

# **Paper 1**

**Foam-oil interactions analysed by static foam tests**



## Foam–oil interactions analyzed by static foam tests

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### Abstract

There have been many foam field applications in the North Sea area in the recent years. One of the key questions of foam stability is the tolerance to presence of oil in the reservoir. In order to understand the influence of oil saturation on foam, more fundamental experimental studies have been performed. The static foam properties have been investigated by variation in surfactant concentration, amount of added oil, and variation in polarity of the oil phase. An alpha-olefin sulfonate surfactant is used in all experiments. The foam generation ability is connected with surfactant concentration. Foam is also formed with the AOS surfactant even below the critical micelle concentration. For the ionic strength area investigated, foam height for AOS solutions does not change, but foam tests with decane and crude oil are stabilized with lower ionic strength. The foam stability in the presence of alkane-type oils is related to the molecular weight of the oil molecule. The foam generation and stability is possibly connected to the surfactant ability to solubilize oil molecules. Alkanes that solubilize in the micelles seem to destabilize the foam. In crude oil systems more complex relations seem to be active. Alkanes with molecular weight higher than decane are too large to be solubilized in the micelles. The molecules will therefore have less ability to be transported out of the foam and oil seems to stabilize the foam. We have used a multivariate analysis to identify the most important factors influencing foam stability in the presence of oil. © 2005 Elsevier B.V. All rights reserved.

**Keywords:** Foam; Foam–oil interactions; Static foam properties; Alpha-olefin sulfonate; Surfactant concentration

### 1. Introduction

Applications of foam within improved oil recovery include foam for mobility control, and the use of foam to shut off unwanted production of gas [1–5]. Several of these projects have been successes, both technical and economical. In spite of this, there are still many challenges to meet in the effort to describe foam properties and especially to predict foam behaviour.

One of the most important factors in EOR application of foam is the influence of oil on foam stability. Foam oil interactions are complex. A lot of core flooding experiments have been performed to evaluate the possibility of foam generation in the presence of oil. Usually, the foam is intended to reduce gas mobility in those zones already flooded by gas. In that aspect, it is important to perform the core flooding experiments with residual oil saturation present in the cores [6–8].

To characterize the strength of the generated foam, the mobility reduction factor (MRF) is often defined [6,9]:

$$\text{MRF} = \frac{\Delta P(\text{foam})}{\Delta P(\text{no-foam})} \quad (1)$$

where MRF is the mobility reduction factor,  $\Delta P$  (foam) and  $\Delta P$  (no-foam): The measured pressure across the porous medium with and without foam, respectively.

In the literature most data suggest efficiency of foams in reducing gas mobility. Some define a critical oil saturation for which foam cannot be formed above that oil saturation (see discussion by Schramm [9]). But several papers show that it is possible to generate strong foams at relatively high oil saturations [6–8].

Another influence of oil present in the core during foam experiment is a reduced propagation velocity of foam through the core [7,8], [10,11]. In 1991 Chou [12] reported that foam propagation without oil depends on the initial condition of the core material. Pre-saturating the core with surfactant prior to

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foam generation seems beneficial both for foam generation and propagation [13].

Foam flow in porous media in the presence of oil is not well understood. Even though core-flooding experiments are very important, the uses of different types of experiments are needed to help understand foam–oil interactions. One suggested method to determine whether oil would destabilize foam has been related to spreading coefficients (Eq. (2)) and entering coefficients (Eq. (3)) [6–9]. The relation to foam stability in the presence of oil is related to a negative entering coefficient, which imply a negative spreading coefficient

$$S = \sigma_{w/g} - \sigma_{w/o} - \sigma_{o/g} \quad (2)$$

where  $S$  is the spreading coefficient,  $\sigma_{w/g}$  the surface tension between water and gas,  $\sigma_{w/o}$  the interfacial tension between water and oil,  $\sigma_{o/g}$  the surface tension between oil and gas

$$E = \sigma_{w/g} + \sigma_{w/o} - \sigma_{o/g} \quad (3)$$

where  $E$  is the entering coefficient.

From experiments in a micro visual cell, Schramm [9,14] has defined three types of foams A, B and C. Type A foams are believed to show best stability in the presence of oil, as this condition refer to both negative entering and spreading coefficients. These foams are believed to show little interactions with crude oil. In addition, a lamella number has been introduced by Schramm [9] to investigate if oil is imbibed in the A suggested expression for the lamella number,  $L$ , has been:

$$L = 0.15 \frac{\sigma_{w/g}}{\sigma_{w/o}} \quad (4)$$

where  $L$  is the lamella number.

For Type A foams the lamella number is less than 1, for type B foams  $1 < L < 7$ , and for type C foams  $L > 7$ .

Wasan et al. [15] relates foam stability in the presence of oil to the stability of a pseudo-emulsion film, generated between the oil droplet and the gas phase. If the pseudo-emulsion film is ruptured, the oil may form a lens at the gas–water interface.

Results of the spreading coefficients and entering coefficients have in some cases correlated with the core flood experiments in the presence of oil [16]. Kristiansen and Holt [17] observed reduced flow resistance in experiments with spreading oils compared to non-spreading oils. Manlowe and Radke [18] has reported results from foam floods in micro models. Their work showed no correlation to spreading or non-spreading oils on foam stability. They believe that the stability of the pseudo-emulsion film is important for foam stability. The same conclusion was found by Koczo et al. [19] for the methods and systems that were investigated.

Many researchers explain defoaming action in oil–water systems with spreading and entering of the oil, in the case when hydrocarbon represents a separate phase in the foaming solution. Others find that there is a lack of correlation between the defoaming ability and spreading of oil. The different results are presented and discussed by Kruglyakov and Vilkova [20], and by Exerowa and Kruglyakov [21].

Mannhardt et al. [6] reports a large amount of experiments and finds it difficult to correlate foam performance in core floods with bulk foam stability, etched-glass micro model observations or interfacial parameters. There has also been a lot of discussion about similarity or lack of similarity between static and dynamic foam test. So far, the literature has not come to a consensus about this matter. There is an obvious difference in the condition of mixing a static foam and generation of foam in porous media. It is also important to be aware that the oil interactions when static mixing distribution of oil into the foam is very different from the situation in a porous medium where foam meets an oil phase. The criteria for stabilization and the foam–oil interactions are expected to be different for static bulk tests and porous media generated foam. This argument may be even stronger with regard to oil tolerance. However, it will be interesting to study static foam properties to see which parameters that are important for foam–oil interaction.

It seems to be two factors that are important for foam stability: the stability of the pseudo-emulsion film and the spreading relation of oil at the water interface.

In this study, we present and discuss static foam tests in relation to physical chemical analysis. The study first investigated static foam properties by varying surfactant concentration, brine ionic strength, and brine composition. Thereafter, systematic foam tests varying oil additive were performed. The organic components were variation in oil polarity, alkane molecular weight, organic acid and base additives, and crude oil with different physical properties. The analysis of the static foam tests has concentrated on foam column height. Foam texture has not been considered in these experiments.

## 2. Materials

The surfactant used was an alpha-olefin sulfonate, AOS, with molecular weight of 324 g/mol. The surfactant is anionic. Alkanes used are pentane, decane, dodecane, tetradecane and hexadecane, and the more polar oils used are toluene and xylene. Methanol, butanol and octanol are the alcohols used, and  $C_9H_{19}COOH$  the acid used. The crude oils denoted a–f, are crude oils from the North Sea. Analyses of the oils, acid and base content, wettability etc. are given in ref. [22]. The synthetic sea water has the following composition: 2.489 wt.% NaCl, 0.173 wt.%  $CaCl_2$ , 1.112 wt.%  $MgCl_2$ , 0.019 wt.%  $NaHCO_3$ , 0.406 wt.%  $Na_2SO_4$ , and 0.067 wt.% KCl.

## 3. Methods

### 3.1. Static foam tests

Foam tests were made by static mixing air into the surfactant solution. Air was dispersed into the 300 ml test solution with a pedal connected to a mixer at a speed of 2000 rounds per minute for 5 min. The mixer was a polymix obtained from

Table 1  
Different variable used in the foam column height testes

Variables in the foam tests
AOS concentration
Brine composition
Additive of alkanes
Additive of alcohol
Hydrocarbons with different polarity
Alkane with additive of octanol and/or C <sub>9</sub> H <sub>19</sub> COOH
Crude oil

Kinematica, type RW20 S12. Tests were mixed in 1000 ml glass cylinders. A cylinder is 44 cm high and is 6 cm in diameter. During mixing there was no restriction on air supply or for the foam volume to grow. After mixing the glass cylinder was closed with a plastic sealing at the top. Foam height was always well below the sealing. In foam tests with oil, the amount of added oil was 1, 5 or 10 wt.%, calculated as a weight fraction of the 300 ml surfactant solution. Oil was added to the surfactant solution before the mixing started. The oil was therefore dispersed in the foam during mixing. In all the experiments the height of the foam column above the liquid phase was measured as a function of time after the end of the mixing. Mixing time and the procedure for the test was the same for all experiments. The experiments were performed at ambient conditions. Foam height was examined by changing a lot of variables. These variables are listed in Table 1.

### 3.1.1. Surfactant concentration

First the AOS concentration was varied from 0.0001 to 2 wt.% AOS. In all other experiments the AOS concentration was kept at 0.5 wt.%.

### 3.1.2. Salt concentration

To test if the salt content in the water would affect the foam column height, it was performed different foam tests with 1 wt.% NaCl, 5 wt.% NaCl, 0.1 wt.% MgCl<sub>2</sub> and 1 wt.% MgCl<sub>2</sub>. Eq. (5) shows how to calculate the ionic strength  $\mu$

$$\mu = \frac{1}{2}([A]Z_A^2 + [B]Z_B^2 + [C]Z_C^2 + \dots) \quad (5)$$

where  $\mu$  is the ionic strength, [A], [B], [C], ... represent the species molar concentration of the ion A, B, C, ... Z<sub>A</sub>, Z<sub>B</sub>, Z<sub>C</sub>, ... are their valences.

Foam heights for tests with organic solvent additive, including alkanes, alcohols, and crude oils were measured.

### 3.1.3. Alkanes

The amount of alkane added was 1 wt.%, and the following alkanes were used: pentane, decane, dodecane, tetradecane and hexadecane. Experiments were also made with 5 and 10 wt.% amount of decane or hexadecane added. To see if the salinity would have any affect on the foam, 5 wt.% decane was added to 1 or 5 wt.% NaCl solution.

### 3.1.4. Alcohols

How different alcohols as methanol, butanol and octanol affect foam were studied. The concentration of alcohol was 1 and 5 wt.%. In addition tests with 0.1 and 0.4 wt.% content of butanol was done.

### 3.1.5. Oil polarity

There were done foam tests with 1 wt.% toluene or 1 wt.% xylene to see how the oil polarity affected foam generation.

### 3.1.6. Acid/base

Octanol and/or C<sub>9</sub>H<sub>19</sub>COOH acid was put in foam tests with 1 wt.% hexadecane to see how acids and bases affected the foam. There were added 1 wt.% organic additive to hexadecane before the hexadecane mixture was added to the surfactant solution.

### 3.1.7. Crude oil

There were finally performed experiments with 1 or 5 wt.% of different crude oils in synthetic sea water, and tests with 5 wt.% of crude oil in 1 wt.% NaCl solution. The oils are named crude oil a–f.

## 3.2. Surface tension measurements

The interfacial tension for the oils and the surface tensions values used to find CMC have been measured with the pendant drop method. The method is for instance described by Adamson [23]. The instrument is a CAM 100 with CAM 200 software, all delivered from KSV Instruments Limited. This instrument have problem with calculating surface/interfacial tension for values smaller and around 1mN/m. This lead to great uncertainties for there values. For the rest of the values the uncertainty is  $\pm 0.5$  mN/m when the instrument is calibrated with the needle method.

## 3.3. Viscosity measurements

The Rheometer used to measure viscosity was a RHEO-LAB MC 120 instrument delivered from Physica. The viscosity was measured at 20 °C, and the shear rate was constant at 100 s<sup>-1</sup>. Measurements were done by measuring the viscosity each 10th second until 20 measurements were recorded.

## 3.4. Spreading experiments

The spreading conditions for the different crude oils on a gas–water interface were analyzed by direct visualized detection. Crude oil and 0.5 wt.% AOS in synthetic sea water was put in a container to equilibrate. After 2–4 weeks ca. 20 ml of the AOS solution was put in a spherical glass container and the neck was sealed with a septum. The container was put upside down, with the septum down. Oil was put in a syringe and the needle through the septum. An oil drop was then pressed out of the syringe, and it was observed whether the oil spread on the surface or not. The needle was not in

Table 2  
Composition of the crude oils

Crude oil	Acid number (mg KOH/g oil)	Base number (mg KOH/g oil)	Paraffin content (wt.%)	Asphaltene content (wt.%)	Interfacial tension (mN/m) <sup>a</sup>
a	0.04 ± 0.01	0.29 ± 0.01	79.4	0.2	0.39
b	3.2 ± 0.1	1.06 ± 0.02	55.0	0.7	0.5
c	0.12 ± 0.02	0.47 ± 0.01	61	0.1	0.7
d	0.12 ± 0.01	1.6 ± 0.2	54.0	6.2	0.33
e	–	–	50	0.7	1.8
f	0.026 ± 0.005	0.146 ± 0.007	63	–	1.6

<sup>a</sup> Measured against a solution of 0.5 wt.% AOS in synthetic sea water.

Table 3  
Crude oil properties

Crude oil	Viscosity (cp)	Spreading coefficient (mN/m) <sup>a</sup>	Lamella number	Foam height (cm) <sup>b</sup>
a	3.1	11.1	10.4	2.2
b	55.1	4.6	8.1	13.0
c	11.1	4.2	5.8	1.0
d	10.7	7.3	12.3	19.9
e	9.1	5.4	2.3	18.4
f	8.4	4.7	2.5	17.6
	±0.5	±0.9		±0.5

<sup>a</sup> Measured against a solution of 0.5 wt.% AOS in synthetic sea water.

<sup>b</sup> Foam column height to solutions of synthetic sea water with 0.5 wt.% AOS and 1 wt.% of different crude oils measured after 180 min.

touch with the water surface. This experiment was done for all the different crude oils.

### 3.5. Multivariate data analyses

Standard multivariate data analyses were used to analyse the results. Foam column height, interfacial tension, spreading coefficient and viscosity measured for the crude oil and acid number, base number, paraffin and asphaltene content, [22], was used as input variables in the multivariable data analyses. The different data are given in Tables 2 and 3. The variables were standardized by the program to make it possible to compare the effects of the different variables. The Principal component analyse, PCA, method used assume a linear combination between the variables. The method was used to look for possible interesting results that otherwise may be difficult to find.

There was also preformed a partial least square regression analyses, PLS, on the dataset. The purpose of this was to further improve understanding of the properties that may affect the foam column height, and to look for possible interactions between these properties.

## 4. Results and discussion

### 4.1. Static foam tests

#### 4.1.1. Effect of surfactant concentration

The critical micelle concentration (CMC) has been measured as a reference for the surfactant system in the brine; see

Table 4  
CMC for AOS as a function of salt concentration

Solution	CMC (wt.%) pendant drop
Synthetic sea water	$2.2 \times 10^{-3}$
1 wt.% NaCl	$2.8 \times 10^{-3}$
5 wt.% NaCl	$1.6 \times 10^{-3}$
1 wt.% MgCl <sub>2</sub>	$3.2 \times 10^{-3}$
	$\pm 0.3 \times 10^{-3}$

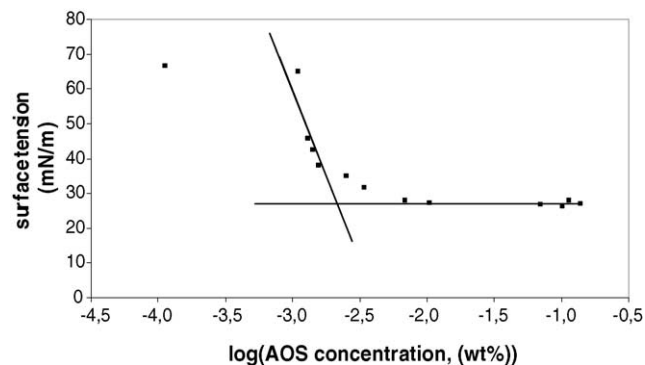


Fig. 1. Example of CMC measurement of AOS, here in synthetic sea water, 25 °C.

Table 4 and Fig. 1. The purpose was to see if formation of static foam was related to the CMC in the brine.

The static tests show that the foam column generated is stable for several days, Fig. 2. There was no foam formed in reference tests without surfactant present, but foam appeared

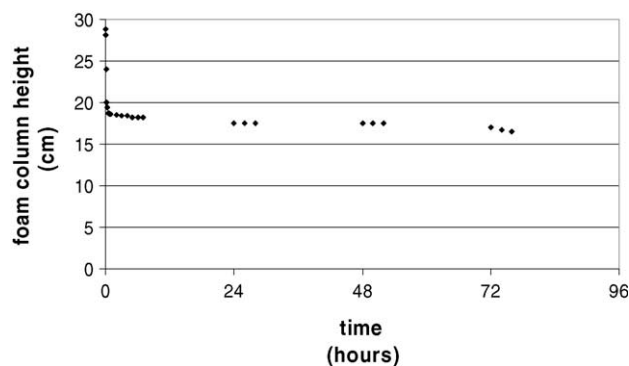


Fig. 2. Foam column height for a solution of AOS (0.5 wt.%) in synthetic sea water measured as a function time.

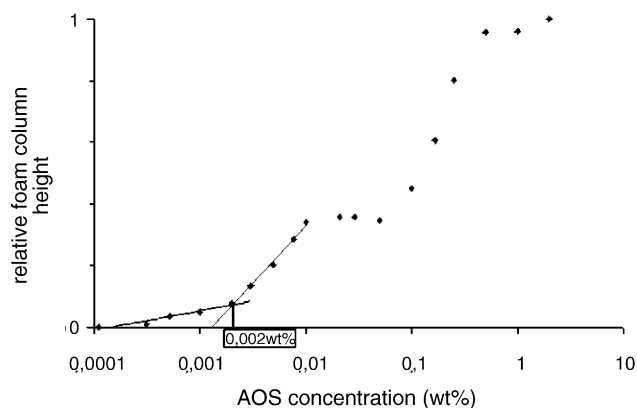


Fig. 3. Relative foam height vs. surfactant concentration. The foam height used is measured 4 h after mixing.

at surfactant concentrations even below CMC (Fig. 1, Table 4 and Fig. 3). The static foam height measurements are an average of 2–4 parallels, and the accuracy was estimated to  $\pm 0.5$  cm. This implies that foam generation can be efficient measure as a function of surfactant concentration. Mannhardt et al. [6] arrived at similar results for static foam tests using the surfactant, Chaser Gr-1080.

Fig. 3 shows the change in relative foam column height at different surfactant concentrations. The foam height reaches a limited foam height at surfactant concentration 0.5 wt.%. All foam heights are normalized by the highest foam height. The relative foam column height does not change when increasing the AOS concentration from 0.01 to 0.1 wt.% ( $5 \times \text{CMC}$ – $50 \times \text{CMC}$ ). In our opinion this may not be related to micellization as such, but could be related to reorganization from spherical to rod-like micelles and further to multilayer laminar or liquid crystalline phases. As the total surfactant concentration increases from a few times CMC to more than 100 times CMC, literature suggest that ionic micelles can at some point undergo a transition from near-spherical to rod-like or other elongated forms [24,25]. Others have reported to find a second CMC at higher concentrations [26]. At this certain concentration there is an indication of a reorganization of the micelles [26]. Abed et al. [27] have studied micellization of  $C_{12}$ – $C_{18}$  alpha-olefin sulfonate. No transition from spherical to cylindrical micellar shape was observed for the experimental concentration range 0–3 wt.%.

#### 4.1.2. Effect of salt

The change in composition and ionic strength of the brine had little effect on the foam column height in experiments without oil added. Ionic strength for the brines calculated with Eq. (5) and foam height is given in Table 5.

In experiments with decane and crude oil present it seems as a low salt concentration increase the stability of the foam. Experiments were run with 0.5 wt.% AOS and 5 wt.% decane in 1 wt.% NaCl, 5 wt.% NaCl and sea water and 5 wt.% of crude oil in synthetic sea water and in 1 wt.% NaCl. For decane and crude oil stable foam is generated at 1 wt.% NaCl

Table 5

The calculated ionic strength in brine compared to measured foam height

Brine	$\mu$ i distilled water (M)	Foam height after 120 min (cm)
1 wt.% NaCl	0.171	18.6
5 wt.% NaCl	0.856	18.3
0.1 wt.% $\text{MgCl}_2$	0.026	18.9
1 wt.% $\text{MgCl}_2$	0.261	18.3
Synthetic sea water	0.822	18.7
		$\pm 0.5$

concentration. Also, reducing the crude oil content to 1 wt.% gave stable foam in synthetic sea water.

The results show that there may be a different influence of brine composition and ionic strength for tests with and without oil present.

#### 4.1.3. Effect of alkanes

In Fig. 4 the foam column height is given as a function of molecular weight of the alkane added. As seen from the figure short chain alkanes tend to destabilize foam, while long chain alkanes gives stable foam. From a visual examination, it even look like long chain alkanes give more stable foam compared to AOS in brine. Drying of liquid films is slower with oil present.

Similar results were found by Suffridge et al. [28] studying  $C_{11}$  and  $C_{18}$ . Lower molecular weight alkanes offered a more unfavorable environment to foam than did higher molecular weight alkanes. Both of the oils gave some foam, but  $C_{18}$  was the most stable one, even more stable than foam generated without oil present, in line with our observations.

On the other hand Meling and Hanssen [29] also studied a series of pure alkanes, but found no general correlation between foam destabilization and oil carbon number. For one surfactant the gas-blocking ability was found to be increasing with increasing oil carbon number. For the other surfactants used the observed trends were rather complex.

Adding an oil soluble dye (Oil Red), tracking the oil phase, to the alkane phase gave a better visualization of the distribution of alkane between the foam and bulk brine phase. Again,

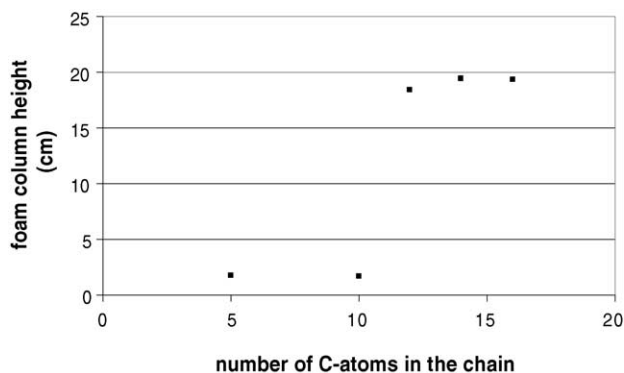


Fig. 4. Foam column height to tests with 0.5 wt.% AOS in synthetic sea water with a content of 1 wt.% alkane. The foam height is measured 2 h after mixing.



it appears to be a difference between long and short-chained alkanes. The dye itself did not affect the result as experiments with and without dye added gave the same results.

The long chain alkanes (carbon number > 10) did not dye the brine phase, just the foam. This indicated that these molecules do not solubilize in the micelles. The short chain alkanes are distributed both in the foam and the bulk brine phase; thus, they have a higher ability to solubilize in the aggregates, in line with other reported results [29,30]. Ceglie et al. [30] also found that when oil chain length is small, as in hexane for example, oil has a strong tendency to penetrate into the micelle aggregate. As the chain length of the oil increases, the penetration of oil becomes progressively more difficult for steric reasons [30]. Thus, the breaking of foam for short chain alkanes is most likely related to the ability to transport oil out of the surfactant film and into the bulk brine by solubilization in micelles. The effect of solubilization has been discussed by Lobo et al. [31] who claim that solubilization reduces foam stability and will also change the micellar interactions [31]. It is indicated that the oil drop size may play an important role in the stability of foam.

Another interesting result was that for long chain alkanes no oil phase between the liquid and foam columns existed. All of the oil must therefore be in the foam structure, even for a 10 wt.% content of alkane. The amount of hexadecane, 1, 5 and 10 wt.%, did not influence the foam column height. The foam structure consists of lamellas. In the experiments performed, we especially discuss the properties of the skeleton of the lamellas. These are thicker for the long chain alkanes than for the short ones. In a study by Aveyard et al. [32] lamellas in foam with added hexadecane has been reported to be thicker than lamellas in foam with shorter chain alkanes (undecane). Foam without oil had the thinnest lamellas.

Generally, any factor, which reduces the rate of drainage downward under gravity from a Plateau border will increase the stability of the film [33]. The hydrophobic effect, [34], can be an example of such a factor. The oil may be present as a continuous phase inside the Plateau borders non-polar oils, like long chain hydrocarbons, will usually give very high stability of asymmetric films [21]. This will lead to a notable foam stabilization as a consequence of slower film thinning and drainage.

The lamella numbers calculated by using Eq. (4) predict type B foams independent of alkane molecular weight. Type B foam has a moderate stability to oil [9]. By definition, for type B foams entering coefficient is positive and the spreading coefficient is negative. This is not in line with our results as all the foam experiments with alkanes show that both the entering and the spreading coefficients are positive, see Table 6. Some of the alkanes give stable foam others do not, even if they are in the same foam group with regard to the lamella number theory.

Further, from Table 6 it is not possible to see any connection between alkane length and spreading coefficient or lamella number. This can be caused by the uncertainty in the measure of the interfacial tension between oil and AOS solution, which

Table 6

Spreading coefficient and lamella number for the different alkanes

Oil	Spreading coefficient (mN/m)	Lamella number
Decane	4.8	5.4
Dodecane	3.0	5.8
Tetradecane	4.5	3.9
Hexadecane	2.1	2.3

Measured against a solution of 0.5 wt.% AOS in synthetic sea water.

is close to 1 mN/m. Aveyard et al. [32] found that the spreading coefficient is negative for undecane and longer alkanes and positive for shorter alkanes. In their experiments, the anionic surfactant bis(2-ethylhexyl) sulfosuccinate was used.

#### 4.1.4. Effect of alcohol

Fig. 5 summarizes static bulk foam tests with added alcohols. The short chain alcohols methanol, and also lower concentration of butanol (conc. <5 wt.%) showed stable foam. High concentration of butanol, and also octanol at the concentrations applied, gave complete destabilization of the foam.

As for the alkanes, molecules that solubilize in the micelles seem to break foam. Methanol is miscible in brine and is known to adsorb into the polar region of [35] solubilized in the micelles, but would prefer a location in the palisade layer of the micelles. For foam tests with 1 wt.% butanol, and tests with 1 wt.% octanol, the alcohol were coloured whit the same Oil Red dye. The test with butanol got a dark red solution and the foam was white. This indicates that there is no butanol in the foam. This will probably cause the foam to stabilize as AOS foam without additives. The test with octanol was a bit different. Octanol was placed as a pink layer between the water solution and the foam column.

#### 4.1.5. Effect of oil polarity

Additives like decane, xylene, or toluene all reduced the static foam height compared to the pure brine–surfactant system. In our experiments almost no foam was formed. It is therefore not possible to make a conclusion of the influence of oil polarity.

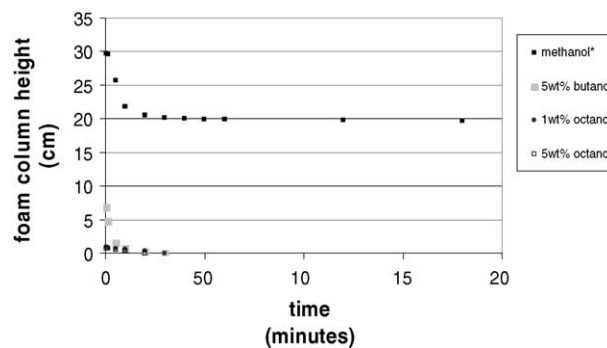


Fig. 5. Effect of alcohol additive on the foam column height for 0.5 wt.% AOS in synthetic sea water. \*Foam column height to foam tests with 1 and 5 wt.% methanol, and foam tests with 0.1, 0.4 and 1 wt.% butanol. All these experiments give almost the same foam height.



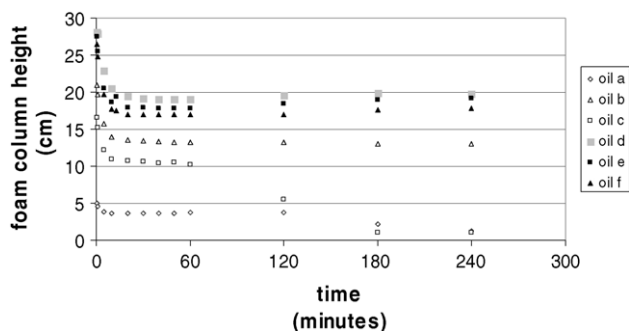


Fig. 6. The plot show foam column height to solutions of synthetic sea water with 0.5 wt.% AOS and 1 wt.% of different crude oils.

#### 4.1.6. Effect of acid and base

Adding 1 wt.% acid or base to the hexadecane content in the foam test did not show a systematic trend for changes in the foam column height. The additives of organic compounds are very small compared to the total volume of liquid in the tests.

#### 4.1.7. Effect of crude oil

Bulk foam tests are also made with crude oils from some North Sea oil reservoirs. The physical properties of the crude oils are a necessity for interpretation of the results. The crude oils have shown different ability to break foam. All the spreading coefficients calculated from interfacial tension measurements are positive for the crude oils. The same result was found from the visual spreading test in the spherical glass container. It was not possible to see any difference in time needed to spread the oil on the water surface. All oils spread very quickly in line with the calculated values.

In Fig. 6 foam generated with 1 wt.% crude oil added in synthetic sea water, show that both stable foam and foam breaking may occur in the presence of crude oils. Similar results were obtained using 5 wt.% oil in 1 wt.% NaCl solution. Results from foam tests with 5 wt.% oil in synthetic sea water are shown in Fig. 7. The generated foams broke down very quickly.

Lamella number calculated by Eq. (4) and the spreading coefficients are presented in Table 3. Oil a, b and d has type

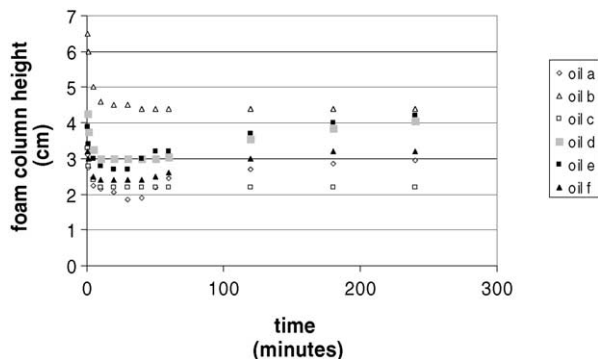


Fig. 7. The plot show foam column height to solutions of synthetic sea water with 0.5 wt.% AOS and 5 wt.% of different crude oils.

C foam, and oil c, e and f have type B foam. All of the crude oils have positive spreading and entering coefficient, indicating type C foams. According to theory, this should have given foams with low or moderate stability to oil. The foam stability in the presence of the different crude oils is mostly not in line with this type of classification. Oil b is for instance very stable in the experiments even if it has type C foam. For the foam tests with 1 wt.% crude oil, both the stable oils b and d have type C foam by using the lamella number theory. The two unstable oils a and c from the experiments have different foam type, a has type C foam and c has type B by theory.

After mixing the small foam bubbles start to coalesce. After some minutes the coalescence rate decreases and the foam texture becomes more stable. The lamellas then start to break up. In the end, there is mostly a lamella skeleton with Plateau borders and with some lamellas left. Some foam experiments will at this point break down completely, while others will have a stable foam skeleton for a long time.

When mixing the static foam tests, oil will be forced into the foam. After mixing, the oil drained out of the foam at different rates. For the crude oils draining of oil lead to an oil phase between the water phase and the foam column. The size of the oil phase varies for the different oils. For the most stable crude oils the oil will stay in the skeleton of the lamellas and in the Plateau borders even after most of the lamellas are broken. It looks like nothing will drain out (see Fig. 8), which is confirmed by no excess oil phase. Oil b and d have such foam. Draining of oil to the junction of the Plateau borders was not observed during the 2 days long experiment. The foam height was stable for 2–3 days until it suddenly cracked and all foam broke down in seconds. Oil e and f gave relatively stable foam for some hours, but the foam is almost broken down after 1 day. In these experiments most of the oil drain out of the foam and only leave oil in the wedges of the Plateau borders during the first hours (Fig. 9), similar to the observation in ref. [9].

#### 4.2. Multivariate data analyses

Interfacial tensions at equilibrium and crude oil viscosity were measured, and corresponding spreading coefficient were calculated. The values for the spreading coefficients and the viscosity are given in Table 3. Acid number, base number, paraffin and asphaltene content for these crude oils have been investigated in earlier studies [22], and are presented in Table 2.

A multivariate data analyse was performed to investigate parameters influencing foam height. The main limitation of multivariate analysis is the assumption of linear relations between the different items. The objects (crude oils) are marked a, b, . . . up to f. The Variables (measured data) that were used are given in Table 7. The biplot for the multivariate analyse are given in Fig. 10. From this first step analysis, it was detected that interfacial tension, acid number and viscosity were

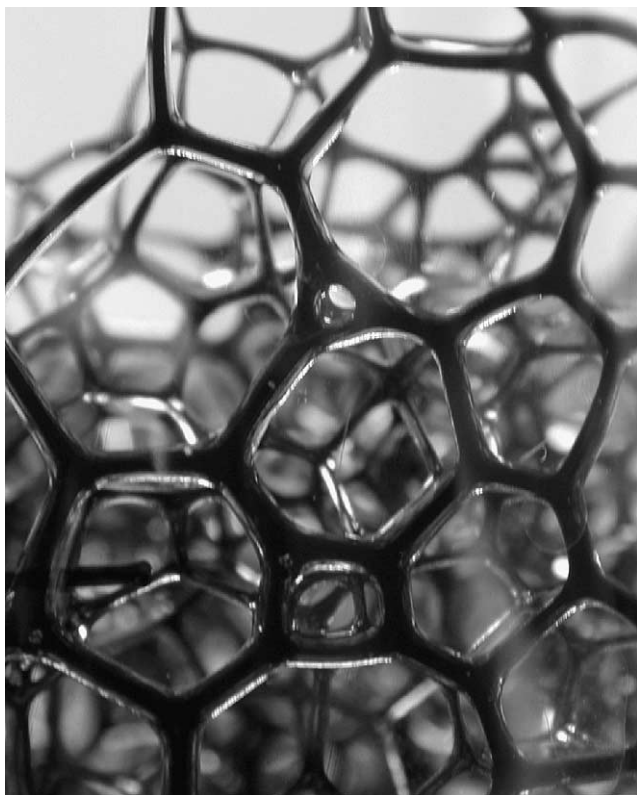


Fig. 8. The picture show foam with much oil in the Plateau borders. The foam is from a foam test with 1 wt.% of oil b in synthetic sea water with 0.5 wt.% AOS content. The picture is taken 24 h after mixing and it is three times enlarged.

less important for the foam stability. These three variables were therefore excluded from the multivariate analyse. Limited variation in the variables can be a reason for exclusion. Therefore it is still possible that they are of importance.



Fig. 9. The picture shows foam with thin Plateau borders and oil in the junction of the Plateau borders. The foam is from a foam test with 5 wt.% of oil e in synthetic sea water with 0.5 wt.% AOS content. The picture is taken 24 h after mixing and it is four times enlarged.

Table 7

The abbreviation for the variable used in the biplot, Fig. 10

Variables	Abbreviation
Asphaltene content	ASPH
Base number	BASE
Interfacial tension between oil and water	IFT
Paraffin content	PAR
Spreading coefficient	S
Acid number	ACID
Foam column height	FCH
Viscosity	VIS

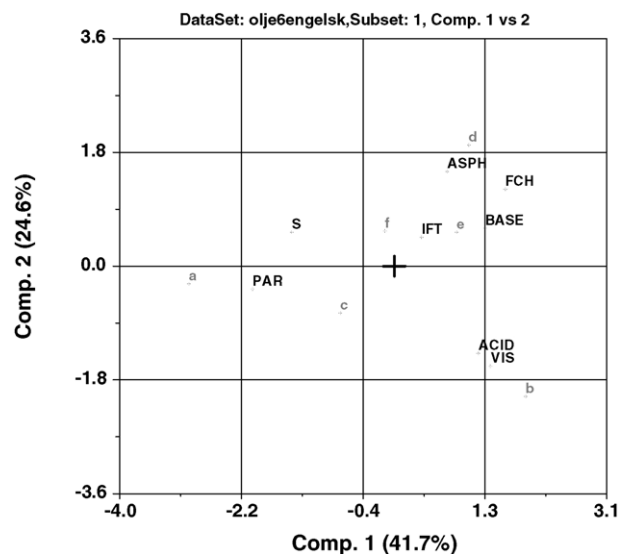


Fig. 10. Biplot from the multivariate data analyses. The biplot show the relation between the objects and the variables.

Fig. 11 shows the impact and importance the variables have on foam column height. Positive values in Fig. 11 increase foam column height.

Higher asphaltene content and higher base number will increase the foam column height. Lower spreading coefficient and lower paraffin content will also increase the foam column

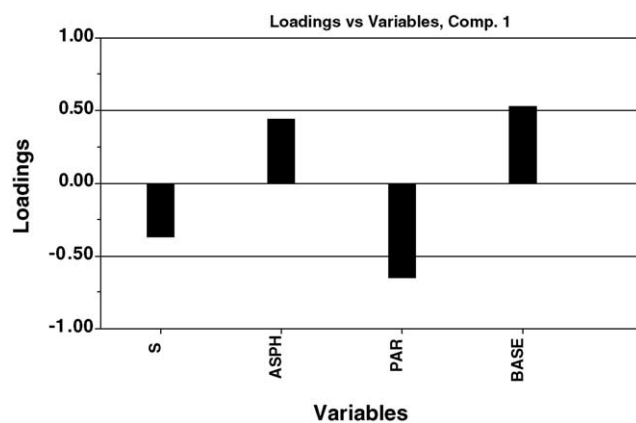


Fig. 11. The diagram shows how the different variables explain the variation in foam column height.

height. The program is not capable of knowing the difference between positive and negative values for the spreading coefficient. So a lower spreading coefficient mean a lower number, but since the values measured are close to zero, a lower value may get negative. The spreading coefficient changes from spreading to non-spreading when passing zero.

During this study it is found that short paraffin will solubilize in the micelles and destabilize the foam. Longer paraffin will not solubilize in the micelles, and the lack of transport from the surfactant film into the bulk liquid phase through solubilization seems to stabilize the foam. These facts can explain why paraffin (smaller molecules) destabilize the foam and asphaltene stabilize the foam. However, asphaltene are large polar molecules and the interaction between asphaltene and a surfactant layer, will be different from the hydrophobic effects expected for paraffins and the surfactant layer.

Evans and Wennerström [36] assumes that a positive spreading coefficient will lead to oil spreading on the liquid surface. This will probably cause the foam to break down faster. All the oils in the dataset have positive spreading coefficients, but stable foams have been generated. It is difficult to explain the different foam column heights from spreading coefficients since all are positive. Koczko et al. [19] assumes that it is the stability of the pseudo-emulsion films that will decide if the oil is spreading or not. The stability of the pseudo-emulsion film is among other things dependent of the van der Waals forces in the water film between the oil and air. Strong van der Waals forces will stabilize the foam, while the foam will break down if the van der Waals forces are weak. It is possible that this can explain why some foam generated with crude oils present are stable, even if all the spreading coefficients are positive. The conditions for pseudo-emulsions are expected not to change with variation in chain length of the added alkane, but the conditions may change when adding different crude oils.

The parameters that seem to be most important for foam height, asphaltene content, base number, spreading coefficient and content of paraffin, were used to make a linear model that could predict foam height. Fig. 12 shows that the

main variables are giving a reasonable prediction of the foam column height for the crude oils.

## 5. Summary

The results in this paper show no obvious connection between spreading coefficient and foam stability. In all the foam tests for alkanes and crude oil, the spreading coefficients are positive. The foam stability is varying even when the interfacial tensions are constant and experiments have shown that foam is stable even if the spreading coefficient is positive. The results clearly demonstrate that negative spreading coefficient is not a necessary condition to get stable foam.

The lamella number has been used to explain oil transport within the lamella. The lamella number is calculated from Eq. (4). Three of the crude oils are type B, the others are type C by theory. One of the most stable crude oils in the experiments has type C foam. For the two crude oils that are not stable in the experiments one has type B foam and the other type C foam by theory. The criteria used in the definition of lamella number cannot predict the stability of foam with added oil in this study. The foam stability in the presence of crude oil is strongly dependent on the amount of crude oil added.

The pseudo-emulsion film has been used as a possible explanation for foam stability, but this is not measured in this study. Therefore, it is still open that pseudo-emulsions can play an important role in foam stability.

The main factors that seem to affect foam stability, in the experiments reported, are salinity and chain length of the hydrocarbon. The salinity has an effect when alkanes or crude oil is added, but is not observed without oil. A reduced salt concentration will stabilize the foam. In some experiments with oil added, no foam is generated in experiments with high salinity, but some foam is generated at low salinity.

The hydrocarbon molecular weight seems to be very important for the foam stability. Decane and shorter alkanes will solubilize in the micelles and these alkanes act to destabilize the foam. The destabilization of the foam can be related to the dynamic solubilization of alkanes into the micelles, thus alkanes may drain out of the Plateau borders. Alkanes longer than decane are too large to be solubilized in the micelles. The molecules will therefore have less ability to be transported out of the foam and seems to stabilize the foam.

## 6. Conclusion

- Static bulk foam made from an AOS surfactant solution generates foam even below CMC. Micellization is not a necessary condition for foam formation.
- A step-wise increase in foam height with increasing surfactant concentration is observed. The change may be associated with reorganization of micelles from a spherical shape to rod-like to a more laminar aggregate structure.

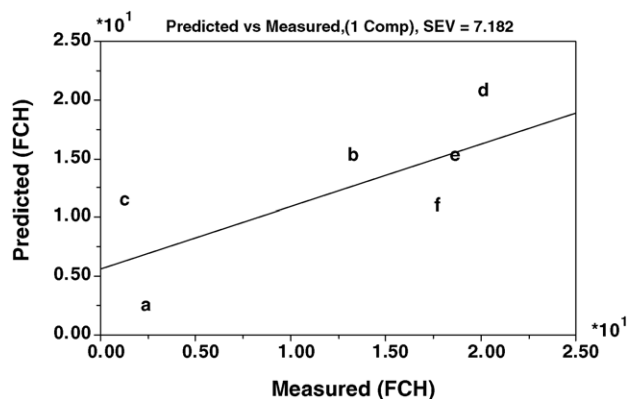


Fig. 12. Predicted foam height from MVA analysis compared to measure foam height.

- For the ionic strengths investigated, changes in ionic strength and ionic composition had little effect on foam column height. Crude oil and decane systems investigated showed a strong dependence on ionic strength.
- Negative spreading coefficient is not a necessary condition for stable foam.
- Foam stability in presence of oil seems to be related to transport properties within the foam. The larger alkanes stabilize foam, while the alkanes with lower molecular weight destabilize the foam. Solubilization can be a possible explanation for the different stability in the static bulk foam tests with contents of different alkanes.
- For crude oil the influence of physical chemistry properties on foam properties are complex. The multivariate data analyses showed that no single factor could explain the complex interactions observed.

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