Abstract

Contact experiments have been performed between an onion lamellar phase and brine, in the SDS/octanol/brine system. Using video microscopy we have studied the nonequilibrium behaviour of the swelling and dissolution process of onions. Experiments at $T = 20^\circ C$ and $30^\circ C$ showed that temperature has a strong effect on their behaviour. At low temperature onions are observed to diffuse away from the onion phase and only swell sightly. However by increasing the temperature we induce the formation of sponge phase ($L_3$) at the onion/brine interface. Onions that initially swell then dissolve into $L_3$ phase expel a stable core which moves to the micellar phase and remains there. Over a longer period of time (several days) we have also observed coalescence leading to the formation of large onions of up to $\sim 100 \mu m$ diameter. These huge onions have a radial distribution of domains, or solvent cavities, within them.
1 Introduction

Surfactant phases can exhibit a variety of interesting behaviour when observed in nonequilibrium experiments \([1]\). Specifically, we are interested in the relaxation behaviour of onion phases. Onions consist of several closed bilayer shells, i.e. multilayer vesicles \([2]\). Their equilibrium properties have been extensively studied with different techniques as well as their flow behaviour using rheology \([2, 3, 4, 5, 6, 7, 8]\). However, only little is known on their behaviour during relaxation to equilibrium. In particular, we investigate the swelling and dissolution of onion phases after concentration quenches. Depending on the conditions onions are expected to swell and to dissolve eventually forming a micellar \((L_1)\) and/or sponge phase \((L_3)\).

Penetration-scan experiments \([9, pp. 535–538]\) provide a useful method for studying surfactant phase behaviour and kinetics \([10, 11, 12, 13, 14]\). These experiments involve placing one phase, e.g. \(L_\alpha\), in a capillary tube and contacting it with another phase, e.g. solvent such as water or brine. At the interface between the two phases a sequence of intermediate, metastable phases may then arise. The structural arrangement of the mesophases is then observed using polarisation microscopy, which also facilitates to identified the formed mesophases by the birefringent textures \([15]\). This technique has recently been used to study the formation and swelling of a lamellar phase by contacting pure surfactant with an aqueous phase \([16, 17, 18]\). In many contact experiments, a crystal or neat surfactant liquid phase is used instead of the lamellar phase. However, in most of these cases a lamellar phase forms almost immediately at the interface, and controls the subsequent evolution. These random oriented bilayers (polycrystalline powder lamellar phase) are not very well-defined microstructures. We thus prefer to perform contact experiments directly with well-characterised lamellar samples, e.g. consisting of onions with a certain size, than with pure surfactant from which the lamellar phase forms in a rather uncontrollable fashion. We exploit the fact that by shearing a lamellar phase its microstructure is changed from the powder state to a close packed array of onions \([2]\).

In this study we perform penetration scans with an onion phase at different temperatures. Changing the temperature of a bilayer system affects various properties of the bilayers, such as fluctuations, bilayer topology and density of defects. This determines the equilibrium phase behaviour and also has important consequences for the non-equilibrium dynamics. In this paper we investigate non-equilibrium behaviour, specifically the swelling and dissolution of onions upon addition of brine. At low temperature onions are observed to disperse and swell slightly when observed over 4 days. Over the same period of time, but at a higher temperature, a variety of phenomenon
can be observed. Initially, the onions disperse and then proceed to swell up to three times their original diameter. The centre of the onion has a core of much larger density than the rest of the onion. Eventually, the onion dissolves forming a sponge phase which can be observed in abundance at the onion/micellar interface. During onion dissolution the core is expelled which then proceeds to diffuse away from the sponge phase until it eventually dissolves in the micellar phase. After 4 days some onions are observed to coalesce forming large onions with diameters of about 100µm.

2 Experimental Section

2.1 Materials
SDS was supplied by Touzard and Matignon, France, (99% purity) and used without further purification. The lamellar phase was prepared by dissolving 9% SDS and 11% octanol in brine (20g/l NaCl in distilled water). This was then left to equilibrate, until the lamellar phase was homogeneous, which took approximately two weeks.

2.2 Preparation of onion phase
To prepare the onion phase, the lamellar phase is sheared in a temperature controlled transparent Couette (light-scattering) cell with a 1mm gap, manufactured by Caplim. In order to obtain onions that are 10µm in diameter the lamellar phase is initially loaded into the cell and then heated to T = 35°C, where the lamellar phase is known to undergo a transition to the sponge phase. The sample is then subjected to a large shear rate of about 200s⁻¹ while the temperature is lowered to T = 30°C. When onions form the light scattered from the sample gives a characteristic ring in the forward direction whose radius is related to the onion size [2][19]. A steady state is assumed to have been reached when no further change in the size of the light-scattering ring is noticed. The sample is then removed from the Couette cell and loaded into the capillary tube or glass slide and cover slip arrangement as described below.

2.3 The contact experiment
The phase penetration scan experiment involves contacting onion phase with brine. This was either done using a glass slide and cover slip or a capillary tube. In the first case the onion phase is placed between a glass slide and a
cover slip, which is raised at one edge by a spacer, and then contacted with brine. This method has the advantage that it allows to produce thin samples and therefore the contrast is high and structures can be studied in detail. In the second method, the capillary tube (4mm × 0.4mm) is gently inserted into the onion phase whereupon capillary action loads the sample into the tube. At the sample end the tube is then sealed, using Araldite glue. Subsequently the sample is observed under a microscope to check that loading did not introduce disruption of the microstructure in the onion phase. The sample is then contacted with brine. This is done outside the microscope using a fine pipette in a controlled and gentle fashion. The sample is then placed on a microscope slide and slightly tilted at one end to keep any trapped air bubbles away from the lamellar/water interface. The capillary tube is completely sealed to prevent any evaporation. Thus this allows us to study the sample for up to 4 days. Disruption of the sample often occurs, when some of the material becomes torn from the interface as water flows in to displace the air. These samples are rejected and only those are further studied which produce a smooth initial interface between onion and aqueous phases.

2.4 Microscopy

Observations were made using an Olympus BX50 microscope in bright-field mode between crossed polarisers with long working distance objectives. In a few cases we applied Normarski DIC which detects changes in refractive index in the sample and gives better contrast in experiments where we use glass slide and coverslip (section 2.3). The evolution of the samples is recorded using a CCD camera and time lapse video recorder together with a framegrabber PC. The contrast of the presented images has been enhanced by thresholding. All experiments were done at a well-defined temperature in a Linkam LTS hot-stage which ensured controlled and stable conditions.

3 Results

Samples composed of onions are contacted with brine at two temperatures, T = 20°C and 30°C, to study temperature effects on swelling and dissolution of lamellar phase.
3.1 Low temperature $T = 20^\circ$C

Onions with a characteristic diameter of $10\mu$m were contacted with brine. The behaviour of the onions following this quench was studied using two different geometries. The first method is optimised for a high resolution of the onion organisation, which is achieved preparing thin samples. The sample is placed between a glass slide and coverslip and then observed using Normarski DIC. Upon contact with brine, onions in the bulk far from the interface remain close packed. Figure 1A shows the hexagonal organisation of the onion phase immediately after preparation. They are spontaneously deformed into this shape due to the low curvature energy cost of the bilayers. After a short time, about 2 minutes, the onions come apart and swell while becoming spherical (figure 1B).

The same experiment was also performed in a capillary tube. Because the capillary tube can be sealed, this allows us to study the long time behaviour without being affected by evaporation. We followed the behaviour of onions close to the interface, but still in bulk. Four days after contact these onions have moved apart, while they are not yet free from the bulk (figure 1C). Outside each onion we have observed a ‘halo’ domain. The walls of these domains are in contact with each other and are observed directly between the onions.

Directly at the interface the onions initially cascade from the interface. Due to their lower density, they move onto the top surface of the glass capillary tube (figure 2A). As the onions detach from the interface, they swell slightly from initially about $10\mu$m to approximately $12 - 14\mu$m (figure 2B). The onions are not found to coalesce and appear to be fairly monodisperse across the whole interface. Furthermore, the internal structure of the onions appears to remain homogeneous throughout the observation period.

3.2 High temperature $T = 30^\circ$C

We have also performed penetration scan experiments on onion samples at a higher temperature $T = 30^\circ$C. After contact with brine, the onions detach from the onion/brine interface and move to the top of the glass capillary tube (figure 3A). In the region of detached and swelling onions, sponge phase ($L_3$) nucleates, at first forming droplets on the capillary tube surface. The $L_3$ droplets then coalesce to form a large region of $L_3$ phase (figure 3B). Since the SDS/octanol bilayers have a lower density than brine we observe the $L_3$ phase on the top surface of the capillary tube.

During the dissolution of onions into the $L_3$ phase, domains within the onion are observed (figure 4). An inner and outer part of the onion can be
distinguished as well as a core. The onion core albeit peculiar seems to be no artifact, because it has been observed in various other systems [20, 21]. As the onion dissolves the interface between the inner and outer domains moves towards the centre of the onion. After the onion dissolves all that is left is a small core of approximately 1µm size. The core undergoes Brownian motion and eventually leaves the $L_3$ phase. Upon leaving the $L_3$ phase the core continues to undergo more vibrant Brownian motion in the micellar phase until it dissolves about 10s later. Figure 5 shows a schematic representation of the vertical profile in the capillary tube.

After 1 day we observe coalescence, where the onions merge together to form larger onions. Since this process is slow, onions can be observed at different stages of coalescence (figure 6). This behaviour is very different from the previous observations at $T = 30^\circ$C. In figure 6C-E we observe one of the largest onions in the system 4 days after contact. At this point in time we only observe a few very large onions since most of the small onions have fused with these.

After coalescence, onions are often observed to show several concentric domains with sharp interfaces. We also observe solvent-like-domains at some of these interfaces. The centre of the onion in this case is very brightly birefringent. This may imply a dense lamellar phase at the core. On close inspection a small inner core in the centre of a bright birefringent lamellar shell is observed (see figures 6C-E). This core is mobile in the centre of the onion and can be observed to undergo Brownian motion while being confined by the shell.

### 3.3 Dilution experiments

In a separate experiment, onions of 10µm diameter are added to solvent and then dispersed by gently shaking the sample. The diluted onion sample is placed in a flat capillary tube and observed at $T = 30^\circ$C for a period of 6 hours. The onions appear to be slightly swollen; some of the onions are as big as 18µm. With these onions we observe swirly defects within the onions (figure 7A). If the onions are kept at high temperature ($T = 30^\circ$C) the onions dissolve after about one day in the brine without further swelling. However, if the temperature is lowered to $T = 20^\circ$C, the onions not only not dissolve, but in addition the defects vanish over time (figure 7B-D). We also noted a slight, but consistent decrease in onion size during this process.

### 4 Discussion
4.1 Onion swelling

An onion phase was contacted with brine at two different temperatures. The swelling and dissolution behaviour was found to depend on temperature and dramatic changes were found. When observed over a one week period at low temperature (T = 20°C) onions remain intact while they detach and diffuse away from the interface. They do not appear to swell by a large amount. In contrast, onions at high temperature (T = 30°C) can swell up to three times their diameter and eventually ‘melt’ into L3 phase. This can be rationalised based on the equilibrium phase behaviour. A lamellar phase can only swell, i.e. accommodate solvent, to a maximum bilayer spacing which is determined by the position of the $L_\alpha$ phase boundary. When it reaches this point the bilayers will reorganise their structure and form sponge phase. At high temperature the maximum swollen lamellar phase can reach a larger layer spacing before transforming to $L_3$ phase than at lower temperatures. This behaviour is reflected in the observed swelling of the onions at higher temperature.

4.2 Onion collapse and cores

At low temperature onions only swell slightly and cores are not observed. However, in the high temperature experiments onions are found to eventually dissolve into $L_3$ phase and expel a stable core. While stable cores have been observed in nonionic/water [20] and AOT/brine [21] mixtures, the present system has some unique features that have not been observed before. During the onion collapse a domain is observed in the onion which shrinks towards the core (figure 4). The core will remain stable only for several minutes and then dissolve in the $L_1$ phase. There are two possible theoretical explanations for the stability of the core.

First we consider a possible kinetic reason for core stability. In order for onions to swell, solvent has to be transported through the layers into the onion. This requires defects, usually necks [22], which nucleate between layers. We can try to estimate the number of defects as a function of the diameter of one shell in the onion, i.e. one bilayer. The density of defects between bilayers was measured using rheology and found to increase drastically with increasing temperature [7]. In particular, at low temperature (T = 20°C) the area density of necks is small ($\phi = 0.02\%$), whereas at a higher temperature (T = 30°C) it is significantly larger ($\phi = 0.4\%$). The diameter of the neck is expected to be of order of the layer thickness, $d \sim 5 \times 10^{-3} \mu m$, which gives the defect area to be $A_d \sim 2 \times 10^{-5} \mu m$. The number of defects $n$ on an onion layer with diameter $D$ is thus estimated as $n \sim D^2 \phi / A_d$. Using
the experimentally measured values of φ at T = 30°C it follows that for onions smaller than \( \sim 0.1\,\mu\text{m} \) there is on average less than one defect and thus swelling might not occur or be very slow. That this size is smaller than the core diameters observed, possibly indicates that more than one defect is required to swell the onion within a reasonable time.

Alternatively for swelling to occur, the distance between bilayers has to increase, while still maintaining the layered structure. To ensure that the layers are not in a bound state, but wish to swell thermodynamically, thermal undulations must be present. In contrast to the lamellar phase, the transition from a bound to an unbound state within the onion has to allow for a tension across the membrane \[23\]. At the core, high curvature can induce a tension which suppresses membrane undulations and thus leads to a bound state. Surfactants in membranes with high curvature, at the core, will diffuse to membranes with a lower curvature. The tension of membranes in the centre will hence be higher than in the rest of the onion. This idea has been developed quantitatively by Diamant \[23\] and successfully predicts that the core will remain in a bound state during the swelling of the onion. Figure 8 shows the calculated density profile of a swollen onion where the bright region corresponds to high density and the dark region to low density. This argument assumes local equilibration of the bilayers within the onion during the swelling process and is thus, in contrast to the first argument, based on thermodynamic, equilibrium principles. Later we give evidence which supports this point of view (section 4.4).

### 4.3 Onion coalescence

Giant onions have been observed as large as 100\( \mu \text{m} \). They can be seen in penetration scans 3-4 days after contact and are the result of onions coalescing (figure 6). In emulsions and vesicles it is well known that droplets can coalesce and merge to form bigger aggregates. The time to coalesce is dependent on the energy barrier that must be surmounted in order to join the surfactant layers, which might either be a mono- or bilayer in the case of emulsions and vesicles, respectively. Once over the barrier they then rapidly merge \[24, 25\]. In the case of (multilamellar) onions one layer has to connect at a time. For the outer onion layer to connect, a neck must form between the two outer bilayers. Once this barrier is passed the onion cannot relax quickly since the next layer has to form a neck and so on. The complete process of coalescence has been observed (figure 6) and takes several days to complete. Also domains or cracks are observed radially in these onions. These may be remains of onions that have joined. After they coalesced fully they leave a scar behind where there is some density variation in the onion. Alterna-
tively there could be thermodynamic reasons for a radial domain structure in some cases [23].

4.4 Onion dilution

After the dilution of onions with brine, we have observed defects in the onions. These defects, which are probably solvent domains have a characteristic 'swirl'. They may be due to the osmotic shock after the onions have been dispersed. Over 4 days these defects disappear, if the onions are kept at a low temperature of 20°C. (In contrast, at 30°C the onions dissolve before the defects can disappear.) Since the onions slightly shrink this suggests that solvent is expelled from the onion. The bilayers within the onion are thus able to reorganise into an energetically more favourable state where there are no internal defects and thus the bilayers can reach a local equilibrium state. This reorganisation does not seem to depend on neck-like defects, since the density of these defects is small at low temperature [7]. This also has important consequences for the stability of cores discussed above (section 4.2). This observation makes the kinetic reason involving necks less likely and thus supports the thermodynamic explanation based on the unbinding theory of an onion.

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Figure 1: Onions in the bulk of the sample after contact of the onion phase with brine at T = 20°C. (A) Hexagonal close packed order before contact. (B) About two minutes after a small dilution, onions are observed to swell slightly. (C) Four days after contact ‘halo’ domains around the onions are observed in the bulk close to the interface (arrows). Images (A) and (B) are obtained using a glass slide and coverslip and observing with Nomarski DIC, while image (C) results from an experiment with a capillary tube using brightfield microscopy.
Figure 2: Onions at the onion/brine interface at $T = 20^\circ$C. (A) After several hours onions detach from the interface. (B) Within 4 days onions swell by a small amount.

Figure 3: Formation of sponge phase ($L_3$) after onion phase (right) is contacted with brine (left) at $T = 30^\circ$C. (A) Interface immediately after contact. (B) Sponge phase begins to form at the onion/brine interface 3 hours after contact.

Figure 4: Optical micrograph of onion kinetics at the micellar/sponge ($L_1/L_3$) interface. Onions (left) dissolve into a region of sponge phase (right). Arrow indicates the progress of a particular onion over time (times shown in minutes).

Figure 5: Schematic diagram of an onion-brine contact experiment at $T = 30^\circ$C. Vertical cross section of the capillary tube after the $L_3$ phase has formed.

Figure 6: Coalescence of onions during a penetration scan at $T = 30^\circ$C. After 2 days (A) large connections form between onions and (B) coalesced double onions with cores are observe. After 4 days (C) big onion in the process of coalescence are observed. (D) Onion with domains viewed using partial cross polars. (E) Closeup of the onion in (D).

Figure 7: Internal defects in a diluted onion dispersion at $T = 30^\circ$C. (A) After 6 hours of swelling (B) - (D) The defects in the onion disappear over 3 days when the temperature is changed to $T = 20^\circ$C.

Figure 8: (A) Calculated density profile of an onion where $\phi$ is the bilayer density and $r$ is the radial position in an onion of radius $R$. (B) Pictorial representation of (A) where the dark regions correspond to regions of low density and bright regions correspond to regions of high density in the onion. (Figure courtesy of H. Diamant [23].)
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