

# Effect of cosurfactant on the free-drainage regime of aqueous foams

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## Abstract

We report results of drainage in aqueous foams of small bubble size  $D$  ( $D = 180 \mu\text{m}$ ) prepared with SDS-dodecanol solutions. We have performed free-drainage experiments in which local drainage rates are measured by electrical conductivity and by light scattering techniques. We have investigated the role of the surfactant–cosurfactant mass ratio on the drainage regime. The results confirm that a drainage regime corresponding to a high surface mobility can indeed be found for such small bubbles, and show that an increase in the cosurfactant content can induce a transition to a low surface mobility drainage regime. We show that the transition is not linked to variations of the bulk properties, but rather to variations of the interfacial properties. However, the results show that the added amount of dodecanol to trigger the transition is quite high, evidencing that the relevant control parameter for drainage regimes includes both bubble size and interfacial contributions.

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## 1. Introduction

Foams are dispersions of gas bubbles in a liquid or solid phase [1]. They have received a lot of interest in the last years because of their applications: cosmetics, detergency, foods, packaging, mineral flotation, etc. The study of the behavior of foams is relevant not only for the design of materials with new physical properties but for the understanding of fundamental phenomena in complex fluids.

Aqueous foams are made from solutions of amphiphilic molecules which adsorb to the air–water interface. These systems are not in equilibrium. They evolve in time by three mechanisms: coarsening, drainage, and film rupture. During coarsening, smaller bubbles dissolve, while bigger ones grow in size due to gas diffusion across the liquid films [1]. This effect depends both on the bubble size, in-

terfacial tension, gas properties, and liquid fraction of the foam:  $\varepsilon = V_{\text{liquid}}/V_{\text{foam}}$ . Drainage, on the other hand, is the gravity-driven flow of the liquid phase inside the liquid channels (Plateau borders, PB) between the gas bubbles. In a “free drainage” experiment, a foam of initially uniform wetness is allowed to drain: the foam dries first at the top, and a dry front propagates downward, while the liquid emerges and accumulates at the bottom. Two drainage regimes have been observed, depending on the “surface mobility” parameter, which incorporates both the bubble size, the interfacial and bulk properties, and which describes the coupling between the bulk flow inside the PBs and the interfacial one at their surfaces [2–7]. When the surface mobility is high, the surface flows with the bulk flow, and water drains without much resistance in the PBs (with a non-zero velocity at the PBs surface). In this limit, the major dissipation eventually takes place in the nodes of the foam [4–7]. On the other hand, for low surface mobility, there is no flow at the PBs surfaces, and a Poiseuille-like flow is established, providing a slower rate of drainage [1–4].

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Note that the drainage rate is also controlled by the gas used, due to a coupling between coarsening and drainage. However, by choosing an insoluble gas or by controlling the bubble size [8], the study of free-drainage without coarsening effects is possible.

In previous free-drainage experiments with SDS foams and SDS-dodecanol foams of small bubble sizes  $D$  ( $D < 200 \mu\text{m}$ ), only the regime corresponding to a high surface mobility was surprisingly observed [7,8], though the surface mobility was supposed to be low (in the models, the surface mobility  $M$  is inversely proportional to the bubble size [2]). However, in these studies, only low concentrations of DOH were used, so that the surfactant–cosurfactant mass ratio,  $k = m_{\text{SDS}}/m_{\text{dodecanol}}$ , was only investigated down to 250.

The aim of this work is to study how the free-drainage behavior of SDS-dodecanol foams, in the case of small bubble size, depend on the surfactant–cosurfactant ratio,  $k$ , in order to better understand the unusual drainage properties of such small bubble foams. We thus report here free-drainage experiments with foams made with different dodecanol contents, as well as different gases.

## 2. Materials

Sodium dodecyl sulfate (SDS, high purity) and dodecanol were supplied by Sigma–Aldrich. All solutions were prepared using ultra-purified water (Millipore); We used two gases for preparing the foams: nitrogen ( $\text{N}_2$ ) and hexafluoroethane ( $\text{C}_2\text{F}_6$ ). The latter is highly insoluble in water and thus strongly reduces coarsening of the bubbles. The surfactant–cosurfactant mass ratios studied were  $k = 100, 12, 8, 5,$  and  $4$ . We also studied foams prepared with pure SDS solutions.

## 3. Methods

### 3.1. Foam preparation

Foams were prepared by the turbulent mixing method [9]. A jet of the surfactant–cosurfactant solution is injected at high pressure (125 PSI) to a mixing chamber through a tiny hole (0.7 mm diameter). To produce the foam, gas is fed into the chamber at high pressure. The resulting foam is conducted to a Plexiglas column (height 1 m, width 25 cm, and thickness 3 cm). This method provides, in a few seconds, large volume of homogeneous foams of uniform initial liquid fraction  $\varepsilon_0$ . In our experiments,  $\varepsilon_0 = 0.08$  and  $0.16$ . The bubble average diameter was  $180 \mu\text{m}$ , and the foams are slightly polydisperse [9].

### 3.2. Drainage experiments

We study the drainage dynamics by two complementary techniques which allow to follow the liquid fraction as a

function of time  $\varepsilon(t)$  in several points of the foam. First, we use electrical conductometry [1], via a set of electrodes installed along the foam container. The setup is similar to that described in Ref. [3]. Locally, the liquid fraction  $\varepsilon$  is proportional to the electrical conductivity  $c$  [10]. The setup provides the liquid fraction profile in the foam at any time. Simultaneously, we use a light scattering method, similar to that reported in Ref. [8]. The foam is uniformly illuminated on one side of the Plexiglas column with white light, and a CCD camera collects the transmitted light on the other side. For a large enough foam thickness  $T$ , providing the limit of multiple scattering of each photon inside the foam, the diffuse transmitted intensity  $I$  can be, as a first approximation, related to the liquid fraction via  $I \propto D/T\sqrt{\varepsilon}$  ( $D$  is the bubble diameter) [11]. Thus, one can straightforwardly infer  $\varepsilon(t)$  from  $I$ , if  $D$  is constant. If  $D$  does not remain constant on the same timescale as the one of the variation of  $\varepsilon$ , treating the data as if  $D$  was constant and comparing them to the conductivity data is a way to evidence effect of coarsening in the drainage rate [8].

### 3.3. Solution properties

The bulk viscosity of all surfactant–cosurfactant solutions were determined with a Brookfield DV-III rheometer. Electrical conductivities of solutions were measured with a Radiometer Analytical DMA-200 apparatus.

## 4. Results and discussion

### 4.1. Effect of gas

Typical conductivity and light scattering curves are shown in Fig. 1, for an equal  $k$  value ( $k = 4$ ), at a given height, and for the two different gases. In this figure, the treatment of the light scattering data is always made by considering the bubble size as a constant. Both experimental

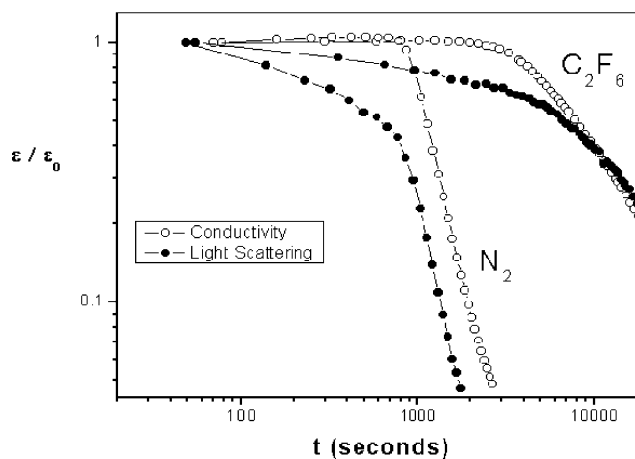


Fig. 1. Effect of gas on the drainage of SDS-dodecanol foams ( $k = 4$ ). The curves correspond to a fixed height, 30 cm below the top of the foam.

techniques produce the same qualitative results, for every studied gas, and this typical behavior is observed for all values of  $k$  and  $\varepsilon_0$ . In this figure, one can see that there are clear differences between the two gases: drainage of foams prepared with  $N_2$  begins sooner as compared with foams prepared with  $C_2F_6$ . In addition, the light scattering and electrical conductometry curves for the foam produced with  $N_2$  strongly separate already at early times, whereas for  $C_2F_6$  there is a relatively good agreement between the two experimental techniques (as already reported for  $k = 250$  [4]). So, these results show that there is a strong bubble growth or coarsening for the  $N_2$  foam, resulting in a strong effect on drainage. As expected the coarsening with  $C_2F_6$  is much lower, as a result of both a low solubility and a diffusivity. Consequently, we have verified that with  $C_2F_6$ , coarsening is low, allowing us to study only the drainage dynamics, out of any coupling with other effects, and its dependence on the amount of cosurfactant.

#### 4.2. Effect of cosurfactant

The light scattering and electrical conductometry experiments produced similar results when the surfactant–cosurfactant mass ratio was changed. In Fig. 2 we plot the free drainage curves obtained with light scattering experiments for foams prepared with  $C_2F_6$  gas; in this picture  $k = 100, 12, 8, 5,$  and  $4$ . The initial liquid fraction in these foams was  $\varepsilon_0 = 0.16$ , and the measurements are made at a fixed position in the foam, 30 cm from the top.

We see that after some time, which depends on the dodecanol content, the drainage rate follows a power law decay, as expected for free-drainage experiments [4,8]. The time where the power law behavior appears is of the order of 1000 s for pure SDS foams, and 3000 s for  $k = 4$ .

From the long time behavior of the liquid fraction, one can determine the flow regime from the exponent of a power

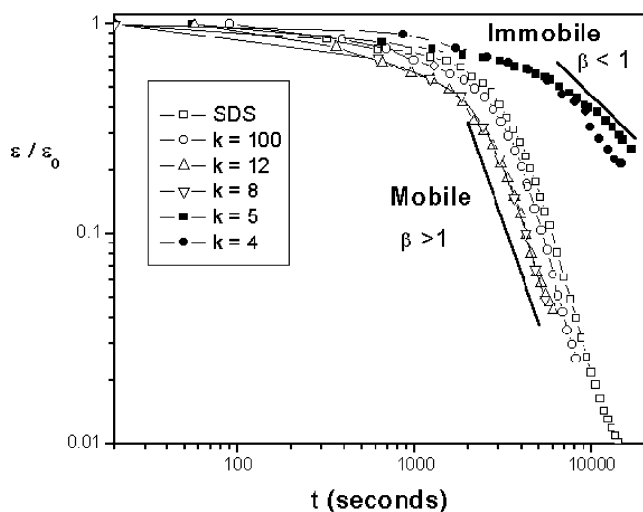


Fig. 2. Effect of cosurfactant on the drainage of SDS-dodecanol foams prepared with  $C_2F_6$  gas. The curves correspond to a fixed height, 30 cm below the top of the foam.

law  $\varepsilon = t^{-\beta}$  [4,9]. The value of the exponent depends on the height in the foam, and on the PB surface mobility. In the case of immobile surfaces (vanishing flow velocity in the walls, and Poiseuille flow) the exponent varies with the height in the range:  $2/3 \leq \beta \leq 1$ . On the other hand, when the PBs walls are mobile the exponent is predicted to be:  $1 \leq \beta \leq 2$ , evidencing a more plug-like type of flow in the PBs. From the exponent of the experimental curves, we see that for low cosurfactant contents ( $k = 100, 12,$  and  $8$ ) we have a high mobility regime, and rather plug-like drainage flows. This behavior agrees with previous observations for  $k = 250$  [4]. On the other hand, for higher cosurfactant contents ( $k = 5$  and  $4$ ) we have found Poiseuille-like flows.

The observed transition from a drainage regime of high surface mobility to a regime of low surface mobility (Poiseuille-like flow) is thus also occurring for the small bubble foams. The surface mobility depends on the interfacial and the bulk properties, it is thus important to check how the bulk properties depend on  $k$ , especially for such high values of  $k$ . We have measured the bulk viscosity  $\eta$  and the electrical conductivity  $\sigma$  of the solutions used for foam production (Fig. 3). The viscosity in the solutions increases slightly when the dodecanol content is increased, whereas the conductivity decreases at the same time. This means that the aggregates in the solution are undergoing a physical transformation. In fact, the effect of cosurfactant is to change the shape and size of the micelles [12]. In our system, the micelles are spherical at low dodecanol contents. As more dodecanol is added, micelles become cylindrical and grow in size, producing the observed effects in  $\eta$  and  $\sigma$ . In the drainage theories, an increase of the bulk viscosity always corresponds to a higher surface mobility [5–7]. Here, we have found an opposite effect: decreasing  $k$  (i.e., increasing the cosurfactant content) means increasing the bulk viscosity, and thus should provide more mobile interfaces, whereas experimentally we have found low surface mobility at low  $k$ ; thus we can conclude that the observed drainage transition is not connected to the variation of the bulk viscosity. Then,

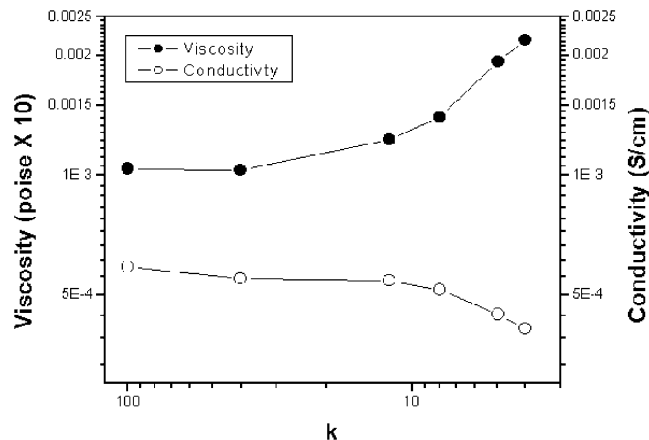


Fig. 3. Bulk viscosity and electrical conductivity of the surfactant–cosurfactant solutions used to prepare the foams.

one can only attribute the drainage regime transition to a change in the interfacial properties. To summarize, we have found that also for small bubble sizes, the cosurfactant can trigger a transition between two different drainage regimes. For low dodecanol contents, the surface mobility is high. On the contrary, when the dodecanol proportion is increased up to  $k = 5$ , the surface mobility becomes low enough to give a flow velocity that vanishes at the walls, and a Poiseuille velocity profile. A surprising result here is that one has to add such large amount of dodecanol ( $k = 5$ ) to trigger the transition (a significant variations of the purely interfacial properties in such systems usually occur at much lower dodecanol concentration [13]). These results confirm the previous surprising observations [7,8] showing that the surface mobility also depends on the bubble size in a way that a high mobility drainage regime is found for small bubble sizes. This effect of bubble size is very robust: to counterbalance it, one has to vary widely the interfacial ones (by adding large amount of dodecanol).

## 5. Conclusions

We have studied the effect of the cosurfactant content on the drainage behavior of aqueous foams of small bubble size ( $D < 200 \mu\text{m}$ ) prepared with SDS-dodecanol solutions. Coarsening effects were minimized by the choice of  $\text{C}_2\text{F}_6$ . The cosurfactant changes the drainage regime in the foams. Addition of dodecanol to the system eventually leads to a

drainage transition which is related to interfacial rather than bulk variations.

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