



Foams Stabilized by Surfactant Precipitates: Criteria for Ultrastability

Li Zhang, Lili Tian, Huiling Du, Stéphan Rouzière, Nan Wang, Anniina Salonen

► To cite this version:

Li Zhang, Lili Tian, Huiling Du, Stéphan Rouzière, Nan Wang, et al.. Foams Stabilized by Surfactant Precipitates: Criteria for Ultrastability. *Langmuir*, 2017, 33 (29), pp.7305-7311. <10.1021/acs.langmuir.7b01962>. <hal-04223337>

HAL Id: hal-04223337

<https://hal.science/hal-04223337v1>

Submitted on 29 Sep 2023

HAL is a multi-disciplinary open access archive for the deposit and dissemination of scientific research documents, whether they are published or not. The documents may come from teaching and research institutions in France or abroad, or from public or private research centers.

L'archive ouverte pluridisciplinaire **HAL**, est destinée au dépôt et à la diffusion de documents scientifiques de niveau recherche, publiés ou non, émanant des établissements d'enseignement et de recherche français ou étrangers, des laboratoires publics ou privés.



HAL Authorization

Foams stabilized by surfactant precipitates: criteria for ultrastability

Li Zhang¹, Lili Tian³, Huiling Du¹, Stéphan Rouzière², Nan Wang^{3*}, Anniina Salonen^{2*}

¹ School of Materials Science and Engineering, Xi'an University of Science and Technology, Xi'an 710054, Shaanxi, China

² Laboratoire de Physique des Solides, CNRS, Univ. Paris Sud, Université Paris Saclay, 91405 Orsay, France

³ Key Laboratory of Space Applied Physics and Chemistry, Ministry of Education, School of Science, Northwestern Polytechnical University, Xi'an 710072, China

Abstract: Foams are *ultrastable* when all the ageing processes arrest. We make such foams by precipitating sodium dodecyl sulphate with potassium chloride during the foaming process. The precipitate crystals adsorb onto the bubble surfaces to arrest coarsening and stop drainage by blocking in the interstices around the bubbles. However, if the concentration of SDS is too high, the foams are no longer ultrastable. The transition is sudden and corresponds to the point at which significant dodecyl sulphate remains in solution. The presence of the non-crystallised surfactant allows the foam to coarsen leading to the eventual disappearance of the foams, even if the crystals in the continuous phase can still block drainage. The transition occurs as the concentration of non-solubilised KCl becomes higher than the concentration of SDS, giving us a linear stability boundary. The system offers an interesting alternative to other types of particles because the surfactant crystals break and reform as the temperature is cycled, which makes for *reusable* solutions and *stimulable* foams.

1. Introduction

Foams are dispersions of gas inside a fluid¹. The bubbles confer the fluids with interesting mechanical and sensorial properties resulting in their use in many applications, such as enhanced oil recovery, mineral flotation, food products, or personal care products. However, their use can be restricted because of their limited stability, for example when product shelf-lives need to be long. This is why there is much interest in increasing the stability of foams and making so-called *ultrastable foams*.

Foams are thermodynamically unstable and age through three destabilization

mechanisms: *drainage*, *coalescence*, and *coarsening*¹. The first one leads to a decrease of the liquid fraction in the foam (making them drier), while the other two result in an increase of the bubble size. In order to make ultrastable foams, these ageing processes need to be strongly slowed down or even arrested.

Recently researchers have shown many different ways of making ultrastable foams². An increased stability is obtained either through the interfaces, for example by irreversibly adsorbing particles or proteins to make highly elastic interfaces which block coarsening^{3–7}. Alternatively the foam can be stabilized by the bulk phase, by making the bulk phase sufficiently elastic to stop coarsening and/or drainage^{8–12}, or to slow down drainage by blocking particles in Plateau borders^{13–15}. A range of different types of particles has been used to stabilise foam. Shrestha and co-workers showed that crystallized fatty acid particles can also be effective^{16,17}. They showed that it is important the fatty acids form α -crystals to be very stable, the foams made from liquid crystalline phases were much less stable. Crystallized fatty acids have been shown also to stabilize non-aqueous foams¹⁸.

Some applications require that the foam is stable until a certain moment in time, at which it should disappear on command (for example for decontamination or cleaning purposes). The foams should be *stimulable*¹⁹. It has been shown that the stability of foam can be controlled by many external stimuli, such as temperature^{20,21}, pH²², light^{23,24} or magnetic field²⁵. Surfactant crystals are interesting as foam stabilisers because they are temperature sensitive, below the Krafft boundary the surfactant is in crystals, but at higher temperatures it is solubilized in micelles. Precipitating surfactant is known to decrease foamability and foam stability^{26–30}. The precipitate particles are less mobile so adsorption onto interfaces is slow. They can also be active antifoam particles and bridge foam films to cause rupture and lead to foam destabilization^{27,30}.

We have recently shown³¹ that by simply adding KCl or NaCl to sodium dodecyl sulfate (SDS) can make ultrastable and temperature stimulable foams. This is because the surfactant precipitates and forms crystals, which cover the bubble surfaces and arrest foam aging. When heated above the precipitation temperature, the crystals melt and the foam starts to age.

In this paper, we explore the reasons behind the extreme stability of the foams made from the mixtures of SDS and KCl. We choose KCl because it is very good at

precipitating SDS^{31,32} and the precipitate is almost exclusively formed of KDS³². At temperatures below the precipitation boundary, the stability of the foams generated with different concentrations of SDS and KCl have been studied. We show that depending on the relative concentrations of SDS and KCl the foam can: age like pure SDS foams, be stabilised against drainage or be ultrastable with arrested drainage and coarsening.

2. Materials and methods

2.1. Material

Sodium dodecyl sulfate (SDS, $\geq 99.0\%$) and potassium chloride (KCl, $\geq 99.0\%$) were purchased from Aladdin (Shanghai, China) and used without further purification. Milli-Q water ($18.2 \text{ M}\Omega\text{cm}$) is used for the preparation of aqueous solutions. In the experiments air was used as gas for all of the experiments. Stock solutions of 2 M KCl and 900 mM SDS are used in the sample preparations. Due to the hydrolysis of the SDS the surfactant stock solution was used within a week of preparation.

2.2. Methods

Making foam. The foams are made using a setup consisting of two disposable syringes connected by a constriction³³, the setup is shown in Figure 1. The volume of a syringe is 10 mL and the diameter of the constriction is 2 mm. One syringe is filled with salt solution and water, and the other with SDS solution and air. This ensures that SDS and salt come into contact only as the foam generation process begins. The foam is formed by pushing the liquid and gas forward and backward through the constriction 20 times. This takes around 30 seconds. The ratio of gas and liquid used to make foam is 4:1, and the total volume of liquid is constant at 2 ml. This means that the maximal foam volume is 10 ml and the minimal initial liquid fraction 20 %.

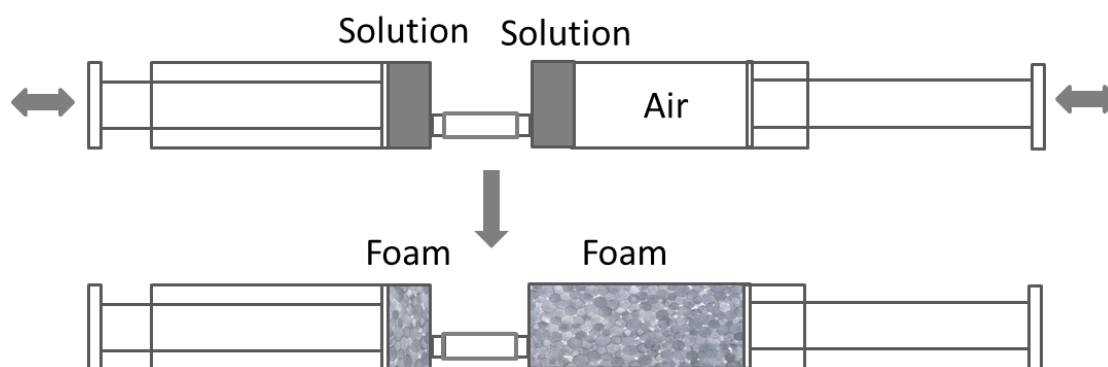


Figure 1 A schematic drawing of the foaming procedure. Two syringes are connected via a shot tube, one of them is filled with surfactant solution and air, and the other with salt solution. The solutions are passed through the connections 20 times at the end of which a homogeneous foam is formed.

Foam stability studies. After making the foam, the samples were transferred into glass vials. Images were taken by a camera every 30 minutes at room temperature. Some samples were photographed every 10 to 20 minutes to follow the initial drainage. Others were photographed under a microscope to observe the bubble surfaces more closely. The samples for microscopy are constrained in cells with a dimension of $1 \times 1 \times 1$ mm and observed from above.

Wide angle X-ray scattering experiments. We have measured the structure of the precipitate using wide x-ray scattering (WAXS). The samples were measured in glass capillaries 1.5 mm in diameter. The capillaries were filled with precipitate separated from the solution by centrifuging at 4000 rpm for 5 minutes. The precipitate was injected into the glass capillaries and they were centrifuged for 5 minutes at 2000 rpm to ensure that the precipitate compacted at the bottom of the capillary, the supernatant was removed using a syringe before measurement.

The samples were measured on a rotating copper anode generator coupled with a multilayer W/Si optics delivering a monochromated X-ray beam (wavelength = 1.542 \AA) of $1 \times 1 \text{ mm}^2$ at the sample position. WAXS images were recorded by an X-ray sensitive image plate detector Mar345 with $150 \text{ }\mu\text{m}$ pixel size. Sample to detector distance was 300 mm and acquisition time for each image was 10 minutes. X-ray diffractogram (intensity as a function of scattering wavevector q) was obtained by performing a radial intensity integration of the image using a home-made software.

Surface tension measurements. We have measured the surface tension of the supernatant collected from precipitated samples. The samples were prepared by mixing appropriate concentrations of 2 M KCl and 500 mM SDS stock solutions with water. The samples were gently shaken and left to equilibrate overnight. The samples were stored at ambient temperature of around $24 \pm 1^\circ\text{C}$.

The next day the samples were centrifuged at 4000 rpm during 5 minutes, after which the precipitate had compacted to the bottom. The supernatant was collected and the surface tension was measured using the Tracker from Teclis, France. The surface tension was followed during 30 minutes.

3. Results and discussion

Three types of foam. We have made foams with different concentrations of SDS (10

– 600 mM) in the presence of varying concentrations of KCl (10 – 500 mM). All the samples studied are below the Krafft boundary and precipitated surfactant crystals eventually form in each sample. The foams are photographed immediately after generation and every half an hour in the first 5 hours and then every few hours over several days. We can divide the foams into three categories depending on their stability and ageing. The foams can be unstable with an ageing similar to standard SDS foam (without salt) these are called type I. The second type of foam, type II is more stable than type I, but disappears through collapse after a few hours. The third type of foam, referred to as type III is classed *ultrastable*, and the foams remain stable for months. Characteristic photographs of the different types of samples are shown in Figure 2 immediately after preparation and 3 hours later, where differences can already be observed.

Both type I (Figure 2 a) and II (Figure 2 b) foams are defined as unstable. The foam ages and eventually disappears. However, they have very different aging. Type I behaves very much like normal surfactant foam. The foam drains, the bubble size increases and the foam starts to collapse from the top of the sample, disappearing in a few hours. The evolution of type II foam is different. After generation some liquid drains out of the foam, but instead of the foam disappearing from the top, it retains its height. The foam becomes a dry network-like structure, which finally, suddenly collapses to the bottom of the sample. The foams of type III are defined as *ultrastable*, even after two months there is considerable foam left. However, within the family of *ultrastable* foams, depending on sample composition the foamability is variable. Some of them foam very poorly (Figure 2 c) and the amount of foam generated is very small, while others can produce quite a lot of *ultrastable* foam, as seen in Figure 2 d.

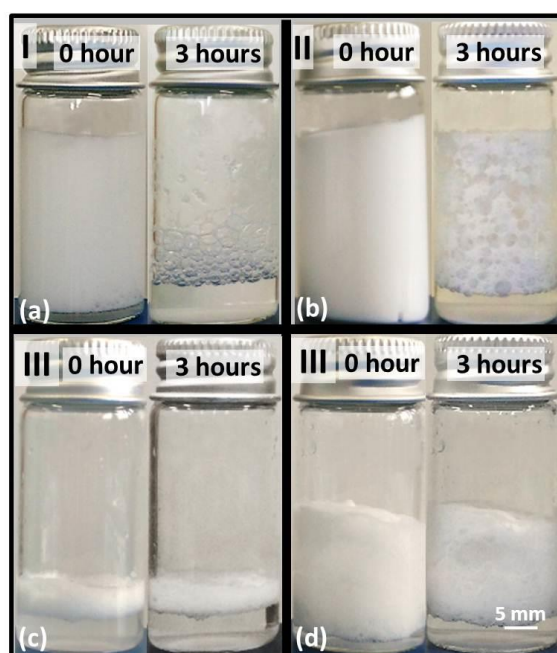


Figure 2. Typical photographs of foams generated when the concentrations of SDS and KCl are varied. Foams I and II are unstable, while foams III are ultrastable. For each foam an image taken shortly after preparation and one taken after 3 hours is shown. The concentration of SDS and KCl in the different samples is as follows: (a) 30 mM KCl and 10 mM SDS, (b) 250 mM KCl and 300 mM SDS, (c) 500 mM KCl and 30 mM SDS and (d) 500 mM KCl and 150 mM SDS.

All the samples have surfactant crystals in them. Photographs taken under the microscope are shown in Figure 3. In type I only a few crystals are seen on the surface of the bubbles after generation (Figure 3 a). In type II foam stability is better and there are more crystals on the bubble surfaces and in the interstices between them (Figure 3 b). The foams are different in type III (Figures 3 c and d), not only are the bubble surfaces completely covered with crystals, there are also crystals visible in the bulk solution. Indeed some of the bubbles are no longer spherical indicating solid-like interfaces³⁴. Therefore, it seems that the amount of crystallized surfactant present is very important and only those bubbles with fully covered surfaces become ultrastable.

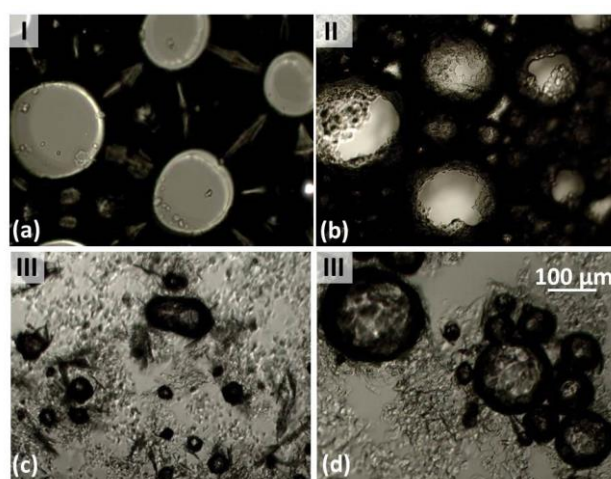


Figure 3 Photographs of bubble surfaces under the microscope after preparation, the concentration in (a) is 30 mM KCl and 10 mM SDS, (b) 250 mM KCl and 300 mM SDS, (c) 250 mM KCl and 60 mM SDS and (d) 250mM KCl and 150 mM SDS.

We have seen that depending on the amounts of SDS and KCl the foam ageing can be very different. Each sample can be classified into one of the three different types of foam. Creating many foams and following their evolution we have constructed a “foam stability” diagram where the three different regions are visible, as shown in Figure 4. Stable foams are only found when the concentration of KCl is superior to the concentration of SDS, while the different unstable foams are formed once the concentration of SDS becomes sufficiently high. The boundary between stable and unstable foam regions can be separated by a straight line with an equation of $[KCl] = [SDS] + 30 \text{ mM}$, drawn in Figure 4. In order to understand the boundary we will have a look at the generation and ageing of the different foam samples in more detail.

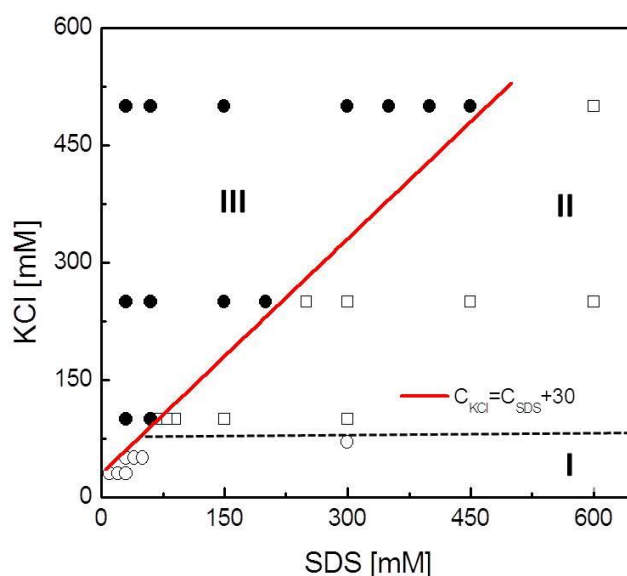


Figure 4 Diagram showing the regions of different types of foam depending on the SDS and the KCl concentrations. The filled symbols indicate ultrastable foams and empty symbols unstable foams. The two unstable foam types I and II are divided by a dashed line as a guide to the eye. The red line shows the boundary between stable and unstable foams and is described by $[KCl] = [SDS] + 30 \text{ mM}$.

Foam generation and ageing. Figure 5 shows the evolution of the normalized foam height (foam height/maximum height) as a function of SDS concentration in the presence of 500 mM KCl. We can see that the amount of foam that can be generated

increases gently from around 0.25 to 0.6 as the SDS concentration increases to 450 mM. As the SDS concentration increases further the foamability suddenly improves and the full sample can be foamed. However, this is also the point at which the foams become unstable (we go from region III to II). Therefore, as soon as the foamability becomes very good, the foam stability suffers. It seems that although the crystals are important in stabilizing the foam, they are detrimental to the foamability.

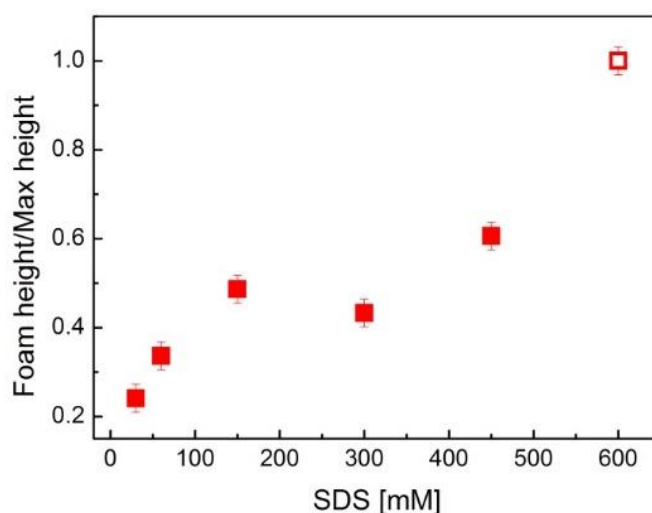


Figure 5 Foam height after generation as a function of the concentration of SDS with 500 mM KCl. The filled symbols indicate ultrastable foams and empty symbols unstable foams.

We know that to make ultrastable foams coalescence, coarsening and drainage need to be stopped. We have followed the drainage of the liquid from the foams by measuring the height of the drained liquid in time from different samples, as shown in Figure 6 (a). The samples are all unstable (regions I and II), where foamability is good and a full sample of foam is made in the beginning. The foams are initially rather wet with a liquid fraction of 20%, and they drain quickly despite the small initial bubble size (around 50 μm in diameter). However, eventually the drainage is slowed down and the height of drained liquid becomes almost constant. The average liquid fraction after 120 minutes is around 5 % in the foams with low concentrations of KDS. This is a reasonable value for the equilibrium liquid fraction of a few centimeters of foam with 200 μm bubbles³⁵. The liquid fraction becomes constant due to the balance between gravity and capillarity, and evolves slowly as the bubble size increases.

The foams in region I (such as 30 mM KCl and 10 mM SDS) drain like the foam made

with 80 mM SDS. In region I the presence of KCl has no effect on the foam aging, because the concentration of KCl is small so the amount of crystals formed is not sufficient to influence foam stability. In region II, the foam drainage slows down as the concentration of KCl increases.

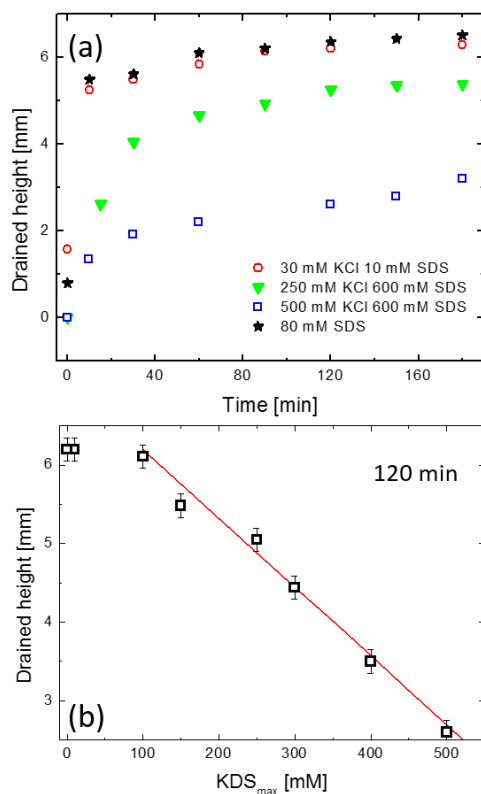


Figure 6 The evolution of the height of drained liquid as a function of time (a) and the maximum concentration of KDS taken as the lower of the values of SDS and KCl (b). (a) The samples in region I is 30 mM KCl and 10 mM SDS (circle); region II are 250 mM KCl and 600 mM SDS (diamond), and 500 mM KCl and 600 mM SDS (square); 80 mM SDS (Up triangle) is considered as the reference sample.

The drainage slows down because the crystals are blocked in the foam skeleton. At a certain point the presence of crystals stops the Plateau borders from decreasing in size, so more water is retained inside the foam than if the Plateau borders could freely continue to drain. The slowing down (eventually leading to blockage) of drainage has been extensively studied by Pitois and co-workers^{13,36,37}. The moment where the drainage blocks depends on the concentration of particles, the higher the concentration the lower the amount of drained liquid. We do not know the exact quantity of precipitate, but in Figure 6 (b) we plot the height of drained liquid as a function of the maximum possible crystal concentration in the sample. The

concentration of KDS that could be precipitated, i.e. for a sample with 30 mM KCl and 10 mM SDS this would be 10 mM, while for a sample with 30 mM KCl and 40 mM SDS this would be 30 mM. The height of drained liquid decreases linearly with the concentration of KDS, this means that the amount of liquid retained in the foam increases linearly with the concentration of precipitate. It is indeed the trapped crystals stabilize the foams.

We can make a simple model to calculate the amount of drained water as a function of the concentration of KDS, and estimate the amount of water bound with the crystals in the foam. We assume that the total volume of liquid (water + crystals) V_{tot} can be divided into three contributions, $V_{\text{tot}} = V_{\text{drain}} + V_{\text{foam}} + V_{\text{crystal}}$. V_{drain} is the amount of drained liquid. V_{foam} is amount of liquid in the foam equilibrium structure, given by the amount of liquid retained in a foam with a low concentration of KDS. V_{crystal} is the volume of KDS + bound water stuck in the foam skeleton. We measure V_{drain} directly, V_{foam} is taken as the volume of water + KDS at the end of the Plateau, so at 100 mM KDS. This leaves us with V_{crystal} , which we calculate from the volume of KDS in the foam, above 100 mM, multiplied by a constant B . B estimates the volume of water that is retained in the foam with the KDS, and it is our only fit parameter. In Figure 6(b), we show in red the line predicting the height of drained liquid from the concentration of KDS. The red line describes the data very well with $B = 3.6$, this means that 1 mm³ of KDS in the foam structure blocks a further 3.6 mm³ of water in the foam. The large amount of water blocked with the particles is probably because of the anisotropic shape of the crystals, which can block the Plateau borders from shrinking without filling them completely.

The foams drain until the bubble structure becomes almost indistinguishable and only a network of crystals remains. The network is not strong enough to support its own weight and collapses once the stress due to the weight of the foam overcomes the yield stress of the crystal network. Assuming a 10 % liquid fraction in the foam, and taking the fluid density as that of water, if we take the height of the foam as 4 cm, the yield stress of the network can be estimated thus to be lower than around 4 Pa.

In the unstable region we have seen that at higher concentrations of SDS and KCl the foams become increasingly stable as the drainage is slowed down by the trapped crystals. However, the foams are not ultrastable as coarsening continues. Figure 7 shows photographs of bubbles evolving in time. All surfaces are not fully covered by

crystals, for example, the bubble surface pointed by the red arrow is “naked”. Initially the bubble is sufficiently large to grow, and after 60 s the “naked” surface has slightly increased before it becomes one of the shrinking bubbles and the “naked” surface starts to decrease (see image at 180 s). It seems that at 300 s crystals cover the whole bubble surface, but despite this the foam remains unstable. The crystals do not completely block as the bubbles shrink, but they continue to desorb or slide past one another to continue to coarsen.

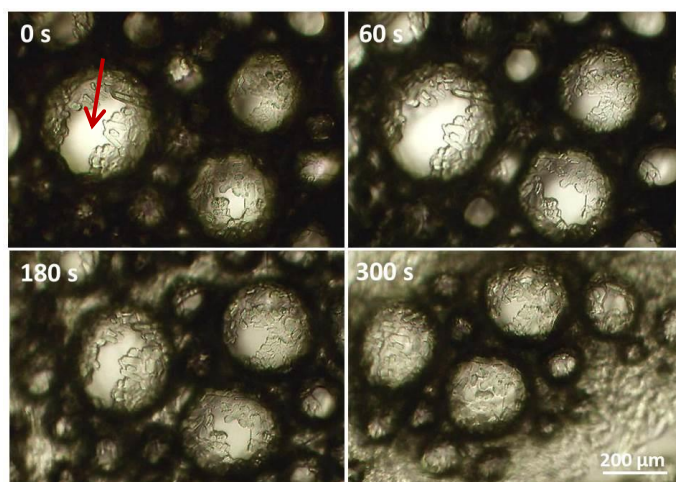


Figure 7 Photographs of the evolution of bubble surfaces with time observed under the microscope. The foam is made with 500 mM KCl and 600 mM SDS and is in the unstable region II.

This is probably because of the excess SDS. Not all of the surfactant has precipitated and the “naked” surfaces are of course covered by DS^- . The SDS at the interface gives it fluidity and the crystals can keep on rearranging as the bubble evolves. Therefore, the foam will continue to coarsen and slowly drain before starting to coalesce.

Crystal structure and supernatant. We have seen how the concentrations of surfactant and salt can lead to very different behavior in foam stability. In order to understand the origin of the change in stability, we have examined the structure of the crystals and the supernatant independently.

We measured the precipitate in four samples, all of them had 250 mM KCl and 150, 200, 250 or 260 mM SDS. The scattered intensity is shown as a function of the q -vector in Figure 8.

The scattering signal from all four samples is very similar. The 3 peaks which are easily identified as arising from a lamellar spacing are obtained at the smallest q -vectors. The position of the peaks is almost unchanged with changing SDS

concentration (a very slight shift to lower q -vectors occurs as SDS concentration increases). We calculate the lamellar spacing, d from the position of the first peak, q_1 as $d = 2\pi/q$ which gives 35 Å. At high q a number of peaks are observed, these indicate the crystallisation of the hydrocarbon chains in the lamellae. All the samples have a very similar structure of the precipitate on either side of the limit of foam stability. Similarly, observations of the crystals under the microscope do not show significant differences in the crystal shape or size, thus we think that neither the crystal structure nor form is responsible for the change.

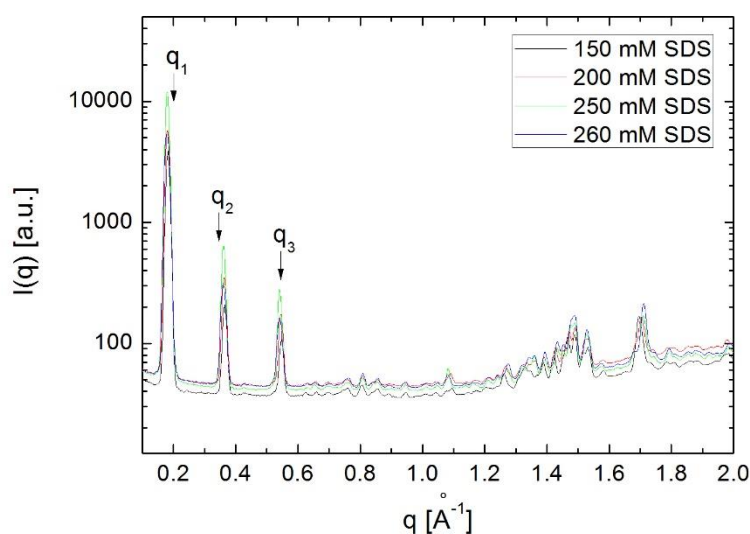


Figure 8 The scattered intensity as a function of the q -vector of precipitate prepared with 250 mM KCl and varying concentrations of SDS. The intensity is plotted in log scale to improve the visibility of peaks 2 and 3.

We have measured the surface tension of the supernatant at increasing SDS concentrations with 250 mM KCl. The dynamic surface tensions are shown in the supporting information in Figure S1, and the values after 30 minutes of equilibration are shown in Figure 9, samples in the stable region III are in filled circles, while samples in the unstable region II are empty circles.

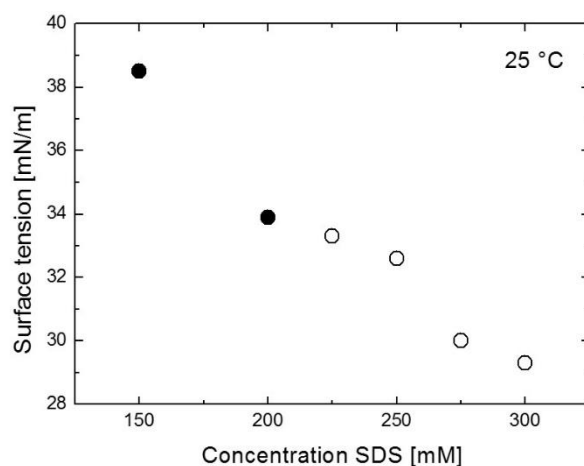


Figure 9 Surface tension of the supernatant after 30 minutes of equilibration for a sample with 250 mM KCl as a function of SDS concentration.

The surface tension decreases as the SDS concentration increases, suggesting that the concentration of SDS in the bulk solution is higher. We have to be careful in analysing these values as the non-precipitated salt concentration will influence the adsorption of the surfactants, and here the ionic background strength is not constant. However, at 150 mM SDS the surface tension is around 38.5 mN/m, which is high considering the concentration of salt in the solution (> 100 mM) so we can infer that the concentration of free SDS is low. The surface tension drops significantly as the SDS concentration increases to 200 mM suggesting that the concentration of non-crystallised SDS is increasing, and continues to do so as the transition from ultrastable to unstable foams is passed.

Some surfactant crystals are known to behave as antifoam particles^{28,29}, we have made foams from the supernatant to explore the possible antifoam nature of our crystals. We find no adverse effects of the crystals on foamability, if anything the supernatant alone foams slightly less well. The resulting photographs are shown in Supporting Information, Figure S2. This further confirms our proposition that the foam stability is decreased below the stability line, because of the presence of free surfactant rather than because of the crystals themselves, although a full study of the contact angles of the particles could give further insight into the stabilization mechanism³⁸.

Criteria for ultrastable foams. The foams made from mixtures of SDS and KCl can have very different stability depending on the concentration of the components.

We can summarise the foams in the different regions is as follows:

Type I – unstable foams at low KCl concentrations (< 30 mM). In these samples the concentration of KCl is very low and the amount of precipitate small. The precipitate has no visible influence on the ageing of the foams.

Type II – unstable foam at high SDS concentrations $[\text{SDS}] > [\text{KCl}] - 30$ mM. The foams are more stable against drainage with increasing concentrations of crystal blocking the Plateau borders. However, the presence of free SDS fluidifies the bubble interfaces and coarsening continues leading to the eventual destabilization of the foam.

Type III – ultrastable foams at high KCl concentrations $[\text{KCl}] > [\text{SDS}] + 30$ mM. The bubbles are covered with crystallized surfactant making the interfaces solid-like. The coarsening process arrests, which also stops drainage and blocks the ageing of the foams.

As the concentration of SDS is increased the transition from stable foams (region III) to unstable foams (region II) occurs along the line given by $[\text{KCl}] = [\text{SDS}] + 30$ mM at 25°C .

We saw that in region II some bubble surfaces were not completely covered by crystals (Figure 7), but by DS^- (with Na^+ or K^+ counter ions close to the interface of course). The surface tension decreases even as the boundary from ultrastable to ageing foams is passed, suggesting that the concentration of surfactant in the supernatant increases.

The surface tension levels off once the equimolar concentration has been passed, which suggests that at this point the surfactant concentration in the bulk has become sufficiently high for micelles to start forming. Wu *et al.*³² studied precipitation of 50 mM SDS solution with added KCl and also saw that the non-precipitated surfactant concentration decreases to only a few mM as the concentration of KCl increases above that of the SDS. The observed increase in foamability as the stability line is crossed also suggests an increase of the SDS concentration in the solution.

The presence of excess surfactant in solution changes the behavior of the foams, they go from purely particle stabilized to stabilized by both particles and surfactants (precipitate + free surfactant), where the surfactants ensure the fluidity of the

interfaces so that the crystals can reorganize and desorb during coarsening. In this case coarsening no longer arrests and the foams are not ultrastable. To understand exactly what determines the position of the boundary we have measured the foam stability at different temperatures, and as temperature is increased or decreased the slope remains the same, but the position of the intercept changes (at 20 °C it is 0 mM and at 30 °C it is 60 mM). This suggests that the intercept is a measure of the concentration of solubilized KCl, denoted $[KCl]_{sol}$. We assume that the concentration of non-precipitated SDS at the transition is negligible, so that the foams become unstable as the concentration of SDS becomes higher than the concentration of non-solubilised KCl. In this case, the increase of $[KCl]_{sol}$ with temperature is observed because of the increased aqueous solubility at higher temperatures. We can test our hypothesis by plotting $[KCl]_{sol}$ as a function of the aqueous solubility of KCl at the studied temperature. In this case we assume that although the solubility of KCl changes in the presence of SDS, its variation with temperature remains the same. The result is in Figure S3 and the relationship is linear, thus backing our explanation of the position of the foam stability line.

We give criteria for making ultrastable foams using precipitated potassium dodecyl sulphate, and show how the critical concentration of KCl required to do so evolves with SDS concentration and temperature. These results will help experimentalist to explore other types of surfactant particles as foam stabilisers, to obtain systems suited for different applications, whether in foods, cosmetics or industrial processes.

4. Conclusions

We explore the generation and stability of foams made with surfactant particles precipitated *in-situ*. We show that potassium dodecyl sulphate crystals can be excellent foam stabilisers and able to arrest all the foam ageing mechanisms. However, if the concentration of surfactant increases above a critical concentration, the foams are no longer so stable. In these conditions, the presence of the crystals can retard drainage, but coarsening will continue leading to the eventual disappearance of the foams. We give the expression for the critical surfactant concentration, which depends on both the KCl concentration and temperature. Physically, at this moment the concentration of non-precipitated surfactant increases strongly and leads to foam ageing. Surfactant precipitates are interesting alternatives as foam stabilizers, because they break upon heating and reform upon

cooling. This makes the foams *stimulable* and the foaming solutions *recyclable*.

Acknowledge: We thank the PhD research startup foundation of Xi'an University of Science and Technology (2017QDJ003), the Natural Science Foundation of China under grant 51372197 and the Key Innovation Team of Shaanxi Province (2014KCT-04). We thank CNES (Hydrodynamics of wet foams) and ESA (Soft Matter Dynamics) for financial support. We thank the financial support by the Fund of the Innovation Base of Graduate Students of NPU.

References:

- (1) Cantat, I.; Cohen-Addad, S.; Elias, F.; Graner, F.; Höhler, R.; Pitois, O.; Rouyer, F.; Saint Jalmes, A. *Les Mousses: Structure et Dynamique*; Belin, 2011.
- (2) Rio, E.; Drenckhan, W.; Salonen, A.; Langevin, D. Unusually Stable Liquid Foams. *Adv. Colloid Interface Sci.* **2014**, *205* (0), 74–86.
- (3) Stocco, A.; Rio, E.; Binks, B.; Langevin, D. Aqueous Foams Stabilized Solely by Particles. *Soft Matter* **2011**, *4*, 1260–1267.
- (4) Du, Z.; Bilbao-Montoya, M. P.; Binks, B. P.; Dickinson, E.; Ettelaie, R.; Murray, B. S. Outstanding Stability of Particle-Stabilized Bubbles. *Langmuir* **2003**, *19* (8), 3106–3108.
- (5) Murray, B. S.; Ettelaie, R. Foam Stability: Proteins and Nanoparticles. *Curr. Opin. Colloid Interface Sci.* **2004**, *9* (5), 314–320.
- (6) Kloek, W.; van Vliet, T.; Meinders, M. Effect of Bulk and Interfacial Rheological Properties on Bubble Dissolution. *J. Colloid Interface Sci.* **2001**, *237* (2), 158–166.
- (7) Salonen, A.; Gay, C.; Maestro, A.; Drenckhan, W.; Rio, E. Arresting Bubble Coarsening: A Two-Bubble Experiment to Investigate Grain Growth in the Presence of Surface Elasticity. *EPL (Europhysics Lett.)* **2016**, *116* (4), 46005.
- (8) Guillermic, R. M.; Salonen, A.; Emile, J.; Saint-Jalmes, A. Surfactant Foams Doped with Laponite: Unusual Behaviors Induced by Aging and Confinement. *Soft Matter* **2009**, *5* (24), 4975–4982.
- (9) Goyon, J.; Bertrand, F.; Pitois, O.; Ovarlez, G. Shear Induced Drainage in Foamy Yield-Stress Fluids. *Phys. Rev. Lett.* **2010**, *104* (12), 128301.
- (10) Salonen, A.; Lhermerout, R.; Rio, E.; Langevin, D.; Saint-Jalmes, A. Dual Gas and Oil Dispersions in Water: Production and Stability of Foamulsion. *Soft Matter* **2012**, *8* (3), 699–706.
- (11) Deleurence, R.; Saison, T.; Lequeux, F.; Monteux, C. Time Scales for Drainage and Imbibition in Gellified Foams: Application to Decontamination Processes. *Soft Matter* **2015**, *11* (35), 7032–7037.
- (12) Lesov, I.; Tcholakova, S.; Denkov, N. Factors Controlling the Formation and Stability of Foams Used as Precursors of Porous Materials. *J. Colloid Interface Sci.* **2014**, *426* (0), 9–21.
- (13) Haffner, B.; Khidas, Y.; Pitois, O. Flow and Jamming of Granular Suspensions in

- Foams. *Soft Matter* **2014**, *10* (18), 3277–3283.
- (14) Varade, D.; Carriere, D.; Arriaga, L. R.; Fameau, A. L.; Rio, E.; Langevin, D.; Drenckhan, W. On the Origin of the Stability of Foams Made from Catanionic Surfactant Mixtures. *Soft Matter* **2011**.
 - (15) Fameau, A.-L.; Salonen, A. Effect of Particles and Aggregated Structures on the Foam Stability and Aging. *Comptes Rendus Phys.* **2014**, *15* (8–9), 748–760.
 - (16) Shrestha, L. K.; Acharya, D. P.; Sharma, S. C.; Aramaki, K.; Asaoka, H.; Ihara, K.; Tsunehiro, T.; Kunieda, H. Aqueous Foam Stabilized by Dispersed Surfactant Solid and Lamellar Liquid Crystalline Phase. *J. Colloid Interface Sci.* **2006**, *301* (1), 274–281.
 - (17) Shrestha, L. K.; Saito, E.; Shrestha, R. G.; Kato, H.; Takase, Y.; Aramaki, K. Foam Stabilized by Dispersed Surfactant Solid and Lamellar Liquid Crystal in Aqueous Systems of Diglycerol Fatty Acid Esters. *Colloids Surfaces A Physicochem. Eng. Asp.* **2007**, *293* (1–3), 262–271.
 - (18) Binks, B. P.; Garvey, E. J.; Elio Vieira, J. Whipped Oil Stabilised by Surfactant Crystals. *Chem. Sci.* **2016**, *7*, 2621–2632.
 - (19) Fameau, A. L.; Carl, A.; Saint-Jalmes, A.; von Klitzing, R. Responsive Aqueous Foams. *Chemphyschem* **2015**, *16* (1), 66–75.
 - (20) Fameau, A.-L.; Saint-Jalmes, A.; Cousin, F.; Houssou, B. H.; Novales, B.; Navailles, L.; Nallet, F.; Gaillard, C.; Boue, F.; Douliez, J.-P. Smart Foams: Switching Reversibly between Ultrastable and Unstable Foams. *Angew. Chemie-International Ed.* **2011**, *50* (36), 8264–8269.
 - (21) Fameau, A.-L.; Lam, S.; Velez, O. D. Multi-Stimuli Responsive Foams Combining Particles and Self-Assembling Fatty Acids. *Chem. Sci.* **2013**, *4* (10), 3874–3881.
 - (22) Binks, B. P.; Murakami, R.; Armes, S. P.; Fujii, S.; Schmid, A. pH-Responsive Aqueous Foams Stabilized by Ionizable Latex Particles pH-Responsive Aqueous Foams Stabilized by Ionizable Latex Particles. *Langmuir* **2007**, *23* (11), 8691–8694.
 - (23) Salonen, A.; Langevin, D.; Perrin, P. Light and Temperature Bi-Responsive Emulsion Foams. *Soft Matter* **2010**, *6* (21), 5308–5311.
 - (24) Chevallier, E.; Saint-Jalmes, A.; Cantat, I.; Lequeux, F.; Monteux, C. Light Induced Flows Opposing Drainage in Foams and Thin-Films Using Photosurfactants. *Soft Matter* **2013**.
 - (25) Lam, S.; Blanco, E.; Smoukov, S. K.; Velikov, K. P.; Velez, O. D. Magnetically Responsive Pickering Foams. *J. Am. Chem. Soc.* **2011**, *133* (35), 13856–13859.
 - (26) Peper, H. THE DEFOAMING OF SYNTHETIC DETERGENT SOLUTIONS BY SOAPS AND FATTY ACIDS. *J. Colloid Sci.* **1958**, *207* (April 1957), 199–207.
 - (27) Zhang, H.; Miller, C. A.; Garrett, P. R.; Raney, K. H. Defoaming Effect of Calcium Soap. *J. Colloid Interface Sci.* **2004**, *279* (2), 539–547.
 - (28) Miller, C. A. Antifoaming in Aqueous Foams. *Curr. Opin. Colloid Interface Sci.* **2008**, *13* (3), 177–182.
 - (29) Garrett, P. R. Defoaming: Antifoams and Mechanical Methods. *Curr. Opin. Colloid Interface Sci.* **2015**, *20* (2), 81–91.
 - (30) Zhang, H.; Miller, C. A.; Garrett, P. R.; Raney, K. H. Mechanism for Defoaming by Oils and Calcium Soap in Aqueous Systems. *J. Colloid Interface Sci.* **2003**, *263* (2), 633–644.

- (31) Zhang, L.; Mikhailovskaya, A.; Yazhgur, P.; Muller, F.; Cousin, F.; Langevin, D.; Wang, N.; Salonen, A. Precipitating Sodium Dodecyl Sulfate to Create Ultrastable and Stimulable Foams. *Angew. Chemie Int. Ed.* **2015**, *54* (33), 9533–9536.
- (32) Wu, B.; Christian, S. D.; Scamehorn, J. F. Recovery of Surfactant from Micellar-Enhanced Ultrafiltration Using a Precipitation Process. *Prog. Colloid Polym. Sci.* **1998**, *109* (Horizons 2000--Aspects of Colloid and Interface Science at the Turn of the Millenium), 60–73.
- (33) Gaillard, T.; Roché, M.; Honorez, C.; Jumeau, M.; Balan, A.; Jedrzejczyk, C.; Drenckhan, W. Controlled Foam Generation Using Cyclic Diphasic Flows through a Constriction. *Int. J. Multiph. Flow* **2017**.
- (34) Subramaniam, A. B.; Abkarian, M.; Mahadevan, L.; Stone, H. A. Non-Spherical Bubbles. *Nature* **2005**, *438* (7070), 930.
- (35) Maestro, A.; Drenckhan, W.; Rio, E.; Höhler, R. Liquid Dispersions under Gravity: Volume Fraction Profile and Osmotic Pressure. *Soft Matter* **2013**, *9* (8), 2531.
- (36) Khidas, Y.; Haffner, B.; Pitois, O. Capture-Induced Transition in Foamy Suspensions. *Soft Matter* **2014**, *10* (23), 4137–4141.
- (37) Haffner, B.; Khidas, Y.; Pitois, O. The Drainage of Foamy Granular Suspensions. *J. Colloid Interface Sci.* **2015**, *458*, 200–208.
- (38) Luangpirom, N.; Dechabumphen, N.; Saiwan, C.; Scamehorn, J. F. Contact Angle of Surfactant Solutions on Precipitated Surfactant Surfaces. *J. Surfactants Deterg.* **2001**, *4* (4), 367–373.

TABLE OF CONTENTS FIGURE

