

## **Paper 2**

**Effect of surfactant structure on foam-oil interactions**

**Comparing fluorinated surfactant and  
alpha olefin sulfonate in static foam tests**



# Effect of surfactant structure on foam–oil interactions Comparing fluorinated surfactant and alpha olefin sulfonate in static foam tests

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## Abstract

There have been many foam field applications in the North Sea in recent years. A key question is the stability of foam in the presence of oil in the reservoir. To understand the influence of oil type and of oil saturation on foam stability and foam generation various fundamental experimental studies have been performed.

In this study results from static foam experiments with a fluorinated surfactant are compared with tests done with an alpha olefin sulfonate [A.K. Vikingstad, A. Skauge, H. Hoiland, M.G. Aarra, *Colloids Surf. A: Physicochem. Eng. Aspects* 260 (2005) 189–198.]. The static foam properties for the two surfactants have been investigated by variation in surfactant concentration, in amount of added oil, and in polarity of the oil phase.

The effectiveness of foam generation is related to surfactant concentration. The fluorinated surfactant gave more stable foam over time at the same surfactant concentration. Foam formed below the critical micelle concentration for both surfactants. Without oil present, both surfactants have foam heights that are independent of ionic strength.

In our opinion, foam stability in the presence of alkane-type oils is related to the molecular weight of the oil molecule. Foam generation and stability is possibly connected to the surfactant's ability to solubilize oil molecules. Foam tests with decane or crude oil stabilized at lower ionic strength for the AOS surfactant. The foam height for the fluorinated surfactant showed little sensitivity to oil.

For the AOS surfactant alkanes that were soluble in the micelles seemed to destabilize the foam. Experiments done with the fluorinated surfactant did not show this behavior. In fact, much more foam was generated in tests with alkanes that solubilize in the micelles than for those that were not. © 2006 Elsevier B.V. All rights reserved.

**Keywords:** Foam; Foam–oil interactions; Static foam properties; Fluorinated surfactant; AOS

## 1. Introduction

The use of foam to improve oil recovery includes control of gas mobility and the shut off of unwanted gas production in production wells [2–6]. Several of these projects have been successful, both technically and economically. There remain, however, many challenges in the description of foam properties and in, particularly, the prediction of foam behavior. One of the most important factors in EOR application of foam is the influence of oil on foam stability.

In our previous paper [1], we presented three main models used to discuss foam–oil stability: spreading and entering coefficients; lamella number; and pseudo-emulsion film models. In the literature, foam stability in the presence of oil is related to a negative entering coefficient ( $E$ ) which implies a negative spreading coefficient ( $S$ ) [7–10].

$$S = \sigma_{w/g} - \sigma_{w/o} - \sigma_{o/g} \quad (1)$$

$\sigma_{w/g}$  is the surface tension between water and gas;  $\sigma_{w/o}$  the interfacial tension between water and oil and  $\sigma_{o/g}$  is the surface tension between oil and gas.

$$E = S + 2\sigma_{o/w} \quad (2)$$

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From experiments in a micro visual cell, Schramm [10,11] has described three types of foams A–C. For Type A foams the lamella number is less than 1, for type B foams  $1 < L < 7$ , and for type C foams  $L > 7$ . Type A foams are believed to show the best stability in the presence of oil with reference to both negative entering and spreading coefficients. A suggested expression for the lamella number,  $L$ , has been:

$$L = 0.15 \frac{\sigma_{w/g}}{\sigma_{w/o}} \quad (3)$$

$L$  is the lamella number.

Another parameter often calculated when discussing antifoam efficiency of oil additives to foam is the bridging coefficient,  $B$ , defined as [12,13]:

$$B = \sigma_{w/g}^2 + \sigma_{w/o}^2 - \sigma_{o/g}^2 \quad (4)$$

For the oil to behave as an antifoaming agent it is necessary, though not sufficient, that the bridging coefficient is positive. A very good discussion of the bridging coefficient is given in Denkov [12].

Several core flood experiments [14,15] have found a correlation between a spreading coefficient, its related entering coefficient, and foam stability in the presence of oil. Others (Manlowe and Radke [16], Koczo et al. [17]) did not find a correlation between the spreading coefficient and foam stability for the methods and systems investigated.

Manlowe and Radke [16], Raterman [18] and Wasan et al. [19] relate the stability of foam in the presence of oil to the stability of a pseudo-emulsion film. A pseudo-emulsion film is a thin water film between the oil phase and the gas phase. If the pseudo-emulsion film is stable the oil will stay in the lamella. If the pseudo-emulsion film is not stable the oil will form a lens on the surface. This can break down the foam.

The role of oil spreading for antifoam activity is a subject of ongoing debate in the literature [12,17,20,21]. A good correlation is often found between antifoam ability and the positive spreading coefficient, but recent studies have raised doubts about this correlation.

Different models to describe foam stability have been successfully applied in different situations. Translating the fundamental mechanisms of foam–oil interactions into generally applicable rules, however, has proven difficult. In our previous work [1], we studied foam–oil interactions for an alpha-olefin sulfonate. Micellization was not a necessary condition for foam formation, and foam could be stable in presence of oil. Crude oil and decane systems investigated showed a strong dependence on ionic strength. We also found that a negative spreading coefficient was not a necessary condition for stable foam; foam stability in the presence of oil seemed rather to be related to transport properties within the foam.

In this study foam–oil interactions for a fluorinated surfactant have been investigated by performing static foam tests. Results are compared and discussed in relation to the results obtained for AOS surfactant. The study first investigated static foam properties by varying the surfactant concentration, brine ionic strength, and brine composition. Thereafter, systematic foam tests were performed by varying oil additives. The organic components

were variation in oil polarity, alkane molecular weight, and crude oils with different physical properties. The analyses of the static foam tests focused on foam stability, that is, measurement of foam column height versus time. Foam texture and foaminess were not considered in these experiments.

Some fluorinated surfactants form foams that are very stable in the presence of oil. Mannhardt et al. [6] have done experiments in which they have added a fluorinated surfactant to different types of surfactants. They found that addition of the fluorinated surfactant enhanced the oil tolerance of some but not all foams. In an investigation of the addition of fluorinated surfactants to foam in different foam experiments, Dalland et al. [14] categorized four of eight fluorinated surfactants as creating oil tolerant foams. The fluorinated surfactants foam showed ranges of oil tolerance from as effective in gas blocking as the best foams known in oil-free systems to even more oil sensitive than foams created by typical conventional surfactants.

Measurements of the interfacial and surface tensions of the surfactants were made and used to calculate the spreading and entering coefficients. The purpose was to look for any correlations between these values and foam performance in the presence of oil. Mannhardt's [6] measurements of interfacial tensions ( $\sigma_{w/o}$ ) for the different surfactants and oil combinations gave approximately the same values. Dalland et al. [14] observed a greater variation in  $\sigma_{w/o}$ , but a similar range in values. The measured surface tension of the oil was also within the same range for all surfactants tested. So according to these studies it looks like the primary factor contributing to the spreading coefficient is variation in the surface tension of the surfactant solution. There seems to be a correlation between a high value of the surfactant surface tension and a positive spreading coefficient.

Holt et al. [22] report different foam stabilization mechanisms with an AOS surfactant and a zwitterionic surfactant. In micro model studies the fluorinated surfactant exhibited a non-entering behavior. For the AOS surfactant, the spreading/entering behavior under micro model conditions was less well defined. Chukwueke [23] has studied AOS and two fluorinated surfactants foam for use in gas shut-off. Core flooding experiments showed that gas blocking performance under reservoir conditions was poor for one of the fluorinated surfactants. AOS combined with a polymer showed good gas blocking, as has also been reported by Aarra et al. [9].

## 2. Materials

The surfactant used was a Perfluoroalkyl betaine, FS-500, supplied by DuPont. The surfactant was zwitterionic. In our previous study [1] we used a C<sub>14</sub>–C<sub>16</sub> alpha-olefin sulfonate surfactant, AOS, with a molecular weight of 324 g/mol. The AOS surfactant is anionic. Alkanes used were pentane, heptane, decane and hexadecane, and the more polar oils used were toluene and xylene. Methanol, butanol and octanol were the alcohols used. The crude oils, denoted a–f, were obtained from the North Sea. The compositions of the crude oils are given in [1]. The synthetic seawater had the following composition: 2.489 wt.% NaCl, 0.173 wt.% Ca Cl<sub>2</sub>, 1.112 wt.% MgCl<sub>2</sub>, 0.019 wt.% NaHCO<sub>3</sub>, 0.406 wt.% Na<sub>2</sub>SO<sub>4</sub>, and 0.067 wt.% KCl.

### 3. Methods

#### 3.1. Static foam tests

Foam tests were made by the static mixing of air into a surfactant solution. Air was dispersed into a 300 ml test solution with a pedal connected to a mixer at a speed of 2000 rounds/min for 5 min. The mixer was a Kinematica polymix, type RW20 S12. Solutions were mixed in 1000 ml glass cylinders, measuring 44 cm high and 6 cm in diameter. During mixing there was unlimited air supply and no restrictions on foam expansion. After mixing the glass cylinder was closed with a plastic seal. Foam height was always well below the top. In foam tests with oil the amount of oil added was 1, 5 or 10 wt.%, calculated as a weight fraction of the 300 ml surfactant solution (wt.%/wt.% assuming a density of 1 g/ml solution). Oil was added to the surfactant solution before mixing. The oil was therefore dispersed throughout the foam during mixing. In each experiment the height of the foam column above the liquid phase was measured as a function of time after mixing. Both the mixing time and the procedure for the test were identical in each experiment. The experiments were performed at ambient conditions. Foam height was examined by changing a great number of variables, as described below. The foam stability, the foam height after 2–4 h was compared for each test. Neither the initial foam volume after mixing nor foaminess were considered. The range of uncertainty for the foam height measurements was  $\pm 0.5$  cm.

##### 3.1.1. Surfactant concentration

First the FS-500 concentration was varied from 0.001 to 1 wt.%. For AOS the surfactant concentration was varied from 0.0001 to 2 wt.%. In all other tests the surfactant concentration a 0.5 wt.% was maintained for both surfactants.

##### 3.1.2. Salt concentration

To test the effect of salt content in the water on foam column height, different foam tests with 1 wt.% NaCl, 5 wt.% NaCl, 1 wt.% MgCl<sub>2</sub> and 5 wt.% MgCl<sub>2</sub> were performed.

##### 3.1.3. Alkanes

The amount of alkane added was 1 wt.%. The following alkanes were used: pentane, heptane, decane, and hexadecane. Tests were also done with 5 and 10 wt.% pentane, decane or hexadecane added.

##### 3.1.4. Alcohols

The effects of alcohols such as methanol, butanol and octanol on foam were studied. The concentration of each alcohol added was 1 and 5 wt.%. Additional tests using 10 wt.% of butanol were done.

##### 3.1.5. Oil polarity

Foam tests with 1 wt.% toluene or 1 wt.% xylene were performed to examine the effect of oil polarity on foam generation.

##### 3.1.6. Crude oil

Lastly, tests were made of 1 or 5 wt.% of different crude oils in synthetic seawater. The oils were named crude oils a–f.

#### 3.2. Surface tension measurements

The interfacial tension of the oils and surface tensions values used to find critical micelle concentrations (CMC) were measured by the Pendant drop method. The method has been described by Adamson [24]. The instrument used was a CAM 100 with CAM 200 software from KSV Instruments Limited. This instrument could not calculate accurately surface-/interfacial tension for values equal to or less than 1 mN/m, leading to significant uncertainties when measuring these values. For values greater than 1 mN/m the uncertainty interval was  $\pm 0.5$  mN/m when the instrument had been calibrated using the needle method.

### 4. Results and discussion

#### 4.1. Static foam tests

##### 4.1.1. Effect of surfactant concentration

CMC were measured as a reference for the surfactant system in synthetic sea water. The purpose was to see if formation of static foam was related to the CMC in synthetic sea water.

The static tests with AOS demonstrated that the foam column generated was stable for several days. The static foam tests with the fluorinated surfactant gave more stable foam over time. This foam was stable for several weeks. Foam did not form in reference tests without surfactant present but did form at surfactant concentrations even below CMC for both surfactants. Holt et al. [22] found that for a C<sub>14</sub>–C<sub>16</sub> AOS no foam was generated for concentrations less than 0.1%.

In our previous paper [1] the change in foam column height at different surfactant concentrations was investigated. For the AOS foam reached a limited height at a surfactant concentration of 0.5 wt.%. The foam column height did not change when the AOS concentration was increased from 0.01 to 0.1 wt.% (5 × CMC to 50 × CMC). The CMC was 0.0022 wt.% for the AOS surfactant. 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 increased from a few times CMC to more than 100 times CMC, the literature suggests that ionic micelles can at some point undergo a transition from near-spherical to rod-like or other elongated forms [25,26]. Others have reported a second CMC at higher concentrations indicating a reorganization of the micelles [27]. Abed et al. [28] have studied micellization of C<sub>12</sub>–C<sub>18</sub> alpha-olefin sulfonate, but did not observe a transition from spherical to cylindrical micellar shape for the experimental concentration range 0–3 wt.%.

Fig. 1 shows foam height versus surfactant concentration for AOS and the fluorinated surfactants. For FS-500 surfactant concentrations above the CMC, 0.0028 wt.%, the foam height increased slowly with surfactant concentration. From 0.01 wt.%

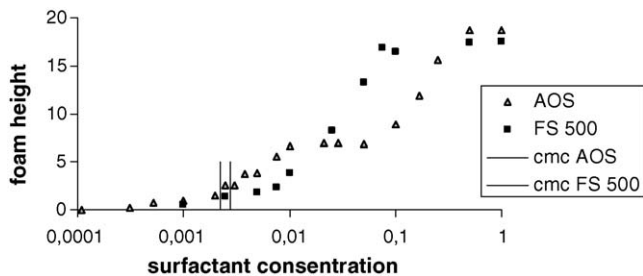


Fig. 1. Foam height vs. surfactant concentration for the fluorinated surfactant and AOS. Foam height was measured 4 h after foam generation.

( $3.5 \times \text{CMC}$ ) surfactant there was a steep increase until the limited foam height was reached ( $<0.1$  wt.%). The CMC values were almost the same for the two surfactants, but the concentration needed to reach the maximum foam height was different. For the fluorinated surfactant a surfactant concentration 35 times the CMC was needed for maximum foam height. For the AOS surfactant a surfactant concentration of more than 100 times the CMC was needed.

#### 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 added oil. The same result was found for both surfactants. The difference in foam height was within the experimental uncertainty for such experiments,  $\pm 0.5$  cm. For the AOS surfactant the foam height after 4 h in synthetic sea water was 18.3 cm. For the other brine solutions the foam height was between 18 and 18.7 cm. For the FS 500 the foam height was 17.4 cm in synthetic sea water and 17.1–17.6 cm for the other brine compositions.

The fluorinated surfactant also generated very stable foam in all tests with different alkanes and crude oil as compared to the AOS surfactant. The results are discussed below. Foam tests with AOS and decane or crude oil formed stable foam at low ionic strength. When changing from synthetic sea water to 1 wt.% NaCl solution the foam height increased from 1.4 to 14.6 cm for foam tests with 1 wt.% decane. For foam tests with AOS and 5 wt.% crude oil the foam height increased from ca. 4 to 17 cm for oil b and from ca. 4 to 21 cm for oil d–f when exchanging the synthetic sea water with 1 wt.% NaCl. For oil a and oil c the foam height was about 2 cm for both brine compositions.

The results show that for the AOS, brine composition influence foam stability with oil present. That is, at high ionic strength, foam stability is reduced.

#### 4.1.3. Effect of alkane

In Fig. 2, the foam column height for foam with AOS is given as a function of the molecular weight of the alkane added. Foam height in foam tests without oil is marked with a line. As seen from the figure short chain alkanes tended to destabilize foam, while long chain alkanes produced stable foam. From a visual examination, it appeared that long chain alkanes produced more stable foam as compared to AOS in brine. Denkov [12] documented the same result by the Ross–Miles method for the surfactant he used. The foam test with hexadecane was more stable than the reference foam test without oil.

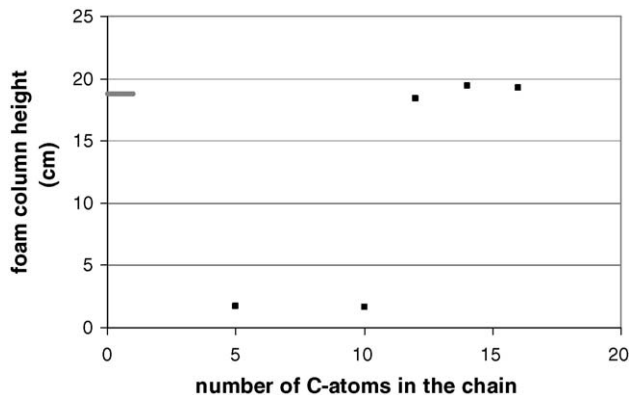


Fig. 2. Foam column height after 2 h for tests with 0.5 wt.% surfactant AOS in synthetic sea water with a content of 1 wt.% alkane. The grey line indicates foam height in tests without oil.

Similar results are also reported by Arnaudov et al. [29]. Draining of liquid films was slower with oil present. Experiments performed by Suffridge et al. [30] studying  $C_{11}$  and  $C_{18}$  in bulk foam tests showed that lower molecular weight alkanes offered a less favorable environment for foam than did higher molecular weight alkanes. Both oils gave some foam, but  $C_{18}$  was the most stable, even more stable than foam generated without oil present [30], consistent with our observations.

Meling and Hanssen [31] report enhanced bulk stability for some foams after the addition of oil. They found no general correlation between bulk foam stability and gas blockage tests performed in glass bead packs. For one surfactant the gas-blocking ability was found to increase with increasing oil carbon number. For the other surfactants used the observed trends were rather complex.

Fig. 3 shows the foam height from tests of the fluorinated surfactant with different alkanes added. Foam heights from foam tests without oil are marked with a line in this figure as well. Foam was generated in every case with each of the different alkanes. For pentane the foam height was nearly twice that seen with the other alkanes or in tests without oil.

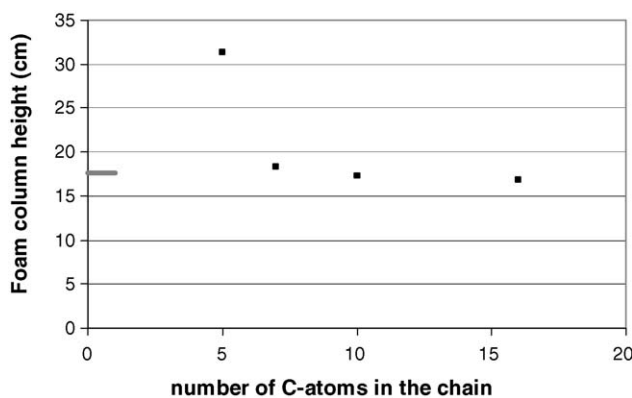


Fig. 3. Foam column height after 2 h for tests with 0.5 wt.% surfactant FS 500 in synthetic sea water with 1 wt.% alkane. The grey line indicates the foam height in foam tests without oil.



#### 4.1.4. Solubilization

Adding a dye (Oil Red) to the alkane phase clearly showed the distribution of alkane between the foam and bulk brine phase. Again, it appeared to be a difference between long versus short chained alkanes. The dye itself did not affect the result as tests with and without the addition of dye gave the same results.

The long chain alkanes (carbon number >10) did not color the brine phase, only the foam for the AOS surfactant. This indicated that these molecules are not solubilizing 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 [31,32]. The effect of solubilization has been discussed by Lobo et al. [33] and is also discussed in our previous paper [1]. For the fluorinated surfactant the change in solubilization is between C<sub>5</sub> and C<sub>7</sub>. Pentane solubilized in the micelles, while heptane and longer alkanes did not. It appeared the Plateau borders with heptane and longer alkanes were thicker than for pentane.

#### 4.1.5. Amount of oil

Another interesting result was that when long chain alkanes were added, there was no oil phase between the liquid and foam columns. All of the oil must therefore have been in the foam structure, even for a 10 wt.% content of alkane. The amount of hexadecane, 1, 5 and 10 wt.%, did not influence foam column height.

The Plateau borders were thicker for the long chain alkanes than for the short ones. Foam Plateau borders for the short alkanes were visually similar to foam Plateau borders in tests without oil. Aveyard et al. [34] also reported thicker lamellas in foam with added hexadecane than lamellas in foam with shorter chain alkanes (undecane). Foam without oil had the thinnest Plateau borders.

#### 4.1.6. Spreading-, entering and bridging-coefficient and lamella number

If we look at one surfactant at a time the spreading coefficients and the lamella number are almost the same for the different alkanes (Tables 1 and 2). The entering coefficients and the bridging coefficients are also shown in Table 1 for the AOS surfactant and in Table 2 for FS-500. For the fluorinated surfactant all the calculated spreading coefficients and lamella numbers indicated stable foam in accordance with theory. For FS-500 the highest foam height was observed with pentane. The foam height was nearly twice the foam height of the other alkanes and foam

Table 1  
Spreading and bridging coefficient and lamella number for the AOS surfactant using different alkanes

Oil	Spreading coefficient (mN/m)	Entering coefficient (mN/m)	Bridging coefficient	Lamella number
Decane	4.8	6.2	234	5.4
Dodecane	3.0	4.2	162	5.8
Tetradecane	4.5	6.5	255	3.9
Hexadecane	2.1	5.1	156	2.3

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

Table 2  
Spreading and bridging coefficient and lamella number for the FS-500 surfactant using different alkanes

Oil	Spreading coefficient (mN/m)	Entering coefficient (mN/m)	Bridging coefficient	Lamella number
Pentane	−5.3	4.7	16	0.4
Decane	−9.7	−1.9	−192	0.6
Hexadecane	−11.8	2.2	−106	0.3

Measured against a solution of 0.5 wt.% FS-500 in synthetic sea water.

height without oil. This result was somewhat surprising as both the entering coefficient was positive and the bridging coefficient was slightly positive.

The spreading coefficients and the lamella number were higher for the AOS surfactant than for the fluorinated surfactant. All the bridging coefficients were large and positive (Table 1). The surface tension for the AOS surfactant was 24 mN/m and for the FS-500 it is 14 mN/m. The varied range in spreading coefficients for the two surfactants could be caused by the great difference in the surfactant surface tension values. Results similar to this can be found in Mannhardt et al. [6] and Dalland et al. [14].

#### 4.1.7. Effect of alcohol

The short chain alcohol methanol and a lower concentration of butanol (conc. <5 wt.%) showed stable foam for the AOS surfactant [1]. At high concentration of butanol and for all concentrations of octanol applied almost no foam was generated. Results were similar for the fluorinated surfactant. The fluorinated surfactant, however, generated stable foam for all concentrations of butanol. Foam tests with methanol and butanol generated an 18–20 cm foam height and tests with octanol generated about a 0.5 cm foam height.

#### 4.1.8. Effect of oil polarity

To investigate the influence of oil polarity on foam stability, additives like xylene or toluene were added to the pure brine surfactant solutions. The results showed that these additives reduced the static foam height significantly as compared to the pure brine—surfactant system. In our tests almost no foam was formed. The foam height was reduced from 17.5 cm in foam tests without oil to 2–4.5 cm foam in tests with xylene or toluene. The result was the same for both surfactants. Based on these studies, it is difficult to make a general conclusion regarding the influence of oil polarity on foam stability.

#### 4.1.9. Effect of crude oil

Bulk foam tests were also made with crude oils from some North Sea oil reservoirs (Figs. 4 and 5). Consideration of the physical properties of the crude oils was necessary for interpretation of the results. The stability of the foam was the same for all the crude oils and the fluorinated surfactant, and the stability was not changed when larger amounts of oil were added. Fig. 5 shows foam height over time for 1 wt.% of the different crude oils in synthetic sea water. For the AOS surfactant the crude oils showed different abilities in breaking down foam [1] (Fig. 4). In

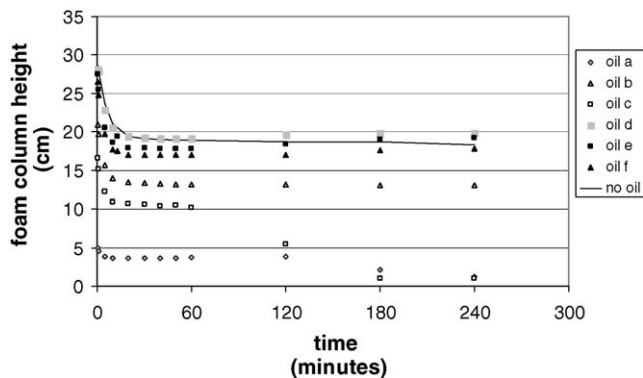


Fig. 4. The plot shows foam column height in solutions of synthetic sea water with 0.5 wt.% AOS and 1 wt.% of different crude oils.

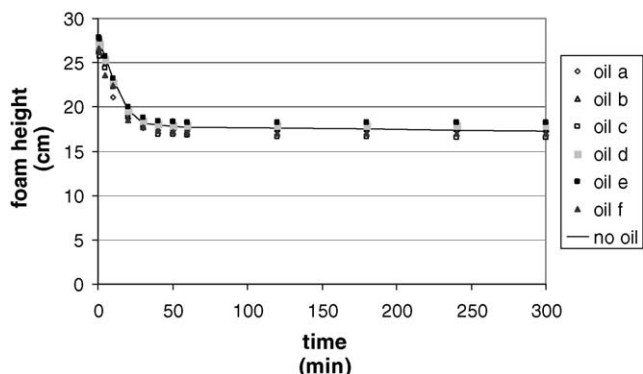


Fig. 5. The plot shows foam column height in solutions of synthetic sea water with 0.5 wt.% FS 500 and 1 wt.% of different crude oils.

both Figs. 4 and 5, foam heights over time for foam tests without oil are marked with a line.

**4.1.9.1. AOS.** The spreading coefficients calculated from interfacial tension measurements for the crude oils were positive for the AOS surfactant (Table 3). By theory, in such a situation the oil would spread at the surface and break the foam. If the spreading coefficient were negative, the literature suggests that the oil would remain a droplet at the surface, and that this defines a necessary condition for stable foam [10]. Our tests show that the AOS surfactant generated stable foam in presence of some of the crude oils. The spreading coefficients were positive for all the crude oil. Tests in which foam was generated with 1 wt.% crude oil added to synthetic sea water demonstrated that both

Table 3  
AOS spreading, entering and bridging coefficient and lamella number for the different crude oils

Oil	Spreading coefficient (mN/m)	Entering coefficient (mN/m)	Bridging coefficient	Lamella number
a	11.1	11.9	489	10.4
b	4.6	5.6	250	8.1
c	4.2	5.6	241	5.8
d	7.3	7.9	353	12.3
e	5.4	9.0	340	2.3
f	4.7	7.9	303	2.5

stable foam and foam breaking may occur in the presence of crude oils (Fig. 4). Similar results were obtained using 5 wt.% oil in 1 wt.% NaCl solution. Foam broke down very quickly in tests with 5 wt.% oil in synthetic sea water.

Lamella numbers as calculated by Eq. (3) are presented in Table 3. Oils a, b and d had type C foam, and oils c, e and f had type B foam. All of the crude oils had positive spreading and entering coefficients, indicating type C foams. For all AOS foams generated in the presence of oil the bridging coefficient was large and positive (Tables 1 and 3). This indicates that the bridging mechanism may induce film rupture [12].

According to theory the values of  $S$ ,  $E$ ,  $B$  and  $L$  show that the AOS surfactant should have given foams with low or moderate stability to oil. Foam stability in the presence of the different crude oils does not seem to have been governed by this type of classification. Oil b was for instance very stable even if it had type C foam. For the foam tests with 1 wt.% crude oil, both the stable oils b and d had type C foam. The two unstable oils a and c had different foam type: oil a had type C foam; oil c had type B. The results indicate that the formation and stability of a pseudo-emulsion film can play a significant role in the stability of these foams. An important question remains: is it possible that electrical repulsion in the pseudo-emulsion film prevents drop entry even in this high salinity environment?

When mixing the static foam tests, oil was forced into the foam. After mixing, each oil type drained out of the foam at a different rate, if at all. If the crude oil drained out of the foam it formed an oil phase between the water phase and the foam column. The size of the oil phase varied for the different oils. The most stable crude oils remained in the Plateau borders, and it appeared that nothing would drain out.

The foam structure was very different for the two surfactants. For the AOS surfactant the stable foam had very thick liquid films (Fig. 6). Oils b and d had such foam. Draining of oil to the Plateau border wedges was not observed during the 2-day long experiment. The foam height was stable for 2–3 days until it suddenly cracked and all of the foam broke down within seconds. Oils e and f gave relatively stable foam for some hours, but the foam was almost completely broken down after 1 day. In these tests most of the oil drained out of the foam and left oil in the Plateau border wedges during the first hours. The Plateau borders in these tests were thin.

**4.1.9.2. FS-500.** The spreading coefficients were negative for all the crude oils (Table 4). According to theory this is a necessary condition for stable foam. The lamella numbers, calculated by using Eq. (3) (Table 4) indicated a type A foam. Type A foams are believed to show best stability in the presence of oil, consistent with both negative entering and spreading coefficients. These foams are believed to show little interaction with crude oil [10]. Some of the entering coefficients for the fluorinated surfactant were positive. This indicated type B foams, which show moderate stability towards oil. For all the crude oils stable foam was observed.

The foam tests with crude oil and the fluorinated surfactant generated foam that was more stable and much denser than the AOS foam (Fig. 7). The oil collected primarily in the Plateau



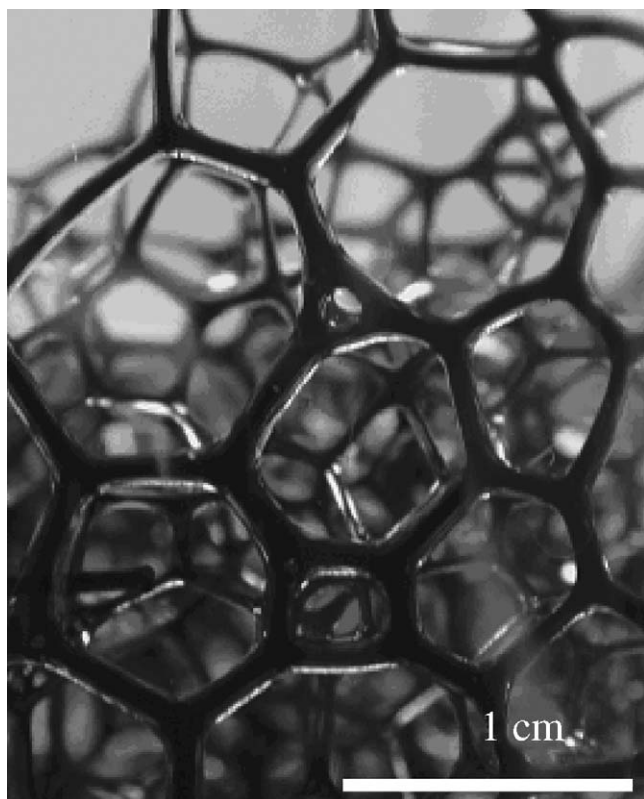


Fig. 6. The picture shows foam with abundant oil in the Plateau borders. The foam is from a foam test with 1 wt.% of oil b in synthetic sea water with 0.5 wt.% AOS content. The picture is taken 24 h after mixing and is enlarged three times.

Table 4  
FS-500 spreading, entering and bridging coefficient and lamella number for the different crude oils

Oil	Spreading coefficient (mN/m)	Entering coefficient (mN/m)	Bridging coefficient	Lamella number
a	-2.7	6.6	72	0.4
b	-8.3	-1.6	-164	0.7
c	-8.9	-2.9	-204	0.8
d	-4.8	8.0	84	0.3
e	-8.4	1.9	-88	0.5
f	-6.3	3.1	-29	0.5

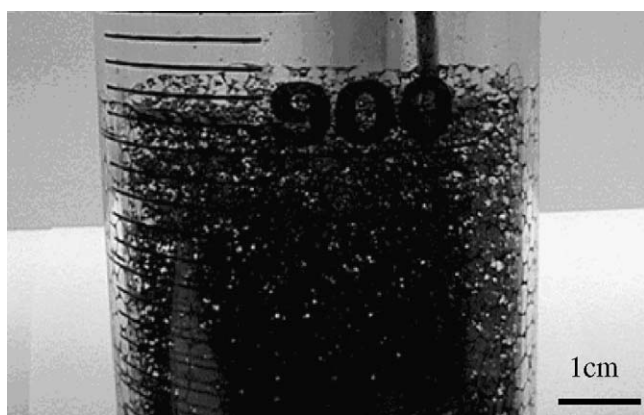


Fig. 7. 5 wt.% crude oil d in synthetic sea water with 0.5 wt.% fluorinated surfactant. The picture is taken 1 day after mixing.

border wedges, but there was some oil throughout the Plateau borders. The foam was stable for many weeks and it seemed that oil did not drain out of the foam.

## 5. Summary

The results of this work show that foam is generated below CMC for both surfactants. Both surfactants reached a constant maximum foam height at 0.1–0.5 wt.% surfactant, but increased concentrations of FS-500 did not show a multiple step increase in foam height.

We found that the limit for solubilization was different for the two surfactants. In foam tests with AOS, decane and alkanes with lower molecular weight were solubilized in the micelles. These light alkanes broke down the foam. The limit for solubilization for the FS-500 was lower. Pentane was solubilized, but alkanes with a higher molecular weight were not. Foam tests with pentane gave much more foam than for the other alkanes with the FS-500 surfactant. Thus, in relation to foam stability there seems to be another effect of solubilization for the fluorinated surfactant than for the AOS. The molecular weight of the surfactants and/or the different structure of the two surfactants could be possible explanations.

The FS-500 surfactant generated stable foam in all tests with oil. The spreading coefficients were negative for all oils investigated with FS-500. The lamella numbers calculated, by using Eq. (3) and its assumptions, were consistent with the values for stable foam as stated by the lamella number theory.

For the AOS surfactant all the spreading coefficients were positive. In spite of this several of the foam tests with oil were stable. The results show that foam could be stable in presence of oil for both surfactants. The variation in spreading coefficient is mainly caused by the different surface tensions for the two surfactants. A lack of correlation between  $S$ ,  $E$ ,  $L$ , and  $B$  and foam stability suggested that properties of the pseudo-emulsion film were of crucial importance for foam stability with the AOS surfactant.

The FS-500 surfactant seemed to give more stable foam than AOS in presence of oil. Visually, the FS-500 foam had a denser bubble concentration than the AOS foam. It was also much more stable over time than the AOS foam. Foam tests with the FS-500 surfactant could be stable for weeks.

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