Angewandte Chemie International Edition

Thermostimulable Materials

International Edition: DOI: 10.1002/anie.201503236
German Edition: DOI: 10.1002/ange.201503236

Precipitating Sodium Dodecyl Sulfate to Create Ultrastable and Stimulable Foams**

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***Abstract:** Ultrastable foams are made very simply by adding salt (NaCl or KCl) to sodium dodecyl sulfate. The addition of high concentrations of salt leads to the precipitation of the surfactant on the bubble surfaces and as crystals in the interstices between the bubbles. As a consequence, the ageing of the foams is stopped to make them stable indefinitely, or until they are heated above the melting temperature of the crystals. The use of KCl is shown to be much more effective than that of NaCl because potassium dodecyl sulfate has a higher melting temperature and faster rates of crystallization. The crystalline structures have been investigated inside the foam using small angle neutron scattering. The larger lattice spacing of the crystals formed with NaCl in comparison with KCl has been evidenced. These simple temperature stimulable foams could have many potential applications.*

Foams are found in a wide variety of applications in industry and personal life, such as firefighting, enhanced oil recovery, mineral flotation, food processing, and personal care products. In some of these applications good foam stability is extremely important. All foams are thermodynamically unstable and are destined to disappear.[1] To prolong their life, various types of stabilizing agents are used, such as surfactants, polymers, proteins, or particles.[1b] These stabilizing agents adsorb onto the surfaces of the bubbles and slow down the different mechanisms by which foams age: drainage, coalescence, and coarsening.

In some cases, foams that are stable for very long periods of time are required, so called ultrastable foams. The processes of coarsening and drainage should be arrested. In the design of such foams, irreversibly adsorbing stabilizing agents are chosen, which makes for highly elastic interfaces which block coarsening.[2] It is also possible to stop ageing by increasing the elasticity of the bulk phase or to slow down drainage by blocking particles in Plateau borders.[2,3] A wide range of systems has been used so far to make these ultrastable foams.[4] An interesting way to make such stable foams was shown by Shrestha et al., who used small crystallized surfactant particles[5] that were trapped inside the foam and arrested the drainage.

In other cases, good foam stability is initially required but at a given moment it should become unstable and disappear. The foams should be stimulable. The stabilizing agents can be chosen such that they respond to one or more external parameters to control foam stability.[4c]

Many commonly used surfactants are charged, so their bulk and interfacial properties depend on the overall electrolyte concentration. Further addition of ions leads to changes in their aqueous solubility, micellar form, and to an increase of their packing at interfaces.[6] The influence of ionic strength on interfacial rheology, film and foam stability has been studied.[7]

It is not only the amount of added salt that is important, the type counts as well.[8] These effects have been rationalized by Collins in his description of matching water affinities.[9] Ions are classed as strongly (kosmotrope) or weakly (chaotrope) hydrated, and matching ions form ion pairs more readily. We choose two salts NaCl and KCl, because Na^+ is a kosmotrope and K^+ is a chaotrope. As surfactant, we choose sodium dodecyl sulfate (SDS), where the sulfate head group is chaotropic.[10]

The alkali dodecyl sulfates have been less studied than the common SDS, but their critical micellar concentrations have been shown to decrease from LiDS to CsDS.[11] Studies on interfaces and thin films have shown the more effective screening by K^+ compared with Na^+ leading to higher surface concentrations.[12] The stability of films and foams is also slightly better with KDS rather than SDS.[12b] However most of the studies are with low or moderate salt concentrations, probably because the addition of higher concentrations of salt is known to lead to precipitation.[13]

Herein, we show that foam stability is controlled by the formation of crystals on the surface of the bubbles and in the aqueous phase. The time it takes for the crystals to form is the key factor to obtain stable foams. These ultrastable foams can be destroyed by heating above the Krafft boundary (below which precipitates form).

Foams were prepared using SDS with added NaCl or KCl. Photographs of these foams as they evolve in time are shown

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[**] We thank Maria Sammalkorpi for interesting discussions on interactions between SDS and salt. This work was supported by the Doctorate Foundation of Northwestern Polytechnical University and the European Space Agency (MAP Hydrodynamics of wet foams).

Supporting information for this article is available on the WWW under http://dx.doi.org/10.1002/anie.201503236.

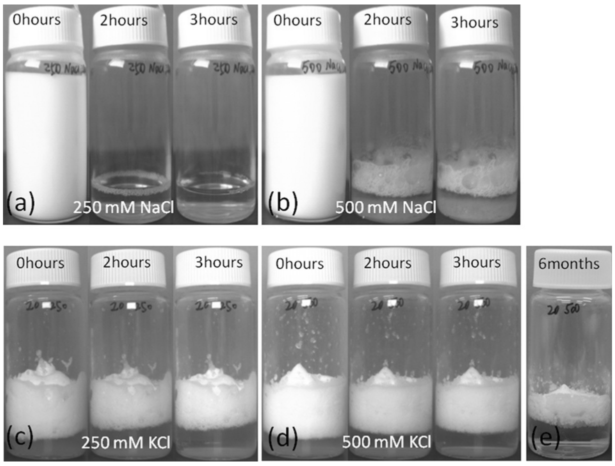

Figure 1. Photographs of foam samples made with 69 mM SDS and a) 250 mM NaCl, b) 500 mM NaCl, c) 250 mM KCl, and d) 500 mM KCl. e) Sample in (d) six months later.

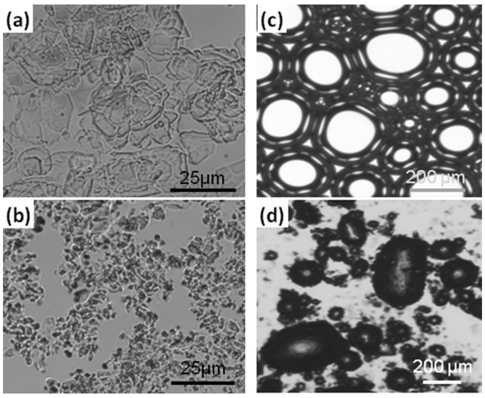

Figure 2. Microscope images of solution with 69 mM SDS and a) 500 mM NaCl and b) 500 mM KCl taken a day after mixing. c), d) Images of bubbles immediately after preparation prepared with the same concentrations: c) NaCl, d) KCl.

Table 1: Temperature at which the crystals are no longer visible in 69 mM SDS in the presence of 250 or 500 mM salt.

c_S [mM]	T_{NaCl} [°C]	T_{KCl} [°C]
250	22.5 ± 0.5	45.0 ± 0.5
500	26.5 ± 0.5	49.0 ± 0.5

in Figure 1. Samples in (a) and (b) were made with 250 mM and 500 mM of NaCl, while samples in Figure 1 c,d and e are with KCl. The solutions with NaCl foam very well; all of the gas is incorporated in the foam. The foam with 250 mM NaCl disappears within 2 h (even more quickly than foam with no added salt). With 500 mM NaCl (Figure 1 b), most of the foam collapses quickly but the remaining foam continues to evolve slowly: the bubble size increases while the height of the foam remains constant over several hours.

The instability of the foam with 250 mM added NaCl could be expected. The screening of the electrostatic repulsion between the two interfaces dominates over the effect of the increased surface concentration of surfactant and the films become unstable. The stability of the foam with 500 mM NaCl after an initial phase of foam collapse is surprising.

The behavior with KCl is very different (Figure 1 c, d). The produced foams are very similar with the two KCl concentrations. Not all of the air can be incorporated into the foam even when the amount of liquid used is increased. We can only make around 8 mL of foam with an initial liquid fraction of around 50 %. We have not been able to make dry foams, only bubbly liquids. In a matter of seconds the bubbles have creamed to the top of the sample, and as they become close packed (liquid fraction around 30–40 %) the drainage slows down dramatically, but continues over several hours before arresting. The coarsening in these samples arrests as well. This leads to ultrastable foams, and as shown in Figure 1 e, the foam is still intact after 6 months.

We also prepared foams from KDS with added KCl (69 mM with 500 mM salt). These are much less convenient to work than their SDS homologues as the KDS solution needs to be heated up above the Krafft boundary (around 50 °C) to prepare the foams. However their appearance and stability are very similar to those from SDS with added KCl.

To understand these differences, we took a closer look at the samples. We can see some precipitate at the bottom of the flask in Figure 1 b, but nothing with KCl (Figure 1 d). We made optical microscopy experiments on bulk samples (without foaming). In both samples the precipitates are composed of crystals. The crystalline domains formed with NaCl (Figure 2 a) are plate-like structures of tens of micrometers in size while the objects with KCl are smaller (Figure 2 b).

The samples were heated to measure the temperature at which the crystals are no longer visible to the eye (Table 1). From these values the enthalpies of dissolution, ΔH, can be estimated using the Van't Hoff equation (Supporting Information, Section S2). We find $\Delta H_{SDS} = 75\ \mathrm{kJ\,mol^{-1}}$ and $\Delta H_{KDS} = 88\ \mathrm{kJ\,mol^{-1}}$. As previously reported by Smith et al.,[14] the enthalpy for the melting of SDS is slightly lower than KDS. However, assuming that the energy gain of sodium is $84\ \mathrm{kJ\,mol^{-1}}$ more than for potassium,[8] the interaction energies are weaker in KDS than in SDS.

Figure 2 c, d show photographs of bubbles taken under the microscope immediately after the generation of foam. The foam with NaCl (Figure 2 c) looks exactly like normal surfactant foam: it is rather wet and the bubbles have a diameter of around 200 μm. The sample with KCl looks nothing like a surfactant foam (Figure 2 d): the bubbles are much smaller (mostly below 100 μm in diameter) and the larger bubbles are not spherical but ellipsoidal.

The presence of elliptical bubbles is surprising as the optimal shape for an air bubble is spherical. A non-spherical shape indicates that the interfaces are solid-like.[15] Therefore coarsening of bubbles is arrested making the foam stable (addition of KCl).

In the foam with 500 mM NaCl, the solution collected at the bottom of the vial is slightly turbid. This means that not all crystals are inside the foam. The solution that drains out of the foams prepared with KCl is transparent, despite a non-foamed solution being turbid. This means that the crystals can become trapped and collect in the plateau borders to stabilize the foam against drainage.[3a,5]

The stability of the KCl foams can therefore be explained by the formation of the crystals on the bubble interfaces and in the interstices between the bubbles. However the relative instability of the foam with 500 mᴍ NaCl is still not entirely clear.

To explain the instability of the NaCl foams, we investigated the kinetics of crystal formation (Supporting Information, Section S3). For the samples shown in Figure 1, it takes tens of minutes for the crystals to appear in the sample with NaCl, but with KCl they appear within seconds of mixing. Therefore in the sample with NaCl the foam has ample time to evolve (coarsen, coalesce, and drain) before the crystals form and can start stabilizing the foams. Similarly, making foams with low concentrations of added KCl (with SDS or KDS) leads to relatively unstable foams, as the crystallization process is slower than the destabilization process (Supporting Information, Section S3).

This means that whether the foam is stabilized depends on the link between the kinetics of crystal formation and the foam ageing times. If crystallization is too slow, the foam has time to evolve and it will partially collapse before the ageing can arrest. The stability of the foams from both SDS and KDS with added KCl suggest that it is not the presence of a mixture of counterions that is determinant in the stabilization process (Na^+ and K^+). The requirement seems to be for the presence of potassium and dodecyl sulfate in sufficient concentration and at a temperature below the Krafft boundary. Of course the position of the Krafft boundary depends on the solution and as such it is sensitive to the type and concentration of ions present, that is, DS^- and Cl^-, with Na^+ and/or K^+.

We carried out SANS measurements on the foams prepared with 69 mᴍ SDS and 500 mᴍ NaCl or KCl to determine the structure of crystallites inside the foam. The scattered intensity as a function of q for the two samples is shown in Figure 3a, where we can see that at low q the intensity decreases as q^{-4}. Such decay is typical of sharp interfaces, such as the surfaces of the bubbles and the crystallites.

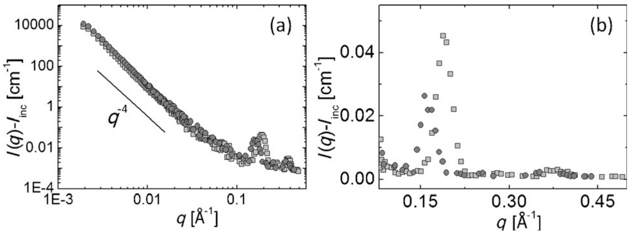

Figure 3. a) The scattered intensity as a function of the scattering wave vector for a foam prepared with 69 mᴍ SDS and 500 mᴍ NaCl (○) and 500 mᴍ KCl (□). b) The high q data shown on a linear scale.

We can also distinguish two peaks arising from the crystal structure in Figure 3b. For the sample with NaCl, the first peak is at $q^* = 0.16$ Å^{-1} and the second at 0.32 Å^{-1}, thus twice the first. The sample with KCl has peaks at 0.19 Å^{-1} and 0.38 Å^{-1}. The structure of SDS crystals has been previously measured; they have been shown to have a lamellar structure where the interplanar distance d depends on the degree of chain tilt and hydration.[16] We measure $d = 39$ Å ($2\pi/q^*$) for the SDS crystals (precipitated with NaCl). This is exactly what has been measured when SDS is crystallized from water; it forms monoclinic weakly hydrated ($SDS{\cdot}1/8\,H_2O$) crystals with $d = 38.9$ Å.[16] The crystals formed with KCl also have a lamellar structure, however the spacing is smaller than with SDS at $d = 33$ Å. Owing to the large difference in the crystallization temperatures, the crystals should be almost exclusively of KDS. This means that the KDS crystals are more tightly spaced than SDS, suggesting that the KDS crystalline unit cell is more strongly tilted.

The photograph of Figure 1e shows that foam prepared with 500 mᴍ of KCl can be stable for at least six months at room temperature. We have shown that the incredible stability of the foam arises from the presence of crystallized KDS both at the surfaces of the bubbles and in the interstices between the bubbles. To break such foam, we heated it to 51 °C to melt the crystals. The images are shown in Figure 4.

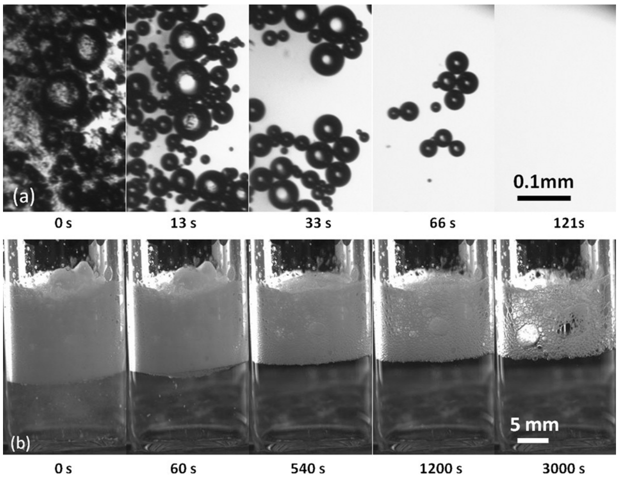

Figure 4. a) Bubbles and b) foams prepared with 69 mᴍ SDS and 500 mᴍ KCl heated suddenly to 51 °C.

The bubbles shown in Figure 4a have rugged surfaces and some precipitate is also found in the surrounding fluid. Very quickly the surface of the bubbles starts to melt, as seen in the photograph taken after 13 s. The bubbles start coarsening and coalescing and then disappear in a few minutes.

We can see the same effect on bulk foam in Figure 4b. Within one minute, the drained solution has become transparent. The foam starts to age as the crystals disappear from the foam, although this probably takes some time as foam is a very poor heat conductor. After 1 min, some liquid has drained, and after around 10 min the bubble size starts to change considerably. The melting of the crystals (bulk and interfacial) transforms the foam into common wet foam, which disappears within a few hours. It is also possible to stop the ageing before all the foam has disappeared by cooling down the sample, to reform a stable foam (Supporting Information, Section S4).

Thus, we show that SDS can be used with KCl to make ultrastable foams, which can be rapidly destabilized using a temperature stimulus. The temperature of destabilization can be easily changed by changing the salt type or the salt concentration. The simplicity of the system makes it interesting for a wide range of applications where fine stability control needs to be combined with low cost.

The addition of salt at a high concentration can be used to make ultrastable foams from SDS. Stable foams are made below the Krafft boundary. However whether the foams are stable or not also depends on the kinetics of crystal formation. This can be tuned by the preparation temperature by changing the type and concentration of added salt. If crystallization is too slow, the foam has time to disappear. If the crystals have time to form on the surfaces of the bubbles the foams are stable over months or until they are heated to melt the crystals at which point they start to age and disappear quickly.

We have shown how the crystallization of surfactant can be used to our advantage in creating ultrastable or/and stimulable foams. We have also seen that the addition of KCl is much more efficient than NaCl. However the detailed mechanisms including the importance of the presence of two types of counterions in the foams with KCl, or the role of the crystal structure on foam stability still require further experiments and/or simulations.

These results are important as they provide a simple way of making very stable foams. They could be used in applications where the shelf-life of a product should be measured in months or years without degradation of the quality of the foam. Thanks to their sensitivity to temperature, they could even be used as simple temperature sensors to indicate prolonged heating during a transport phase. However their main quality is their simplicity, superstability, and stimulability, which make them viable for more applications.

Keywords: crystal engineering · foams · materials science · salt effect · sodium dodecyl sulfate

How to cite: *Angew. Chem. Int. Ed.* **2015**, *54*, 9533–9536
Angew. Chem. **2015**, *127*, 9669–9672

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Received: April 9, 2015
Revised: May 17, 2015