Differences between protein and surfactant foams: Microscopic properties, stability and coarsening

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Abstract

We report results on foamability, stability and coarsening of foams made either of surfactant (SDS) or of milk protein (casein) solutions. Studies have been performed at the scales of the gas–liquid interface, thin liquid film and bubble size, in order to find the correlations between these different scales, and to elucidate the microscopic origins of the macroscopic features. For both systems, foamability concentration thresholds have been measured, and a bubble size dependence has been found. A clear correlation between the stability of an isolated thin film and the foam stability is always evidenced. However, the mechanism of stability of the casein thin films is different from the surfactant one, and related to the confinement and percolation of casein aggregates. We also report results on coarsening at constant liquid fraction, showing that the protein foams coarsen more slowly than the surfactant ones, and that it is due to differences in thin film thickness.

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1. Introduction

Aqueous foams are familiarly stabilized by small soap molecules (surfactant), when they are used in the field of detergency, cleaning etc. [1,2]. Oppositely, for the food-related applications, foams are mostly stabilized by protein molecules [1]. In spite of their wide use in food products, the stabilization mechanisms are not yet completely known for these protein foams, as well as the conditions required for good foaming (or foamability). For small surfactants, the properties at liquid interfaces or in bulk, the stabilization mechanisms are not yet completely known for these protein foams, as well as the conditions required for good foaming (or foamability). For small surfactants, the properties at liquid interfaces or in bulk, the stabilization mechanisms are not yet completely known for these protein foams, as well as the conditions required for good foaming (or foamability). For small surfactants, the properties at liquid interfaces or in bulk, the stabilization mechanisms are not yet completely known for these protein foams, as well as the conditions required for good foaming (or foamability). For small surfactants, the properties at liquid interfaces or in bulk, the stabilization mechanisms are not yet completely known for these protein foams, as well as the conditions required for good foaming (or foamability). For small surfactants, the properties at liquid interfaces or in bulk, the stabilization mechanisms are not yet completely known for these protein foams, as well as the conditions required for good foaming (or foamability). For small surfactants, the properties at liquid interfaces or in bulk, the stabilization mechanisms are not yet completely known for these protein foams, as well as the conditions required for good foaming (or foamability). For small surfactants, the properties at liquid interfaces or in bulk, the stabilization mechanisms are not yet completely known for these protein foams, as well as the conditions required for good foaming (or foamability). For small surfactants, the properties at liquid interfaces or in bulk, the stabilization mechanisms are not yet completely known for these protein foams, as well as the conditions required for good foaming (or foamability).
2. Materials and methods

The two widely used surfactant systems (SDS) and a protein (casein) solutions. We present results obtained at the different length scales of a foam, from the smallest one of the gas-liquid interface to the macroscopic scale, where foaming and coarsening are studied. This allows us to investigate and find some correlations between the properties at all these different scales.

one of the capillary, and it is then possible to extract the surface tension via the Laplace equation. This technique is especially well-suited for the very short times range (down to ms). In the second technique, the surface tension is deduced from the droplet (or bubble) shape, pending (or rising) at the tip of a syringe (oriented downward or upward) [1].

3. Results

3.1. Foamability

Fig. 1 shows typical data found with the foamability setup. The height of foam in the column is plotted as a function of time, for different casein concentrations $c$ (fixed bubble size). The arrow indicates the increase of the concentrations. At low $c$, almost no foam is produced, and the coefficient $K \approx 0.1$. This corresponds to many bubble ruptures, with most of the injected gas not being actually incorporated in the foam. For the highest concentrations, the curve becomes linear, and the amount of foam (at any given time) becomes almost independent of $c$. In that regime, the foaming is optimal and all the gas is entrapped into the foam ($K \approx 0.9$, also meaning that the foams produced are rather dry). With casein solutions, and for any bubble sizes, the curve $K(c)$ presents a well-defined range of concentration where $K$ rises from 0.1 to 0.9 (S-shape curve), meaning that there is really a threshold in concentration for foamability. Thus, defining a single threshold concentration $c_s$ (with $K(c_s) = 0.5$) appears meaningful. Our results on casein solutions show that $c_s$ strongly depends on the bubble size, but not on the injected gas flow rate (typically varied from 0.1 to 1 L/min). Same trends have been found while performing the measurements with SDS, where it is also easy to determine a concentration threshold $c_s$. The dependence of $c_s$ with bubble size is reported in Fig. 2; both for casein and SDS, it is found that $c_s$ increases with $d$, and in the range investigated here, the dependence is somehow linear (with $c_s(\text{SDS}) > c_s(\text{CAS})$). Note that for SDS we have found that $c_s$ is always a few times lower than the cmc (2.8 g/L). For casein, a typical mean value of $c_s$ is 0.2 g/L, and one has now to figure out from which microscopic parameters and stabilization mechanism this typical value emerges. Preliminary experiments on SDS/casein mixtures show that these solutions have unexpectedly high foamability. The mixtures actually foam better than what could be expected from the foaming of each solution taken separately, possibly evidencing some synergistic effects. This remains to be studied in a systematic and detailed way, and it is an ongoing work.

3.2. Coarsening at constant liquid fraction

With casein and SDS concentrations well above the foamability threshold ($c(\text{SDS}) = 8$ g/L, and $c(\text{CAS}) = 5$ g/L), stable foams are obtained for the coarsening studies. For the gas, we used either N$_2$ or perfluorohexane C$_2$F$_6$. With the latter, one obtains low coarsening rates, meaning also low drainage rates [16–21,22], with which the measurements are easier to perform, but providing less bubble size variations. Fig. 3 shows...
the results obtained for the time evolution of $d(t)$ for casein and SDS foams, both at a constant liquid fraction $\epsilon = 0.15$, with almost equal $d_0$ (with casein, the mean bubble diameter is slightly smaller than for SDS) and made of $N_2$. Both data sets can be fitted by the predicted law (solid line) described previously. However, we found that the corresponding $t_c$ are different: $t_c$ (casein) = 980 s and $t_c$ (SDS) = 190 s (so that $t_c$(casein)/$t_c$(SDS) $\approx$ 5). The coarsening rate is thus significantly smaller for the casein foams, at a fixed liquid fraction and bubble size. A similar ratio for $t_c$ (casein)/$t_c$(SDS) $\approx$ 0.15, was found with C$_2$F$_6$, showing that this effect is independent of the gas.

3.3. Surface tension

As the adsorption of the surfactants or of the caseins proceeds at the air–liquid interface, its surface tension decreases. For surfactants, at any given concentrations, an equilibrium is usually obtained within the first minute. For casein (as for most proteins) the adsorption is much slower, and the dynamics strongly depends on the bulk concentration. In fact, if one wants to correlate surface tension and foamability, it is important to determine a typical adsorption time, after which it is relevant to know the surface tension. As a first attempt, we have considered the time taken by a bubble between its creation on the frit and its arrival on the above foam (where it hits the other bubbles, and get jammed). It is indeed during that time that adsorption is possible. In our setup, we have measured the maximum bubble pressure, after 3 s (and corresponding to a bubble diameter $d \approx$ 1.5–2 mm). Measurements with the pendent drop technique provides the same results, but with slightly less accuracy. Here again, we have found a difference between the two type of solutions. For casein, after these 3 s, almost no adsorption is detected in the range of concentration tested: the surface tension remains close to the one of pure water. For the SDS, the adsorption is much more active at these small timescales, as the surface tension significantly decreases with increasing the concentration.

3.4. Thin film studies

The structure, thickness and disjoining pressure curves of small surfactant, like SDS, have been extensively studied, especially with the thin film balance\cite{3,4}. Here, for the SDS, we have recovered some classical results. Under an applied pressure step, films get formed, then always thin in a few seconds, down to very small thickness (around 10 nm). They usually remain very flat and uniform, though some dimples can be trapped in the first drainage stage (at the highest concentrations). A transition from the common black film (CBF) to the Newton black film (NBF)\cite{3,4} is also sometimes observed, before film rupture. At the lowest concentrations ($\epsilon < 0.2$ g/L), the films are strongly unstable and break in a few seconds, and it is only for $\epsilon > 0.6$ g/L that they are getting quite stable (at least for a few minutes). At this stage, it is however indeed difficult to determine a precise concentration threshold for film stability, as it would require a complete statistical study and a large number of measurements to reduce the error bars.

Regarding the casein films, Fig. 5 represents top views of the thin films at three concentrations. One important observation is that these films are always heterogeneous in thickness with the presence of thick spots (or bumps), which density in the film depends on the bulk concentration. In Fig. 5a, with $\epsilon = 0.05$ g/L (representative of the low concentration range, $\epsilon < 0.1$ g/L), only a few thick regions are detected, while most of the film gets rapidly very thin, and eventually breaks. The sizes and thickness of these regions are respectively on the order of a few microns and hundred of nanometers. These thick spots can be interpreted as confined casein aggregates, containing probably many casein micelles, which are trapped in the films, and cannot flow. The density of aggregates, for which the thin film becomes stable typically corresponds to the image in Fig. 5b ($\epsilon = 0.3$ g/L). At that stage, it seems that the aggregates are no longer isolated from each others in the film; but on the contrary, they get connected, providing some rigid and thick bridges between the sides of the film (possibly similar to a percolation process), and a coverage of approximately 50% of the film. At the highest concentrations, the film is completely filled with aggregates and

Fig. 4. Surface tensions, after 3 s, measured by the maximum bubble pressure method, as a function of the SDS and casein concentration.

Fig. 5. Top views of casein thin films, obtained with the thin film balance apparatus, at three different casein bulk concentrations: (a) $\epsilon = 0.05$ g/L, (b) $\epsilon = 0.3$ g/L and (c) $\epsilon = 0.8$ g/L, showing the thickness heterogeneity, and the presence of thick regions (confined casein aggregates), which surface density depends on the concentration. The thin films become stable as soon as these confined aggregates can percolate (b).
its surface is quite corrugated. The films are then extremely stable: they almost do not thin or drain under an increased pressure, as they appear as "gelified" in all their volume. In that concentration range (Fig. 5c), the film resemble very much to those observed for mixed surfactant/polyelectrolytes films, close to the precipitation conditions [23]. The addition of SDS strongly changes the film morphology: starting with $c = 0.5 \, \text{g/L}$ of casein, and with only a small SDS amount of 0.1 g/L added, almost all the thick regions have been removed and the films simply resemble to those of pure SDS. So it seems that the pre-adsorption of SDS prevent the confinement of the casein aggregates in the film. These results cannot be easily linked to those on the foamability of mixtures. In order to understand the 3D behavior of these foams, the structure and the composition of the mixed SDS/casein interfacial layers and thin films remain to be determined. Note finally that other studies with only pure β-casein solutions [24], or only non-aggregated sub-micelles of casein [25] have shown that the films are more homogeneous in morphology and thickness, with stepwise thinning.

4. Discussion

We can now check if the results obtained at these different length scales allow us to explain the foamability and coarsening. Results. It is also interesting to test if the results obtained on isolated single foam structures (interface and thin film) are consistent with the 3D behavior. First let us look at the SDS results. The typical bubble diameter in the surface tension measurement is 1.5–2 mm, and at this size corresponds a 3D foamability threshold, $d_3 \approx 2 \, \text{mm}$ (Fig. 2). At such a $c_s$, it is found that some significant adsorption has actually occurred within the first 3 s (with a decrease of almost 10 mN/m when compared to pure water). As usually expected for surfactant, it appears that there are some clear connection between surfactant adsorption and foamability. However, we have already pointed out that the $c_s$ values are smaller than the cmc, here one can see how far the surface density needed for foam stability (corresponding to a surface tension of 62 mN/m) is below the maximum possible coverage (corresponding to a surface tension of 36 mN/m at the cmc). The SDS thin film studies show that the threshold of film stability, though difficult to determine, is roughly in agreement with the foamability one, and it is here also possible to make a clear connection between these two length scales. The fact that the thin films are flat and thin is indeed consistent with homogeneously covered surfaces. Moreover, when they are stable, the disjoining pressure curves can be nicely interpreted by DLVO models, for which the main repulsive contribution is an electrostatic one, corresponding to homogeneously charged surfaces [3,4].

So, it seems that the mechanisms of stability of the casein and SDS foams are quite different. For the casein solutions, when the bubbles get in contact and packed at the bottom of a foam sample, their surfaces seem to be poorly covered (high surface tensions). But stable foams can nevertheless be produced, due to the confinement of casein aggregates between the bubbles in the thin films. These aggregates, which were not previously completely adsorbed on the surfaces finally provide the film (and the foam) stability, possibly via a percolation process. Such a percolation of the aggregates may rigidify the film, avoiding any more flow or drainage, and preventing large areas of the film to get to very low unstable thickness. Here again, it is interesting to note that this mechanism (simple confinement and percolation of aggregates, without previous adsorption) may not be relevant only for the casein solutions, but could be also valid for foams and emulsions stabilized by other high molecular weight molecules (other proteins or solid particles, for which the adsorption at a liquid interface is not fast and efficient). Note however, as for the low molecular weight surfactant systems, that we are discussing here a possible origin for the thin film stability with large molecules, but that the foamability itself of protein solutions depends obviously strongly on the protein chemistry [9].

These results also show that independent measurements of dynamic surface tension are not relevant for explaining or predicting the protein solution foamability. It may be important to note that for these surface tension measurements, the bubble is fixed and no motion occurs in the fluid, which is not the case in the real situation where the bubble is rising upwards. However, it is not clear if the motion of the
bubble can result in a different, and possibly higher, surface adsorption coverage. In fact, the duration of the bubble motion remains short (3 s), a time which remains small when compared to the typical anchoring times (time needed for a single casein to completely and definitively adsorb at the interface); moreover, it is possible that the anchoring efficiency may be actually reduced by the relative bubble motion. So, in spite of the bubble rising into the solution, the bubble surfaces are still probably widely uncovered when they finally hit each other in the foam. It would then be interesting to be able to measure the effective in situ surface tension, once the bubbles are in contact, and with the aggregates finally adsorbed.

With these results on the mechanisms of foam stabilization, we can now look at the linear dependence of the threshold concentration \( c_t \) with the bubble diameter. For a surfactant, to any given bulk concentration corresponds a single surface density (surface tension), at long times and at equilibrium. This means that, at equilibrium, surfaces are covered at the same surface density whatever their areas, avoiding then any bubble size dependence. As we have found a different behavior, a first hypothesis is that this effect is related to the dynamics of adsorption (before the equilibrium), with intermediate surface densities depending on the size of the bubble. One can also wonder if, even with equal mean surface density, bigger surface density gradients could occur for larger bubble surfaces, providing more film rupturing (and thus necessitating higher bulk concentration to avoid them). For the casein, the situation is somehow similar, and it is possible that for large bubble surfaces, big areas of very thin and unstable thickness can occur, making the films more fragile. In the same time, it is also not obvious that, for a given bulk concentration, the effective surface density of aggregates confined in the film, or even their size, is independent of the film area. Clearly, more experiments on the microscopic properties, corresponding to various bubble sizes, are needed to elucidate completely these macroscopic bubble size effects.

We can finally check if our results allow us to explain the differences in the coarsening rates. As reported before, the ratio \( \frac{c_t}{\gamma_{\text{SDS}}} \) is \( \approx 5 \). Back to the model predicting \( c_t \), we can first check if it can explain this result. For these two experiments the liquid fraction, gas and initial bubble diameter can be considered as identical. Regarding the surface tensions, for SDS \( \gamma = 36 \text{ mN/m} \) since the concentration is above the cmc, for the casein, we also take the value corresponding to the maximum coverage since the bulk concentration is very high, meaning that the surfaces are completely saturated of casein. In fact, at these concentrations, the initial surface tension (measured by the pendant drop technique) after a few seconds is already close to the equilibrium value at longer times, \( \gamma = 42 \text{ mN/m} \). So the differences between the surface tension is finally also small. In fact, our studies have shown that the only significant difference is in the thin film thickness. For the SDS films, a mean thickness (for a liquid fraction of 0.15, and at low capillary pressures) is between 30 and 40 nm, whereas a mean value can be approximated to be around 200–250 nm for the casein (Fig. 5c), so a typical thickness ratio \( h_{\text{casein}}/h_{\text{SDS}} \) \( \approx 5–7 \). It is thus reasonably possible to explain the differences in coarsening rates simply by the differences in film thickness. The agreement is in fact even better if one also include the small surface tension difference. So, these results tend to prove that no new contributions coming from the viscoelastic or other interfacial properties have to be taken into account regarding the coarsening process, as it has also been found with measurements on isolated bubble covered by casein molecules [27]. Note finally that the same difference of coarsening rates between SDS and casein foams has been recovered in an indirect manner, via rheological creep experiments which provide information on the role of coarsening in macroscopic stress relaxation, and on coarsening rates [12].

5. Conclusions

We have reported comparisons between surfactant (SDS) and protein (casein) foam properties, measured at different length scales. It is found that the microscopic origins of foam stability is quite different for SDS and casein foams. For surfactant solution, the repulsive interaction between the adsorbed layers provides the thin film and foam stability. The surface density is then an important parameter, and independent dynamic surface tension measurements are thus instructive. For casein foams, the mechanism of stability is related to the confinement of aggregates within the thin films, trapped there when bubbles come in contact (and not previously adsorbed). The film stability threshold appears to correspond to the percolation of these aggregates in the film. With this type of stabilization mechanism, which could be relevant for systems stabilized by other large proteins or solid particles, dynamic surface tension on single interfaces cannot be linked to macroscopic foamability. However, for both casein and SDS, it is found that there are always clear correlations between the stability of a single thin film and the one of the foam.

A new experimental setup for studying coarsening at constant liquid fraction (cell rotation, coupled to a light scattering measurement method) has been presented, allowing us to measure the time evolution of the mean bubble size inside a foam. It is then found that differences in thin film thickness can explain the ones seen on the coarsening rates. With this setup, more results are now being collected: other chemicals, gas, liquid fractions, or initial bubble size distribution.

Finally, though our results for mixtures of casein and SDS are preliminary, and as also reported from rheology experiments [12], it appears that the properties of such surfactant/protein solutions and foams seems to be rather different from the ones of their pure components, probably because of interactions both in the bulk and at the gas-liquid interfaces, which remains to be identified.
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