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Transition from a foam-like to an onion-like nanostructure in water-rich L₃ phases

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Abstract: In dilute water-surfactant systems L₃ phases are found in which bilayers interconnect to form a sample-spanning sponge-like structure. From our previous study of the system water/NaCl-AOT (sodium bis(2-ethylhexyl) sulfo succinate) we know that a transition of this sponge-like structure to an oil-continuous foam-like structure occurs upon addition of minute amounts of oil (about 3 wt%, α = 0.03) in the L₃ channel at a constant surfactant mass fraction of γ = 0.15 and T = 25 °C. The aim of the present study was to verify if the same transition occurs at γ = 0.25. To achieve this goal, we determined the relevant part of the phase diagram and studied the electrical conductivities and viscosities within the narrow one-phase L₃ channel. Although the electrical conductivities and viscosities change qualitatively like those observed at γ = 0.15 we did not observe a sponge-like structure at γ = 0.25 in the oil-free system (α = 0) with freeze-fracture electron microscopy (FFEM) and freeze fracture direct imaging (FFDI). Together with the FFEM/FFDI images and SANS/SAXS curves we provide experimental evidence for a structural transition with decreasing oil content from a thermodynamically stable foam-like to a thermodynamically stable onion-like nanostructure at γ = 0.25 rather than to a sponge-like structure as is the case at γ = 0.15.

Keywords: L₃ phase; foam-like structure; onion-like structure; transition and structure in L₃ channel

1 Introduction

An L₃ phase was found for systems with non-ionic [1–5] and ionic [6–10] surfactants. The L₃ phase is typically connected with a sponge-like structure, which is a bicontinuous structure consisting of a surfactant bilayer that separates two continuous water phases (see Figure 1, top, left). However, there is hidden evidence for the formation of thermodynamically stable onion-like structures (see Figure 1, bottom, left) in the L₃ channel [3, 11, 12]. In the presence of oil, the surfactant bilayer can be swollen with oil but the system is still water-continuous. However, there is also hidden evidence that the addition of oil may lead to the formation of a foam-like, oil-continuous structure (see Figure 1, right) in the L₃ channel [13–21]. Hidden evidence means that there was no clear experimental evidence for a thermodynamically stable foam-like nanostructure and a thermodynamically stable onion-like nanostructure, respectively, but only assumptions that such structures could exist. The quoted studies read as if no one really dared to challenge the generally accepted (a) sponge-like structure of the L₃ phase and (b) thermodynamic instability of onion-like structures. A summary of the literature about foam-like and onion-like structures is provided in the introductions of [22, 23], respectively. We will show and discuss in the present study that both thermodynamically stable foam-like and thermodynamically stable onion-like structures can be formed in the L₃ phase.

In our previous study [22] we presented clear experimental evidence for the formation of a thermodynamically stable oil-continuous foam-like structure in the homogeneous channel of the L₃ phase. The system under study consisted of the aqueous phase water/NaCl, the oil hexyl methacrylate (C₆MA), and the surfactant sodium bis(2-ethylhexyl) sul fosuccinate (AOT). Note that other than Jahn and Strey [15] and Chen et al. [16] we did not use n-decane as oil but hexyl methacrylate (C₆MA) since our ultimate goal is to polymerize the continuous oil (monomer) phase, i.e. to synthesize nanoporous polymers. We located the isothermal L₃ channel at a constant surfactant mass fraction of γ = 0.15: the channel starts at the oil-free system and evolves with increasing oil mass...
fraction towards lower NaCl mass fractions. Viscosity and conductivity measurements as well as freeze fracture electron microscopy (FFEM) images support a transition from a sponge-like structure in the oil-free system to a foam-like structure for an oil mass fraction of $\alpha = 0.06$ with decreasing $\gamma$ and $\varepsilon$ [22]. (right) Transition from a sponge-like to an onion-like structure in the oil-free system ($\alpha = 0$) with increasing $\gamma$ and $\varepsilon$ [23]. *Reprinted with permission from ref. 8. Copyright 1990 American Chemical Society.

increase the NaCl mass fraction with decreasing oil mass fraction in order to stay in the one-phase L$_3$ channel. Our expectations were clear: (i) a transition from the foam-like back to the sponge-like structure and (ii) smaller domain sizes for the resulting sponge-like structure compared to the values obtained at $\gamma = 0.15$. To our big surprise, we did not find a sponge-like structure in the oil-free system. The study at hand is about the never reported transition from a foam-like to an onion-like structure in the one-phase L$_3$ channel, i.e. about a transition between two thermodynamically stable structures hardly discussed in connection with the L$_3$ phase. We measured the extension of the L$_3$ channel as a function of the oil and the NaCl concentration and traced the structural transition within the L$_3$ phase by viscosity and conductivity measurements. Complementary freeze fracture electron microscope (FFEM) and freeze fracture direct imaging (FFDI) images support the difference between the structures in the oil-free system at $\gamma = 0.15$ and $\gamma = 0.25$, respectively.

2 Materials and methods

2.1 Materials

Pure water from the PURELAB® flex type 1 water system (Veolia Water, Paris, France) and sodium chloride (NaCl, analytical grade) from Merck KGaA (Darmstadt, Germany) were used for brine. The surfactant sodium bis(2-ethylhexyl) sulfosuccinate (AOT, purity > 99 %, BioXtra) was purchased from Sigma-Aldrich (St. Louis, United States) and hexyl methacrylate (C$_6$MA, purity > 98 %, stabilized with MEHQ) from Tokyo Chemical Industry Co, Ltd (TCI, Tokyo, Japan). All chemicals were used without further purification.

2.2 Phase studies

Samples consisting of NaCl solution called brine (A), C$_6$MA (B), and AOT (C) were weighed into test tubes with a volume of 15 mL and a Teflon-coated magnetic stir bar was added. The test tubes were sealed with a polyethylene stopper and placed in a transparent water basin with the DC30 thermostat from Thermo Haake (Karlsruhe, Germany) and the GMH3700 temperature sensor from GHM Messtechnik GmbH (Regenstauf, Germany). The water basin temperature was changed in suitable steps to detect the phase boundaries. Visual determination in diffuse and transmitted light was used to determine the number of phases and their appearance in equilibrium. The quaternary system can be described with three mass fractions, namely alpha ($\alpha$), the mass fraction of oil in the total mass of oil and brine

$$\alpha = \frac{m_o}{m_o + m_b}$$  \hspace{1cm} (1)

gamma ($\gamma$), the mass fraction of surfactant in the whole sample

$$\gamma = \frac{m_c}{m_o + m_b + m_c}$$  \hspace{1cm} (2)

**Figure 1:** Structures of the L$_3$ phase of the system water/NaCl – C$_6$MA – AOT at $T = 25$ °C. (top) Transition from a sponge-like to a foam-like structure at a constant surfactant mass fraction of $\gamma = 0.15$ with increasing oil mass fraction $\alpha$ and decreasing NaCl mass fraction $\varepsilon$ [22]. (right) Decreasing domain size of the foam-like structure at $\alpha = 0.06$ with increasing $\gamma$ and $\varepsilon$ [22] (bottom) Transition from a foam-like to an onion-like structure at $\gamma = 0.25$ with decreasing $\alpha$ and increasing $\varepsilon$ (this study). (left) Transition from a sponge-like to an onion-like structure in the oil-free system ($\alpha = 0$) with increasing $\gamma$ and $\varepsilon$ [23]. *Reprinted with permission from ref. 8. Copyright 1990 American Chemical Society.
and epsilon (ε), the mass fraction of NaCl in the brine

$$\varepsilon = \frac{m_{NaCl}}{m_A}$$  \hspace{1cm} (3)

### 2.3 Electrical conductivity and viscosity measurements

#### 2.3.1 Conductivity

The conductivity measuring cell LTA 1 from Wissenschaftlich-Technische Werkstätten GmbH (WTW, Weilheim in Oberbayern, Germany) and the LCR meter HMB818 from Rohde & Schwarz GmbH & Co. KG (Munich, Germany) were used to determine conductivity. The conductivity measuring cell was placed in closed test tubes (10 mL) containing the samples and a Teflon-coated magnetic stir bar. The temperature of the samples was controlled via a water basin using the DC30 thermostat from Thermo Haake (Karlsruhe, Germany) and the GME3700 temperature sensor from GME Messtechnik GmbH (Regenstauf, Germany). The conductivities were recorded 300 s after the temperature was reached.

#### 2.3.2 Viscosity

The rheometer Physica MCR 501 from Anton Paar GmbH (Graz, Austria) was used to determine the shear viscosities with a steel cone-plate geometry (50 mm, 1°, CP50-1/TTG, Anton Paar, Graz, Austria). The study was performed with a cone-plate gap of $d = 0.101$ mm, shear rates of from $\dot{\gamma} = 100$ $s^{-1}$ to 0.01 $s^{-1}$, and at a temperature of $T = 25$ °C controlled by the AWC 100 cooling unit from JULABO Labortechnik GmbH (Seelbach, Germany). The viscosity was independent of the shear rate for all samples (s. Figure S1 in Supplementary Material), i.e. all samples are Newtonian fluids, as was already found by Snabre and Porte in 1990 for the L3 phase at similar surfactant concentrations [24]. In Figure 3 the viscosities measured at $\dot{\gamma} = 10$ $s^{-1}$ are plotted.

### 2.4 Freeze fracture electron microscopy (FFEM) and freeze fracture direct imaging (FFDI)

The NaCl mass fraction in the samples was adjusted so that the middle temperature of the L3 phase was $T \sim 23.5$ °C to allow easy sample preparation at room temperature ($23.5 \pm 1$ °C).

#### 2.4.1 FFEM

Sandwiches (consisting of two outer copper plates and two inner bare copper grids) containing liquid samples at the L3 phase temperature were rapidly frozen in liquid ethane using a plunging device. The frozen sandwiches were fractured under liquid nitrogen and the grids were transferred (without contamination in the air) in the vacuum chamber of the freeze fracture and etching system EM BAF060 from Leica Microsystems GmbH (Wetzlar, Germany). In EM BAF060, the specimen stage was cooled to $T = -150$ °C. Fractured frozen surfaces of the samples were shadowed with platinum-carbon (~2 nm) at 45° and coated with a layer of pure carbon (~20 nm) at 90°. The replicas were cleaned with ethanol and acetone, dried, and examined with the EM10 transmission electron microscope from Carl Zeiss AG (Oberkochen, Germany) at 60 kV.

#### 2.4.2 FFDI

Two copper plates and two copper grids with a holey carbon film (Quantifoil Multi A 200 mesh) were used for FFDI to form a sandwich. Exactly as for FFEM, the sandwich with the liquid sample was quickly frozen in liquid ethane and broken under liquid nitrogen. The grid was mounted on a cryo-specimen holder (CT3500, Oxford Instruments, Oxford, UK) in the GA G34-215 cryo box from Zeiss (Oberkochen, Germany) and transported to the TEM. The sample was viewed in the LEO EM 912 Ω transmission electron microscope from Zeiss (Oberkochen, Germany) at 120 kV. The temperature of the cryo sample holder was consistently between $T = -162$ °C and -168 °C.

### 2.5 SAXS

SAXS analysis of the H$_2$O/NaCl–AOT system was performed using a XEUSAXS/WAXS system from Xenocs (France) equipped with a GeniX Cu$_{Kα}$ ultra-low-divergence source ($λ = 1.541$ Å, Xenocs) and a Pilatus 300K hybrid pixel detector from Dectris (Switzerland). The sample was measured at a sample-to-detector distance of 0.8 m, which allowed the investigation of a $q$ range from 0.02 Å$^{-1}$ to 0.4 Å$^{-1}$. For the measurements, the sample was positioned in a flow-through Kapton capillary (1 mm inner diameter) from GoodFellow GmbH (Germany) in a Linkam stage from Linkam Scientific (UK) at a temperature of 25 °C. Fostrot software (V3.3.4) was used to analyze the obtained 2D data [25]. The scattering of the sample was normalized with respect to incident intensity, sample thickness, acquisition time, transmission, and background scattering signal of the setup. Glassy carbon type 2 was used as a standard for normalization to incident intensity [26].

### 3 Results

For the sake of comparison, we will show the results of the present study together with the results of our previous study [22]. Note that we will discuss the results starting with the oil-containing system from which we take out hexyl methacrylate as indicated in Figure 1 with the lower arrow pointing from right to left.

#### 3.1 Phase diagram

We discussed in detail in our previous study [22] that a combination of an $ε$- and an $α$-variation allows one to find an isothermal L3 channel at $T = 25$ °C and a constant surfactant mass fraction, namely $γ = 0.15$ (Figure 2 (left)). Looking at Figure 2 (left) one sees how the narrow L3 channel shifts to higher $ε$-values (higher electrolyte mass fractions) with decreasing $α$-values (decreasing oil mass fraction). The same holds true for the L3 channel measured at $T = 25$ °C and a constant surfactant mass fraction of $γ = 0.25$ (Figure 2 (right)). The major difference is the width of the L3 channel which is significantly larger for the system with the higher surfactant mass fraction. This observation is in line with the phase diagrams of typical microemulsions for which the region in the phase diagram becomes broader with increasing surfactant mass fraction: the smaller the structures the more the tuning parameter (here the electrolyte content) must be changed.
3.2 Viscosities and conductivities

In order to learn more about the structure in the L3 channel we carried out conductivity and viscosity measurements in analogy to our previous study. The results are shown in Figure 3. Looking at the viscosities first, one sees that the data measured at $\gamma = 0.15$ (Figure 3 (left)) and those measured at $\gamma = 0.25$ (Figure 3 (right)) are qualitatively the same. As regards a quantitative comparison one sees two differences at the higher surfactant mass fraction of $\gamma = 0.25$: (i) the decrease of the viscosity with decreasing oil content happens at higher oil mass fractions ($\alpha \leq 0.05$ as opposed to $\alpha \leq 0.03$ at $\gamma = 0.15$) and (ii) the viscosities are higher and constant for $\alpha \leq 0.03$. The steep decrease of the viscosity by a factor of 20 is in line with the results published by Wolf et al. [21] and we attributed this change to the transition from a foam-like to a sponge-like structure in our previous study [22]. Since the trends are the same at both surfactant mass fractions one is tempted to argue that the changes observed at $\gamma = 0.25$ with decreasing oil mass fraction can again be assigned to a transition from a foam-like to a sponge-like structure. The higher absolute viscosities at the lower $\alpha$-values are simply due to the higher amount of surfactant. However, the images obtained with Freeze Fracture Electron Microscopy (FFEM) and with Freeze Fracture Direct Imaging (FFDI) are not in line with a sponge-like structure at $\gamma = 0.25$ as will be shown further below.

Before discussing the conductivity data, we like to recall that all of our samples are Newtonian fluids, i.e. we did not observe shear thinning. Shear thinning is reported by Bergenholtz and Wagner [27] for a lamellar phase containing 17 wt% AOT. Comparing our system with the one studied by Bergenholtz and Wagner [27] one sees that (i) the viscosities of our samples are one order of magnitude lower ((0.2–0.3) Pa s as opposed to $\sim 8$ Pa s) and (ii) the diameter of our onions is also one order of magnitude smaller ((85 ± 30) nm as opposed to 1000 nm–2500 nm). Shear thinning was also observed and discussed by Gentile et al. [28] for a sample with 40 wt% C16E4 in D2O. Again, the viscosities are much higher compared to our samples ((10–30) Pa s as opposed to (0.2–0.3) Pa s) and the diameters of the onions are much larger (375 nm–450 nm as opposed to (85 ± 30) nm). In addition to the different viscosities and onion sizes, the rigidity of the AOT...
bilayers may also play a role for the absence of shear thinning in our L3 phase: if it was larger than that of the C10E4 bilayers, a higher energy would be required to obtain shear-induced transitions as discussed by Gentile et al. [28].

We discussed in our previous study that we expected a water-continuous system throughout the whole L3 channel but that the conductivity data revealed a water-continuous phase only for oil mass fractions $\alpha \leq 0.045$, i.e. a transition from an oil-continuous to a water-continuous phase with decreasing $\alpha$. We recall that we identified the oil-continuous phase as a foam-like structure (see Figure 1, right). Being more precise one should say an “inverted foam-like structure” since the aqueous phase is the dispersed phase. Comparing the conductivity data measured at $\gamma = 0.15$ (Figure 3 (left)) with those measured at $\gamma = 0.25$ (Figure 3 (right)) one sees that qualitatively they are the same as was the case for the viscosities. The same holds true for the relative conductivities $\kappa/\kappa^0$ which are plotted versus the oil mass fraction $\alpha$ in Figure 4. Note that the maxima of the two $\kappa/\kappa^0(\alpha)$-curves correspond to the intersections between the $\eta(\alpha)$-curve and the $\kappa(\alpha)$-curve shown in Figure 3. Quantitatively, however, there are two differences at the higher surfactant mass fraction of $\gamma = 0.25$: (i) the system becomes water-continuous for oil mass fractions $\alpha \leq 0.07$ (as opposed to $\alpha \leq 0.047$ at $\gamma = 0.15$), i.e. the transition from an oil-continuous to a water-continuous phase happens at higher oil mass fractions and (ii) the relative conductivities $\kappa/\kappa^0$ are lower for oil mass fractions on the left hand side of the maximum: for the oil-free system we obtain $\kappa/\kappa^0 = 0.61$ for $\gamma = 0.15$ as opposed to $\kappa/\kappa^0 = 0.50$ for $\gamma = 0.25$. These values are in line with the trend described with equation (3) in Strey et al. [9] for the relative self-diffusion coefficients, i.e. the values indicate a sponge-like structure in which the conductivity is the more hindered the higher the amount of the membrane, i.e. of the surfactant bilayer. However, the images obtained with Freeze Fracture Electron Microscopy (FFEM) and with Freeze Fracture Direct Imaging (FFDI) are not in line with a sponge-like structure at $\gamma = 0.25$ as will be shown in the following.

3.3 FFEM and FFDI images

To visualize the transition from the foam-like to the onion-like structure we took FFEM and FFDI images at various $\alpha$-values within the L3 channel, examples of which are shown in Figures 5 and 6. As was the case for all samples, the NaCl content was adjusted to allow for a sample preparation at room temperature ($T = (23.5 \pm 1.0)$ °C). The exact sample compositions are given in the figures. Three representative FFEM images are shown in Figure 5 (right) and are compared with FFDI images taken at $\gamma = 0.15$ for the same $\alpha$-values (Figure 5 (left)). The same FFEM images are shown in Figure 6 (right) and are complemented with the respective FFDI images which clearly show the same overall structures. Let us now have a closer look at Figure 5. We know from our previous study [22] that the two samples with $\alpha = 0.06$ have a foam-like structure (Figure 5, top) and that the oil-free sample with $\gamma = 0.15$ has a sponge-like structure (Figure 5, bottom left). The two open questions are: (1) Which structure is formed in the oil-free system at $\gamma = 0.25$? (2) How do the structural transitions take place?

*Answer to Question 1:* According to Strey et al. (s. Figure 6 in ref. 9) the characteristic domain size of a sponge-like phase at a surfactant mass fraction of $\gamma = 0.25$ is $D = 11.6$ nm (compared to $D = 19.5$ nm at $\gamma = 0.15$). Looking at Figure 5 (bottom right) and at Table 1 one sees that the size of the observed structure is about one order of magnitude larger. The FFEM images also reveal the existence of layered structures (see green arrow in Figure 5). We recall that the viscosity reaches a minimum and the conductivity a maximum in the oil-free system, i.e. that the system must be
Taken these observations together we suggest an onion-like structure as will be discussed in more detail in Section 4. Note that the onions are the polyhedra seen in Figure 5 (bottom right). Fractures through the onions are very seldom (green arrow in Figure 5), since the fracture always happens at the weakest point, which is the midplane of the bilayers.

**Answer to Question 2 and Corrigendum**: What we need to rationalize is the structural transition from a foam-like to a sponge-like structure at \( \gamma = 0.15 \) and from a foam-like to an onion-like structure at \( \gamma = 0.25 \). We know from the conductivity data that at both surfactant mass fractions the structure becomes more and more water-continuous with decreasing \( \alpha \). Moreover, we see the same intermediate structure in both cases (Figure 5 (middle)) with coexisting large and small structures. For the sample with \( \gamma = 0.15 \) and \( \alpha = 0.012 \) we see the same pattern in Figure 7 (right) in ref. 22. However, in our previous study we assigned this pattern to a “large” and a “small” foam-like structure, which we now must correct. From the FFEM images it is clear that the large structures are regions of brine: in mixtures of water and bilayer structures the fracture occurs at the weakest spot which is the hydrophobic side of the surfactant layers [30, 31]. In other words, the transition from the sponge-like to
the foam-like structure is not continuous with the two structures coexisting in between as described in [22]. Instead, we identified brine polyhedra which coexist with small structures — the latter always have diameters of (20–30) nm (see Table 1). We will suggest a structure for the transition state in Section 4.

### 3.4 SAXS and SANS curves

To provide further experimental evidence for the formation of onions we measured a SAXS curve of the oil-free sample at $\gamma = 0.25$ in which we expected to see the first order Bragg peak of the layered structure. Unfortunately, this peak is not visible as shown in Figure 7 (green circles) where the green arrow points to the $q$-value at which the peak is expected. The disappearance of the Bragg peak, i.e. the dominant minimum in the SAXS curve, is a known phenomenon for AOT and was discussed by Nallet et al. [32] and Skouri et al. [33]. However, SANS curves support the formation of onions as will be discussed further below. For the study at hand we show two SANS curves from Strey et al. [9] for the very same system (open circles in Figure 7). We also measured two SANS curves which we will show in a follow-up study [23] because the concentrations are higher than 25 wt%, namely 33 wt% and 45 wt%, while the concentrations measured by Strey et al. [9] of 19 wt% and 28 wt% are similar to ours and thus the SANS and the SAXS curves can be compared. Note that the NaCl concentration $\varepsilon$ was always adjusted in order to stay in the isotropic $L_3$ channel.

Looking at Figure 7 one sees that the SANS curves can be fitted with curves (solid lines) that contain two contributions (dotted lines and dashed-dotted lines). As expected, we have one contribution from the layered structure (dotted lines): the filled arrows point to the first order Bragg peaks. From the respective Bragg peak positions one can calculate the mean distance between the bilayers which is $d = 14.6$ nm for $\gamma = 0.19$ and $d = 9.1$ nm for $\gamma = 0.28$. Since the mean distance is proportional to the membrane volume fraction one can

![Figure 7: Small angle X-ray scattering (SAXS) curve (green circles) measured at $T = 25^\circ$C and small angle neutron scattering (SANS) curves (open circles) measured at $T = 20^\circ$C of the oil-free system H$_2$O/NaCl-AOT in bulk contrast. Surfactant concentrations are given in mass fractions. The SANS data are taken from a study published by Strey et al. [9] (Figure 5, curves c and d).](image-url)

### Table 1: Oil mass fraction $\alpha$, surfactant mass fraction $\gamma$, and NaCl mass fraction $\varepsilon$ (the NaCl mass fraction was partially adjusted for a preparation at $T = (23.5 \pm 1)^\circ$C). Structure sizes determined from FFEM or FFDI images $D_{\text{FFEM/FFDI}}$ and the number of measured structures $N$ from which $D_{\text{FFEM/FFDI}}$ was determined. See Corrigendum for structures at $\gamma = 0.15$ as discussed in Section 3 of this manuscript.

<table>
<thead>
<tr>
<th>$\alpha$</th>
<th>$\gamma$</th>
<th>$\varepsilon$</th>
<th>$D_{\text{FFEM/FFDI}}$/nm</th>
<th>$N$</th>
<th>Structure</th>
<th>Image</th>
</tr>
</thead>
<tbody>
<tr>
<td>0.06$^a$</td>
<td>0.15</td>
<td>0.0030</td>
<td>$36 \pm 7^a$</td>
<td>170</td>
<td>Foam-like</td>
<td>Figure 5 (top, left)</td>
</tr>
<tr>
<td>0.037$^a$</td>
<td>0.15</td>
<td>0.0058</td>
<td>$35 \pm 8^a$</td>
<td>90</td>
<td>Foam-like</td>
<td>Ref. 22 Figure 6 (bottom, left)</td>
</tr>
<tr>
<td>0.023$^a$</td>
<td>0.15</td>
<td>0.009</td>
<td>$24 \pm 7$</td>
<td>80</td>
<td>Vesicles</td>
<td>Figure 5 (middle, left)</td>
</tr>
<tr>
<td>0.012$^a$</td>
<td>0.15</td>
<td>0.013</td>
<td>$145 \pm 42$</td>
<td>80</td>
<td>Brine polyhedra</td>
<td>Figure 5 (middle, left)</td>
</tr>
<tr>
<td>0.005</td>
<td>0.15</td>
<td>0.021</td>
<td>$23 \pm 5$</td>
<td>50</td>
<td>Vesicles</td>
<td>Ref. 22 Figure 7 (right)</td>
</tr>
<tr>
<td>0.006$^b$</td>
<td>0.25</td>
<td>0.0076</td>
<td>$170 \pm 60$</td>
<td>50</td>
<td>Brine polyhedra</td>
<td>Ref. 22 Figure 7 (right)</td>
</tr>
<tr>
<td>0.04$^b$</td>
<td>0.25</td>
<td>0.009</td>
<td>$32 - 34^b$</td>
<td>40</td>
<td>Sponge-like</td>
<td>Ref. 22 Figure 7 (left)</td>
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<tr>
<td>0.02$^b$</td>
<td>0.25</td>
<td>0.015</td>
<td>$69 \pm 19$</td>
<td>40</td>
<td>Sponge-like</td>
<td>Figure 5 (bottom, left)</td>
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<tr>
<td>0.01$^b$</td>
<td>0.25</td>
<td>0.021</td>
<td>$38\times (20 \text{ to } &gt;50)$</td>
<td>40</td>
<td>Sponge-like</td>
<td>Figure 5 (top, right)</td>
</tr>
<tr>
<td>0.005</td>
<td>0.25</td>
<td>0.0076</td>
<td>$19 \pm 3^b$</td>
<td>80</td>
<td>Foam-like</td>
<td>Figure 5 (top, right)</td>
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<td>0.005</td>
<td>0.25</td>
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<td>$25 \pm 7$</td>
<td>50</td>
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<tr>
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<td>0.025</td>
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<td>50</td>
<td>Brine polyhedra</td>
<td>Figure 6 (middle, left)</td>
</tr>
<tr>
<td>0.005</td>
<td>0.25</td>
<td>0.025</td>
<td>$24 \pm 5$</td>
<td>100</td>
<td>Vesicles</td>
<td>Figure 5 (middle, right)</td>
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<tr>
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<td>0.025</td>
<td>$155 \pm 45$</td>
<td>50</td>
<td>Brine polyhedra</td>
<td>Figure 5 (middle, right)</td>
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<td>0.026</td>
<td>$85 \pm 30$</td>
<td>200</td>
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<td>$130 \pm 60$</td>
<td>100</td>
<td>Onion-like</td>
<td>Figure 6 (bottom, right)</td>
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</table>

$^a$Taken from [22] A = FFEM B = FFDI
estimate that $d = 12$ nm for $\gamma = 0.25$. The second contribution can be assigned to the onions (dashed-dotted lines): the open arrows point to the maximum of the dashed-dotted lines. Note that the bump is only visible for $\gamma = 0.19$ because the $q$-range for $\gamma = 0.28$ is not large (low) enough. What supports the existence of the bump at low $q$-values for the sample with $\gamma = 0.28$ is the fact that the intensity of a SANS curve of an $L_3$ phase with a sponge-like structure continuously increases with decreasing $q$, i.e. there is no real maximum. We will show in our follow-up study [23] of the oil-free system how the maximum at low $q$-values evolves with increasing surfactant concentration. Taking the fits for granted, one can calculate a characteristic distance from the respective peak positions which is $D = 70$ nm for $\gamma = 0.19$ and $D = 50$ nm for $\gamma = 0.28$. These distances are perfectly in line with the structure sizes determined by TEM for $\gamma = 0.25$, namely $D_{\text{FFDI}} = (85 \pm 30)$ nm and $D_{\text{FFEM}} = (130 \pm 60)$ nm (see Table 1), which we assigned to the diameter of the onions. Note that the structure sizes extracted from the SANS curves are calculated for the maximum of the fit but that the broad peak indicates a large size distribution of the onions, which is in line with the TEM images. A more detailed analysis of additional SAXS and SANS curves of the oil-free system goes beyond the scope of the present study and will be dealt with in a follow-up study [23].

4 Discussion

In our previous study we offered no explanation for the transition of a sponge-like to a foam-like structure with increasing oil mass fraction $\alpha$. However, if we look at the transition in the opposite direction, i.e. if we start with the foam-like structure, we can at least explain why this structure must collapse with decreasing oil mass fraction. In Figure 8 we schematically show two extreme cases. On the left, one sees that the foam-like structure has a continuous oil phase which separates the brine droplets. The oil can penetrate in the surfactant tails and it can “fill” the Plateau borders which reduces the curvature of the surfactant monolayer in these regions. On the right, one sees that the brine droplets are separated by surfactant bilayers and the Plateau borders are covered with highly curved monolayers. Coming from the oil-containing system one can argue that the curvature of the monolayer covering the Plateau borders gets more and more negative with decreasing oil mass fraction. This can be compensated to some extent because a decrease of $\alpha$ is accompanied by an increase of the salt mass fraction $\varepsilon$: the higher the $\varepsilon$-value the more the electrostatic head group repulsions are screened allowing for a more negatively curved monolayer. However, at an oil mass fraction of $\alpha \leq 0.045$ at $\gamma = 0.15$ and $\alpha \leq 0.07$ at $\gamma = 0.25$, respectively, the curvature becomes too negative and the system adapts to a more favorable structure, which is sponge-like at low surfactant mass fractions and onion-like at high surfactant mass fractions in the oil-free systems. In both cases, bilayers with low curvatures instead of highly curved monolayers are formed. The fact that the transition to the water-continuous phase at $\gamma = 0.25$ happens at higher $\alpha$-content than for $\gamma = 0.15$ can be explained by the fact that the foam-like structure at $\gamma = 0.25$ is smaller and hence the Plateau borders (the monolayers) are more curved. Thus, the driving force for the collapse, i.e. for the adaption of a less curved surfactant layer, kicks in at higher $\alpha$-values.

Having offered an explanation for the collapse of the foam-like structure, we now have a look at the structure(s) that form after the collapse. Other than expected and postulated in [22] there is no gradual transition from the foam-like to the sponge-like/onion-like structure with the two structures coexisting in between. Although the viscosity and conductivity data could be interpreted in this way, the FFEM/FFDI images speak a different language. We identified in Section 3 brine polyhedra which coexist with small structures in the transition state – the latter always have diameters of $(20–30)$ nm (see Table 1). We recall (i) that the transition state must be water-continuous, (ii) that small amounts of oil must be solubilized somewhere, and (iii) that the samples are homogeneous in the whole $L_3$ channel. A transition state that is in line with all experimental results is schematically shown in Figure 9. We suggest the coexistence of brine polyhedra separated by oil-swollen bilayers with vesicles surrounded by oil-swollen bilayers. The schematic drawing in Figure 9 is an analogy to a thermodynamically stable bicontinuous microemulsion suggested by Talmon and Prager [34]: the water domain of the microemulsion is the polyhedron brine domain in our case, while the oil domain of the microemulsion is the vesicle domain. The two domains of the microemulsion are separated by a surfactant monolayer, while in our case they are separated by an open interface as shown in Figure 9 (top, right). The sequence of “vesicle domain – brine polyhedron – vesicle domain”
(pink arrows in Figure 9) leads to the high conductivity, while the sequence of brine polyhedra is non-conducting (dashed arrows in Figure 9) due to the oil swollen bilayer between two brine polyhedra. The open interfaces between the brine polyhedra and vesicle domains are curved as seen in Figure 5 (black arrows). The white arrows in Figure 5 show the brine polyhedra with flat surfaces resulting from fractures through the oil swollen bilayers which separate two polyhedra. Speculative as it may be, we assign the formation of the transition state to a coalescence event known from liquid foams: the lower the amount of oil, the thinner become the oil-swollen bilayers. The thinner the bilayers the more prone they are to rupture. After each film rupture the system needs to accommodate excess oil and surfactant: the oil rounds off the polyhedra, while the surfactant creates additional interfaces. For the formation of vesicles with oil-swollen bilayers one needs four interfaces for two separate vesicles instead of two for two separate water droplets in our foam-like structure. While coalescence in a macroscopic liquid foam leads to phase separation, it leads to the formation of two microscopic domains (vesicle domain and brine polyhedra) in case of our nanofoams. A schematic drawing of the coalescence event is shown in Figure S2 in Supplementary Material.

Finally, we need to discuss the formation of a sponge-like and an onion-like structure, respectively, from the transition state. We know from our previous study that even at an oil mass fraction as low as \( \alpha = 0.012 \) we have vesicles and polyhedra coexisting with sponge-like structures (see Figure 7 in [22]). How and why the vesicles/polyhedra form a sponge-like or onion-like phase, depending on the surfactant concentration, in the oil-poor system is not clarified yet. For what we can offer as explanation, however, is the final state in the oil-free system. Porte et al. [35] argued that the sponge-like L3 phase is entropically favoured over the ordered structure of the Lα phase but that an elastic energy price (bending energy) has to be paid for its formation. This price increases with increasing surfactant mass fraction since more bilayers need to be bent. At \( \gamma = 0.15 \) the entropy gain is obviously larger than the energy price, while at \( \gamma = 0.25 \) the energy price is larger than the entropy gain, which is why no sponge-like structure is formed anymore. The observed transition to an onion-like structure at the higher surfactant mass fraction is a logical consequence because (a) the bilayer structure is kept and (b) the bending energy is reduced compared to the sponge-like structure. In Figure 10 we provide a schematic drawing of the onion-like structure in the oil-free system. Looking at Table 1 one sees that the onion size is \((85 \pm 30) \text{ nm}\) from FFDI-und \((130 \pm 60) \text{ nm}\) from FFEM-images, i.e. we are dealing with a broad size distribution. The \(d\)-spacing of our system estimated from SANS curves (i.e. the \(d\)-spacing for 25 wt% surfactant) is \(-12 \text{ nm}\) (s. Section 3.4 “SAXS and SANS curves”). Thus, the formation of onions with 4–13 bilayers is possible.

5 Conclusions

We studied the isotropic L3 channel of the system H2O/NaCl – hexyl methacrylate (C6MA, oil) – AOT (sodium bis(2-ethylhexyl) sulfosuccinate) at \( T = 25 \text{ °C} \) and at a
constant surfactant mass fraction of $y = 0.25$ as a function of the oil and the NaCl mass fractions. For the study we combined viscosity measurements, conductivity measurements, freeze fracture electron microscopy (FFEM) images, freeze fracture direct imaging (FFDI) images as well as SANS- and SAXS-measurements. All experimental results are in line with (a) a transition from a thermodynamically stable onion-like to a thermodynamically stable foam-like structure with increasing oil and decreasing NaCl mass fraction and (b) a transition state consisting of two domains, namely domains with brine polyhedra and domains with vesicles. In a follow-up study we will investigate the oil-free system in more detail focusing on the transition from the sponge-like structure at $y = 0.15$ to the onion-like structure at $y = 0.25$. Apart from viscosity and conductivity data, we will present telling FFEM- and FFDI-images as well as SAXS- and SANS-curves, which support the formation of onions in the $L_3$ channel at higher surfactant concentrations.

In conclusion we found that in the presence of small amounts of oil and electrolyte the formation of a foam-like structure is the normal and not the exceptional case for AOT. The foam-like structure is favored because the distance between two opposing head groups (larger domain size, see Table 1 in [22]) and between two neighboring head groups (less negative curvature) are larger compared to the sponge-like structure. We recall that oil is required for the formation of a foam-like structure in the $L_3$ phase. Thus, we speculate that foam-like and onion-like structures are also present in other ionic systems if the specific conditions are met. The driving force is always the same: the strong head group repulsions in the monolayer which oppose the negative curvature of the sponge-like structure. Most publications about $L_3$ phases of systems with ionic surfactants are more than 30 years old, i.e. they were written when the idea of a sponge-like phase was brand new. This raises the question: Were structures other than the sponge-like simply overlooked or not searched for? We hope that this provoking question triggers future research activities.

As regards nonionic alkyl polyethylene glycol ethers (C$E_i$ surfactants), the sponge-like structure may be favored because the flexible head groups give rise to a lot of conformational entropy: more conformations are possible if the head groups are directed into a continuous water phase (sponge-like structure) as opposed to a confined water droplet (foam-like structure). To the best of our knowledge, there is no experimental evidence so far that foam-like or onion-like structures exist in the $L_3$ phase of C$E_i$ surfactants. We will challenge this statement in a follow-up study.

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References


23. P. Menold et al.: Transition from a foam-like to an onion-like nanostructure


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