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# Transitions induced by shear in surfactant phases and relaxation of the shear-induced phases

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## Abstract

The surfactant sodium bis(2-ethylhexyl) sulphosuccinate (AOT) in water forms lamellar phases at low salinities and sponge phases at higher salinities. For the lowest salinities, the lamellar phase contains many onion defects and is very viscous and elastic. At higher salinities but still in the lamellar phase, the sample has a low viscosity. The sponge phase is a Newtonian fluid with a very low viscosity. When either the low-viscosity lamellar or the sponge phase are sheared, they exhibit a transition, after a long time, to a phase which has the same rheological properties and the same texture as the very viscous lamellar 'onion' phase. The random nature of the transition suggests that the formation of the shear-induced phase is due to activated processes, which we discuss here. In addition, the relaxation of the shear-induced phases is very slow; some of its relaxation mechanisms are described.

## 1. Introduction

The large length scales of structures present in complex fluids compared to molecular lengths can lead to interactions between the structure of the fluid and the flow field, if the complex fluid is sheared. The flow can affect the organization of the fluid, modifying its viscoelastic properties. This feature has attracted much attention during the last few years, both from an experimental point of view and from a theoretical one [1].

We focus here on the modifications of equilibrium structures observed in phases of surfactant solutions under shear [2, 3]. The modifications that we study are: in one case a change in the texture of the phase, i.e. in the type and number of defects present; and, as a second case, a shear-induced phase transition. In both cases, the shear-induced phase is formed after a certain time. To get some insight into the effect of flow on structure, we have developed models based on nucleation processes. These models are suggested by the observed random characteristics of the time necessary to provoke the shear-induced changes in the solutions.

In addition, the shear-induced phases return very slowly to the equilibrium phases after stopping the shear. We describe some surprising processes observed during the relaxation of a shear-induced lamellar phase that relaxes towards the equilibrium sponge phase structure.

The system that we study is a mixture of 7 wt% of the anionic commercial surfactant sodium bis(2-ethylhexyl) sulphosuccinate (AOT), in brine at  $20 \pm 0.1$  °C. For low salinities ( $s < 1.5$  wt%), the equilibrium phase is a lamellar phase ( $L_\alpha$ ). For high salinities ( $1.75$  wt%  $< s < 2.1$  wt%) the equilibrium phase is a sponge phase ( $L_3$ ) which is a bicontinuous structure. For intermediate salinities ( $1.5$  wt%  $< s < 1.75$  wt%), a coexistence of these two phases is observed [4].

The texture and the hydrodynamic properties of the lamellar phase depend upon the salinity [2, 3]. For  $s < 0.9$  wt%, this phase is very viscous and elastic like a gel and contains many onion defects embedded in a lamellar matrix. These defects are bilayers rolled up around each other forming spheres of different sizes ranging from a few  $\mu\text{m}$  to a few tens of  $\mu\text{m}$ . For  $s > 0.9$  wt%, the lamellar phase has a low viscosity and exhibits oily streaks in a black homeotropic background when a thin sample is observed between crossed polarizers.

The AOT in brine forms bilayers, the topology of which is given, to a first approximation, neglecting the entropy, by the minimization of the elastic energy [5]:

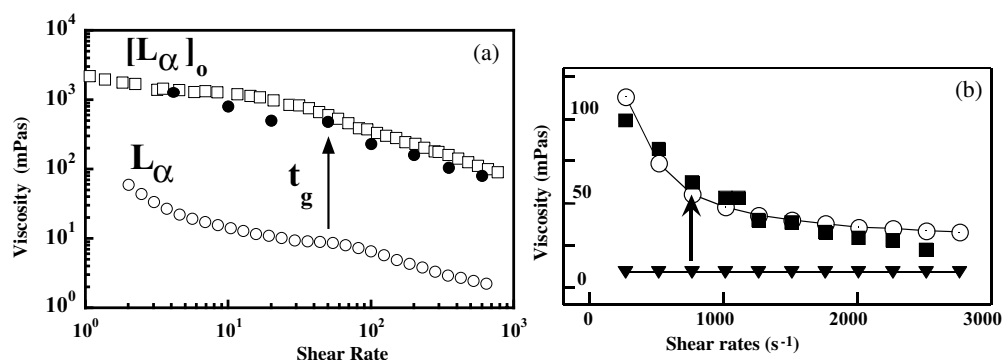
$$E = \int dA \left[ \frac{K}{2} \left( \frac{1}{R_1} + \frac{1}{R_2} \right) + \bar{K} \left( \frac{1}{R_1 R_2} \right) \right]$$

where  $R_1$  and  $R_2$  are the principal radii of curvature of the bilayer, and  $K$  and  $\bar{K}$  are the bending elastic constant and the saddle-splay modulus respectively; the integral is over the surface area. Experiments show that  $K$  is roughly independent of  $s$  for the AOT system while  $\bar{K}$  is affected by the salt which screens the electrostatic repulsions between polar heads.  $\bar{K}$  is negative at low salinities and increases with the salinity. This is in qualitative agreement with the experimental phase diagram. A very negative value of  $\bar{K}/K$  ( $\bar{K}/K < -2$ ) favours a spherical topology (vesicles or onions) while a negative and smaller value of  $\bar{K}/K$  ( $-2 < \bar{K}/K < 0$ ) favours a lamellar phase. For  $\bar{K} \sim 0$ , the formation of a sponge phase can be anticipated. Moreover, experiments seem to show that onion defects at low salinities are equilibrium structures, in agreement with this analysis [6].

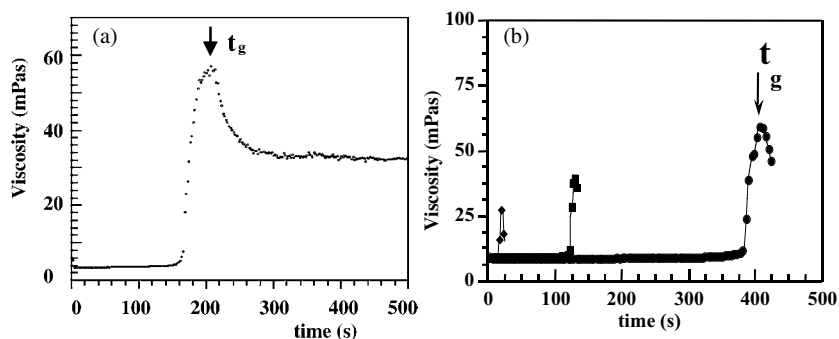
In the following, the lamellar phase with onion defects obtained for  $s < 0.9$  wt% will be called the ‘onion phase’ and denoted as  $(L_\alpha)_0$ , while the lamellar phase with oily streaks obtained at higher salinities will be called the lamellar phase and denoted as  $L_\alpha$ .

## 2. Shear-induced transitions

Rheological measurements on these phases were performed on a Reologica Stress-Tech rheometer with a Couette geometry. The inner rotating cylinder was cone shaped at the bottom in order to provide a uniform shear rate everywhere inside the Couette cell. The rheological behaviour of the ‘onion phase’ is the simplest among those of the three phases considered here. This phase was found to be very viscous and to be shear thinning (figures 1(a), (b)). When examining the sample, its elastic properties are evident, but this was not studied here. The rheological behaviours of the lamellar and sponge phases are more complicated because the viscosity is not only a function of the shear, but also a function of the time of application of the shear. Figures 2(a) and (b) depict the measurements of the viscosity as a function of time for respectively a lamellar phase and a sponge phase as a function of time for different fixed shear rates. For a long period of time, the viscosity is found to be almost constant (lamellar phase) or constant (sponge phase). After this period, a sudden and steep increase of the viscosity occurs over time, to a value that is higher by roughly an order of magnitude for the sponge phase [3] and two orders of magnitude for the lamellar phase [2]. When the viscosity reaches its maximum, a part of the viscoelastic and turbid gel formed in the cell is expelled from the gap of the Couette cell; this is the reason for the apparent decrease in viscosity after the maximum.



**Figure 1.** Viscosity as a function of shear rate for the different phases. (a) Squares: viscosity of the ‘onion phase’  $[L_{\alpha}]_0$  (0.7 wt%); white circles: viscosity of the equilibrium lamellar phase  $L_{\alpha}$  ( $s = 1.35$  wt%); black circles: viscosity of the sheared lamellar phase (at its maximum of viscosity). (b) Circles: viscosity of the onion phase ( $s = 0.6$  wt%); diamonds: viscosity of the equilibrium sponge phase ( $s = 1.8$  wt%); squares: viscosity of the sheared sponge phase (at its maximum of viscosity). The viscosities of the sheared lamellar phase and that of the sheared sponge phase are very similar to that of the ‘onion phase’.



**Figure 2.** Viscosity as a function of time for the lamellar and the sponge phase. We observe the shear-induced formation of a very viscous gel after a delay. (a) For the lamellar phase ( $s = 1.5$  wt%) and  $\dot{\gamma} = 1000$  s $^{-1}$ . (b) For the sponge phase and different (constant) shear rates ( $s = 1.8$  wt%). Rectangles: 750 s $^{-1}$ ; squares: 1250 s $^{-1}$ ; circles: 2000 s $^{-1}$ .

The values of the viscosity measured at the plateau for short shearing times and the maximum of the viscosity are plotted in figures 1(a) and (b) for the lamellar phase and the sponge phase respectively. The viscosity of an ‘onion phase’,  $(L_{\alpha})_0$ , is plotted in the same figure for comparison.

The conclusions from these different measurements are the following:

- The lamellar phase is a shear-thinning fluid which, under shear, suddenly transforms to a phase which has the same rheological properties as the ‘onion phase’ obtained at equilibrium at lower salinities.
- The sponge phase is a Newtonian fluid with a low viscosity which also transforms very suddenly under shear to a phase with the same rheological properties as the ‘onion phase’ obtained at equilibrium at lower salinities.
- The time of shearing needed to observe the transition decreases with increasing shear rate.

These conclusions suggest that the viscoelastic sheared phases obtained by shearing the lamellar phases or the sponge phases have a microstructure similar to that of the ‘onion phase’

obtained at equilibrium at low salinities, and that consequently the shear induces a texture transition in the lamellar phase and a phase transition in the sponge phase. This hypothesis was confirmed by studying the evolution of the textures of the phases subjected to a constant shear [2, 3]. The study was performed at a macroscopic scale in a transparent Couette cell and at a microscopic scale in a transparent cone-plate cell placed directly under a polarized microscope.

The texture of the phase induced by shearing the lamellar phase ( $L_\alpha$ ) at the maximum of viscosity is very similar to the texture of the equilibrium phase obtained at low salinities,  $(L_\alpha)_0$ . One observes the presence of a high density of onions in a birefringent lamellar matrix. Moreover, during the shearing of the lamellar phase, one observes a continuous increase of the number of onions which are absent in the equilibrium lamellar phase. Under shear, these onions align to form long chains. The alignment of the optical axis of the lamellar matrix in the flow allows for an easy observation of this texture (figures 3(a)).

The observation of the texture of the sheared sponge phase at its maximum of viscosity shows the same features as the onion phase obtained at low salinities: here also, the shear induces an onion phase [3]. However, the detailed mechanism of formation of the  $(L_\alpha)_0$  phase is different. During the long period of time for which the viscosity of the sheared sponge phase is constant, macroscopic observation shows that the phase appears isotropic, without any structure. Then, suddenly, the onion phase is observed to nucleate locally and grow quickly, rapidly invading the full sample cell (figure 3(b)).

Repeating the same experiments many times, taking great care to conduct the experiments in exactly the same way, the time of ‘gelification’, i.e. the time of shearing,  $t_g$ , necessary to reach the maximum of the viscosity is not well defined, neither for the lamellar nor for the sponge phase [2,3]. Figures 4(a) and (b) depict the experimentally determined probability distribution  $p(t_g)$  of the gel time  $t_g$  for a lamellar and a sponge phase. The probability distribution has a very different shape for the two different phases. However, for the two cases, the random character of  $t_g$  suggests a nucleation process [7].

In contrast to what is observed for the sponge phase, the probability distribution  $p(t_g)$  for the lamellar-to-onion transition is a function that is roughly symmetric around its mean value. Consequently the lamellar phase–onion phase transition cannot result from a single activated process as is the case for the sponge-to-onion transition. Moreover, this is confirmed by the observed continuous increase of the number of onions in the sheared lamellar phase (figure 3(a)). This last observation suggests that it is a large number of activated processes that finally lead to the onion phase, each event corresponding for instance to the formation of a single onion. If this were the case, the probability that we observe a single event at time  $t$  is given by a Poisson distribution:  $p(t) = \Gamma e^{-\Gamma t}$ . For successive and independent random events, the probability that we observe  $N$  events, the event number  $N$  at time  $t$ , is given by [2]

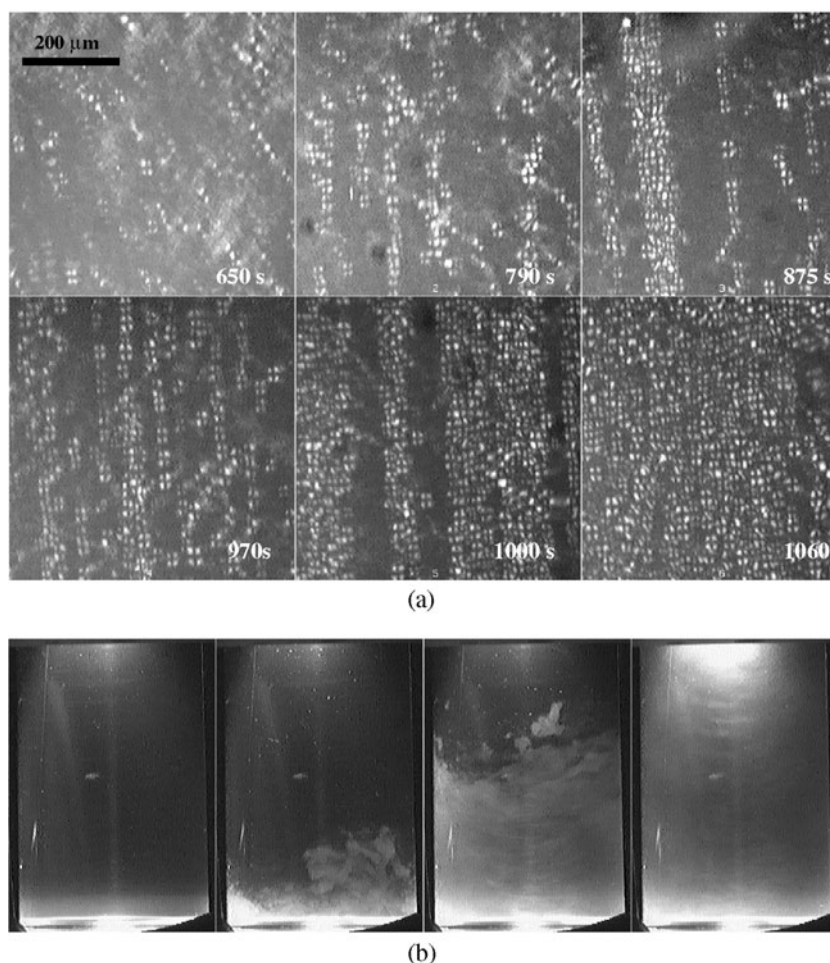
$$p(N, t) = N\Gamma(1 - e^{-\Gamma t})^{N-1}e^{-\Gamma t}.$$

The maximum of this distribution occurs for

$$t_{\max} = \ln(N)/\Gamma.$$

For large  $N$ , this distribution is centred around  $t = t_{\max}$  ( $\neq 0$ ) and the ratio of  $t_{\max}$  to the width of the distribution is equal to  $\ln(N)/e$ : the relative width of the distribution decreases with the number of events  $N$ .

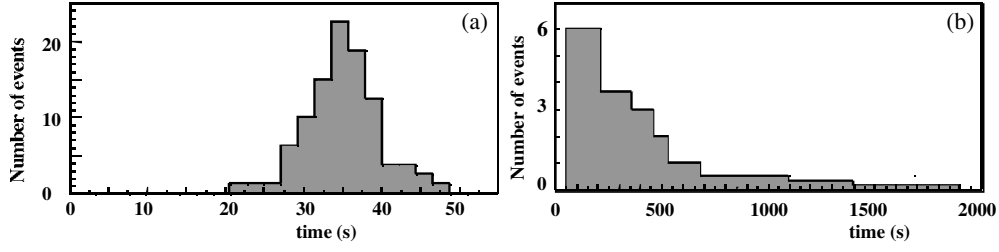
If we suppose that each such event indeed corresponds to the nucleation of an onion defect, the estimation of the number of onion defects in the Couette cell from the microscopy images gives  $N \approx 10^9$ , leading to  $\ln(N)/e \approx 7.7$ . This is of the same order of magnitude as, though somewhat larger than, the ratio of the maximum of the distribution over its width deduced from the experimental probability distributions; from those we find a ratio between 3.4 and 6.8.



**Figure 3.** Images of a lamellar phase and a sponge phase during the shear. (a) A sequence of images obtains at a microscopic scale, in a transparent cone-plate cell, during the shear of a lamellar phase ( $s = 0.3$  wt%). One observes a continuous increase of the number of aligned onions which are absent in the equilibrium phase. The time of shearing is indicated on each image. (b) A sequence of images, at a macroscopic scale, taken using a transparent Couette cell, showing the nucleation and growth of the shear-induced phase (time between images: 15 s). In the first image, before the nucleation, no birefringence is observed (the light at the bottom of the cell is due to a reflection on the cell). The three following images show the birefringent phase invading the cell. The last one was taken at  $t_g$ .

In view of the simplicity of the model, these differences are not very surprising. In practice, the probability of nucleation of an onion defect will not be constant as is supposed in the above reasoning for two reasons. First, the volume of sheared lamellar phase decreases when onion defects nucleate. Second, due to the formation of the viscous shear-induced phase, the shear rate will no longer be perfectly constant in the gap. Therefore these simple considerations provide a coherent picture of the shear-induced lamellar-to-onion transition.

Next, we consider the sponge-to-onion transition. For the sponge phase under shear,  $p(t_g)$  vanishes for low  $t_g$  ( $t_g < 40$  s) and is exponential for larger  $t_g$  ( $t_g > 40$  s). The shape of the distribution suggests that the sponge-to-onion transition results from a single activated process: the nucleation of a single nucleus of onion phase followed by a rapid growth of this



**Figure 4.** Distribution of the random gel times  $t_g$  (times of shearing to get the maximum of the viscosity). (a) For a lamellar phase ( $s = 1.15$  wt%,  $\dot{\gamma} = 200$  s $^{-1}$ ) and 80 measurements. (b) For a sponge phase ( $s = 1.8$  wt%,  $\dot{\gamma} = 1200$  s $^{-1}$ ) and 80 measurements.

nucleus. This is in agreement with the macroscopic observations in the transparent Couette cell of a sudden and local appearance followed by the growth of the shear-induced onion phase during the shearing (figure 3(b)). The time necessary for the growth of the nucleus up to the observation of the maximum of viscosity is in the experiment of figure 4(b) of the order of 30 s. In reality, it is probably slightly longer, because in a rheological experiment, the nucleation and the first steps of the growth are not observed; the initial nucleus is too small to induce a measurable increase in viscosity.

If we consider that the shear-induced phase forms by an activated (nucleation) process, the nucleation rate  $\Gamma$  is an exponential function of the activation energy  $E_a$  [7]:

$$\Gamma = \Gamma_0 e^{-E_a/k_B T}$$

where  $\Gamma_0$  is an attempt frequency.

The energy  $E_a$  needed to nucleate a droplet (the nucleus) results from a competition between the cost in surface energy of the droplet and the gain in bulk energy and is given by [7]

$$E_a \approx \sigma^d / (-\Delta E)^{d-1}$$

where  $d$  is the dimensionality of the nucleus,  $\sigma$  the surface energy and  $\Delta E$  is the difference in bulk energy between the lamellar and sponge phases. For the sheared system, it is the shear rate  $\dot{\gamma}$  that causes the transitions. This implies necessarily that  $\Delta E$  is a function of  $\dot{\gamma}$ ;  $\Delta E > 0$  for  $\dot{\gamma} = 0$  because the sponge phase is the equilibrium phase when the shear vanishes. However,  $\Delta E$  has to become negative when the phases are sheared, since a transition from the sponge to the onion phase is observed. If we expand to first order in  $(\dot{\gamma} - \dot{\gamma}_0)$ , it follows that [3]

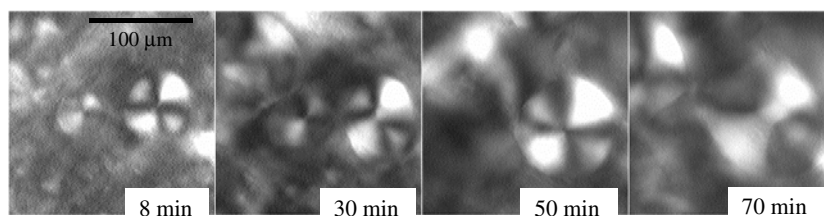
$$\Delta E \sim (\dot{\gamma} - \dot{\gamma}_0)$$

where  $\dot{\gamma}_0$  is a critical shear rate needed to induce the transition.

The time that one has to wait before nucleation is observed is inversely proportional to the nucleation rate [7]. Therefore, within this model, one expects the mean value of the time of nucleation to vary as [3]

$$\ln(t_{\text{nuc}}) \sim \frac{1}{(\dot{\gamma} - \dot{\gamma}_0)^{d-1}} + \text{constant}.$$

Different experiments indicate that the best fit of our data with this equation is obtained for  $d = 2$  [3], implying that the nucleus is two dimensional, its third dimension being imposed by a natural length scale of the phases, the distance between lamellae in the lamellar phase for instance. However, the fits are not good enough to allow for a definitive conclusion; more experiments over a larger range of shear rates would be necessary to firmly establish this proposition.



**Figure 5.** Microscopy images of the relaxation of the sheared sponge phase during the first hour, observed between crossed polarizers. One of the onions grows (at the centre, on the right), while another one (at the centre, on the left) disappears.

### 3. Relaxation of the shear-induced onion phase

The ‘onion phases’ obtained by shearing the lamellar phase or the sponge phase are out of equilibrium when the shear is stopped. They relax slowly to the equilibrium phase. Different mechanisms of this relaxation were observed. Here, we describe some of these for the relaxation of the onion phase obtained by shearing the sponge phase. It is the easiest relaxation to study by polarized microscopy because the sponge phase is optically isotropic while the initial onion phase is optically anisotropic. The two phases are therefore easily distinguishable by polarized microscopy.

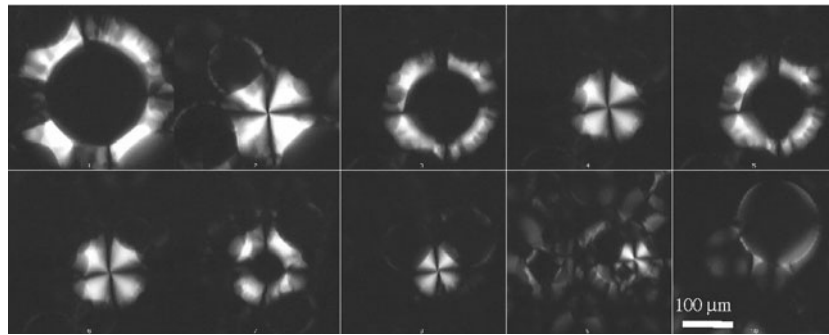
The relaxation was observed in the bulk of the sample in a thick cell. This accounts for the fact that the quality of the images is not perfect. The relaxation near the walls of the cell (and consequently also in a thin cell) is different and more rapid. Unlike the swelling and subsequent dissolution of onions studied by Cates and collaborators [8], the  $L_\alpha \rightarrow L_3$  transition observed during the relaxation is between a metastable phase and a stable phase having the same (or almost the same) composition.

When the sample is studied just after cessation of shear, the onion phase contains many onion defects embedded in a lamellar matrix. During the first hour of relaxation, the number of onion defects decreases. Some of them grow in size from a few tens to a few hundreds of microns, while others disappear (figure 5). At the same time, the lamellar matrix appears to relax more rapidly than the onion defects: its birefringence decreases progressively in time.

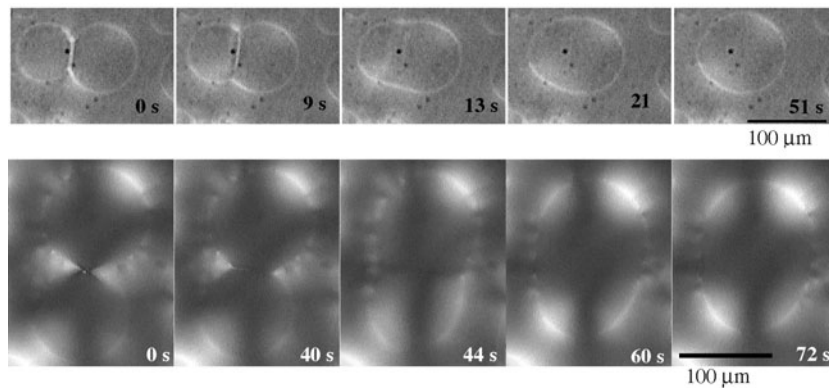
On a longer timescale, a new phenomenon appears. The inside of the onions starts to relax: in the centre of each onion a sphere of isotropic phase is observed to grow. The onions look like bubbles made of a thick spherical layer of lamellar phase within the sponge phase and containing a sponge phase (figure 6). At the same time, their radius continues to increase slowly over several hours. However, from time to time, a bubble collapses. When this happens, its size decreases quickly (in a few seconds) and the sponge phase that it contained is lost. Most of the time, the sponge phase that was expelled from the bubble forms a new and very thin bubble, again of sponge phase surrounded by a very thin layer of the birefringent phase that remains attached to the original onion defect. Subsequently, the same process may start all over again. However, the total volume of the birefringent phase progressively decreases during these processes, disappearing completely in the end.

During the final hours of the relaxation process (10–24 h after the initial shearing), the density of bubbles with a thin wall of birefringent phase is sufficient to allow observation of coalescence of these bubbles (figures 7). The wall between two bubbles breaks and the two bubbles form a roughly ellipsoidal bubble which is observed to relax to a spherical shape. If  $l_{\max}$  and  $l_{\min}$  are the two axes of the ellipsoid, the characteristic relaxation time  $\tau$  for the bubble shape is given by





**Figure 6.** Relaxation of the inside of one onion of the sheared sponge phase over a long time. First image (5 h after the beginning of the relaxation): the inside of the onion relaxes and becomes optically isotropic (it appears black between crossed polarizers). The onion looks like a bubble. Following images: from time to time, one observes a quick collapse of the bubble (a few seconds) followed by a slow growth of the onion (a few tens of minutes). This sequence of images was taken over a period of 3 h just before and just after a collapse. Most of the time, the sponge phase expelled from the bubble forms new and thin bubbles (second image).



**Figure 7.** Two sequences showing the coalescence of thin bubbles of sponge phase surrounded by a thin film of lamellar phase observed more than 7 h after the beginning of the relaxation of a sheared sponge phase. These images are obtained by polarized microscopy between crossed polarizers (images at the bottom) and uncrossed polarizers (upper images). The portions of the walls of the bubbles which are oriented in the same direction as the axes of the crossed polarizers appear black, showing that these walls are made of lamellar phase.

$$\frac{l_{\max}}{l_{\min}} = 1 + e^{-t/\tau}.$$

The coalescence of bubbles in the viscous regime was studied by Taylor [9]. Neglecting the viscoelasticity of the wall by taking into account only the interfacial tension  $\sigma$  between the two phases and the viscosity  $\eta$  of the sponge phase [9], we have

$$\tau = 2.2 \frac{\eta R}{\sigma}$$

where  $R$  is the final radius of the bubble.

Consequently, from the relaxation time of the bubble, one can deduce the interfacial tension between the sponge phase at thermal equilibrium and the metastable lamellar phase surrounding the bubbles. Table 1 gives the values deduced from the experiment, from which  $\sigma$  is found to be a function of the salinity.

**Table 1.** Values deduced from the experiment.

Salinity (wt%)	1.8	1.9	2
$\sigma$ (mN m <sup>-1</sup> )	$(1 \pm 0.25) \times 10^{-5}$	$(1.7 \pm 0.5) \times 10^{-5}$	$(3 \pm 1) \times 10^{-5}$

This interfacial tension is ultralow, about 10–100 times smaller than the interfacial tension which can be measured between a lamellar phase and a sponge phase coexisting in equilibrium. However, this low value is only ten times smaller than the estimated interfacial tension between the L<sub>3</sub> phase and the nucleus of lamellar phase estimated from the nucleation experiments. This is in agreement with a critical shear rate  $\dot{\gamma}_0$  close to zero, since at this critical shear rate the interfacial tension must vanish [3]. Moreover, this low interfacial tension can be explained by the similar compositions of the two phases.

#### 4. Summary and conclusions

We report on new shear-induced transitions in surfactant systems from low-viscosity equilibrium phases to a high-viscosity gel-like phase. The first transition that we consider is a texture transition in a lamellar phase [2]. The shear induces a high density of onion defects that do not exist at equilibrium. The second transition that we study is a shear-induced phase transition from a low-viscosity sponge phase to a high-viscosity ‘onion phase’ [3]. The phases induced by the shear are very similar to the ‘onion phases’ obtained at lower salinities at equilibrium: they have the same rheological behaviour, and the same microscopic texture.

The random nature of the experimental ‘gel’ time can be explained by considering activated processes. For the sponge-to-onion phase transition, a single activated nucleation process followed by a rapid growth of the nucleus of the onion phase agrees with the experimental results. For the lamellar-to-onion transition, the transition results from a large number of sequential activated processes.

The relaxation of the onion phase induced by shearing a sponge phase shows complex processes during the relaxation. The formation and coalescence of bubbles of sponge phase with thin walls of lamellar phase allow for the measurement of the interfacial tension between the sponge phase at thermal equilibrium and the metastable lamellar phase. These tensions are ultralow, of the order of  $10^{-5}$  mN m<sup>-1</sup>.

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#### References

- [1] For a review, see e.g., Onuki A 1997 *J. Phys.: Condens. Matter* **9** 6119  
 For onion phases, see e.g., Diat O and Roux D 1995 *Langmuir* **11** 1392  
 For sponge phases see e.g., Yamamoto J and Tanaka H 1996 *Phys. Rev. Lett.* **77** 4390  
 Mahjoub H F, Bourgaux C, Sergot P and Kléman M 1998 *Phys. Rev. Lett.* **81** 2076  
 Mahjoub H F, McGrath K M and Kléman M 1996 *Langmuir* **12** 3131  
 Huse D A and Leibler S 1988 *J. Physique* **49** 605  
 Cates M E and Milner S T 1989 *Phys. Rev. Lett.* **62** 1856  
 Bruinsma R and Rabin Y 1992 *Phys. Rev. A* **45** 994  
 [2] Léon A, Bonn D, Meunier J, Al-Kahwaji A, Greffier O and Kellay H 2000 *Phys. Rev. Lett.* **84** 1335

- 
- [3] Léon A, Bonn D, Meunier J, Al-Kahwaji A and Kellay H 2001 *Phys. Rev. Lett.* **86** 938
  - [4] Ghosh O and Miller C A 1987 *J. Phys. Chem.* **91** 4528  
Skouri M, Marignan J, Appell J and Porte G 1991 *J. Physique II* **1** 1121
  - [5] Helfrich W 1978 *Z. Naturf. a* **33** 305  
Helfrich W and Servuss R-M 1984 *Nuovo Cimento D* **3** 137
  - [6] van der Linden E and Buytenhek C J 1997 *Physica A* **245** 1
  - [7] Gunton J D, San Miguel M and Sahni P S 1983 *Phase Transitions and Critical Phenomena* vol 8, ed C Domb and J Lebowitz (London: Academic)
  - [8] Buchanan M, Arrauld J and Cates M E 1998 *Langmuir* **14** 7371  
Diamant H and Cates M E 2001 *Eur. Phys. J. E* **4** 223
  - [9] Taylor G I 1934 *Proc. R. Soc. A* **146** 501