on the formation of O/W nano-emulsions, by low-energy emulsification methods, suitable for pharmaceutical applications. *European Journal of Pharmaceutical Science*, **26**(5), 438-45 (2005).
- [16] Brown, B., & Goodman, J.E., *High-intensity ultrasonics: Industrial applications*. Princeton, N.J. (1965).
- [17] Caneba, G.T., Dutta, C., Agrawal, V., & Rao, M., Novel ultrasonic dispersion of carbon nanotubes. *Journal of Minerals and Materials Characterization and Engineering*, **9**(3), 165-181 (2010).
- [18] Farajzadeh, R., Andrianov, A., Krastev, R., Hirasaki, G.J., & Rossen, W.R., Foam-oil interaction in porous media: implications for foam assisted enhanced oil recovery. *Advances in Colloid and Interface Science*, 183-184, 1-13 (2012).
- [19] Li, X., Karakashev, S.I. Evans, G.M., & Stevenson, P., Effect of environmental humidity on static foam stability. *Langmuir*, **28**(9), 4060-8 (2012).
- [20] 1173, A.D., Standard Test Method for Foaming properties of Surface Active Agents. *Annual Book of ASTM Standards*, **15.04**, 1-2 (2001).
- [21] Branson. Available from: http://www.emersonindustrial.com/en-US/documentcenter/BransonUltrasonics/Bench_Top_Cleaners/Branson-Manuals/mini_manual_12_00-2200-3200-5200-8200.pdf.