Application Report

Characterization of liquid foams

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Drop Shape Analyzer – DSA100R

Characterization of liquid foams by the determination of surface rheological properties of surfactant solutions

Abstract

The phenomenon of foaming is of particular interest in many different industrial branches. Producer of personal care products, fire extinguishing foams, flotation process froths, breweries, and more can be interested in the formation of particular stable or unstable foams. Despite the importance of foams in technological processes there is still a lack of simple as well as sound methods for foam characterization. Until today, the Ross-Miles Foam Height Test [1] is a standard testing method, despite of the major drawback of being very time consuming. In this note we show that by determination of the surface rheological parameter E´ and E´´ (i.e. the elastic and viscous moduli) with the EDM/ODM module, we quantify a critical factor for foamability and foam stability. The measurement takes place prior to foaming and allows optimization of formulations without time consuming in situ testing.

Method

To determine the rheological behavior of a surface or interface, a mechanical stress is applied to the interface by means of an oscillation or expansion of a drop. We observe the change of surface or interfacial tension as a reaction to the applied mechanical stress. From the phase shift between these signals, the elastic modulus E´ and the viscous modulus E´´ can be calculated.

Experimental section

In this study we compare two different formulations of personal care products in terms of foamability and foam stability. The foamability of a surfactant solution (i.e. the initial foam height) and the stability of the foam with increasing time depend on the rate of film drainage (induced by gravity or surface tension induced film pressure differences), the rate of gas diffusion through the lamella, electrical double layer effects, and the surface rheological properties of the lamella. Even though the surface rheological behavior is not the only factor to control the stability of a foam, in applications it appears to be the critical one [2].

In order to compare the results obtained from the surface viscosity characterization with the real behavior of the foams, we performed a simple foam height test with each 40mL of 1000ppm solutions of both samples. The foam was obtained by shaking the sample vessels.

The results of this test are summarized in table 1 and figure 1. Table 1 shows the measured foam heights at different times, figure 1 shows the relative foam heights calculated as

initial foam height / foam height at time X

vs. time.

Time [min]	Foam height Sample 1 [mm]	Foam height Sample 2 [mm]
0	9,6	11,3
1	6,7	9,8
2	6	9,1
5	5,8	8,1
10	5,6	7,7

Tab. 1: Decrease of the foam height with time

From figure 1 it is obvious that foaming of sample 2 yields a more stable foam than foaming sample 1.

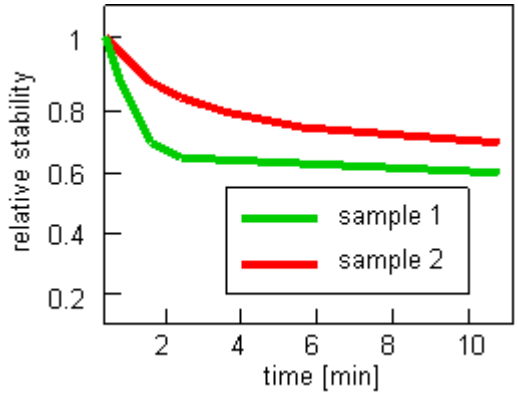

Fig 1: Decrease of the relative foam height with time

We will now see that this results can be predicted by a surface rheology characterization with the EDM/ODM technique.

Though the EDM/ODM module offers different methods to determine the surface rheological parameters E´ and E´´ (i.e. the pendant drop method, the circular drop method and the expanding drop method), first of all the proper measuring mode has to be chosen.

For the characterization of the stability of a foam, the rheological properties of the liquid/air interface have to be determined. In this case, the change of the surface tension of a drop due to the mechanical change of the surface area can easily be determined by the optical pendant drop method. Thereby, the contour of an image of the drop is fitted mathematically (see fig. 2). With the information of the density of the liquid, the size of the drop and the mathematical fit of the drop contour, the surface tension of the liquid can be calculated. A prerequisite for this method is that the pendant drop is significantly deformed by the influence of the gravity, in other words, that the contour of the drop differs significantly from a circular shape. This will be the case in any liquid/air system.

(Is, e.g., the stability of an emulsion of interest, an interface of two liquids has to be created. For this purpose, usually the liquid with the heavy density has to form a pendant drop inside the liquid with the lower density. It then may happen that the difference of the densities of the liquids is low. In this case, a pendant drop of the heavy density phase will have always an almost circular shape when inserted into the liquid with the lower density. Then the pendant drop method fails and the circular shape method needs to be applied).

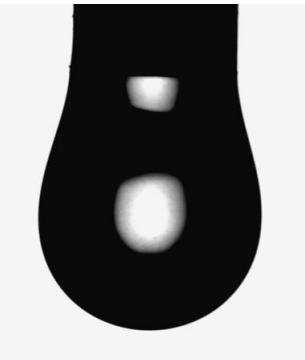

Fig 2: Image of a pendant drop in air

For our measurements, 1000ppm solutions of both samples were prepared and filled into the EDM/ODM module. A pendant drop was oscillated with a magnitude and frequency at which the drop showed a significant change in surface tension due to the mechanical de- and increase of the drop surface. The parameters for the measurement are summarized in table 2.

Incident frequency [Hz]	0,2
Drop volume change [%]	15
Initial drop size [µL]	10

Tab. 2: instrument settings for the measurement

Figure 3 shows (schematically) the incoming signal.

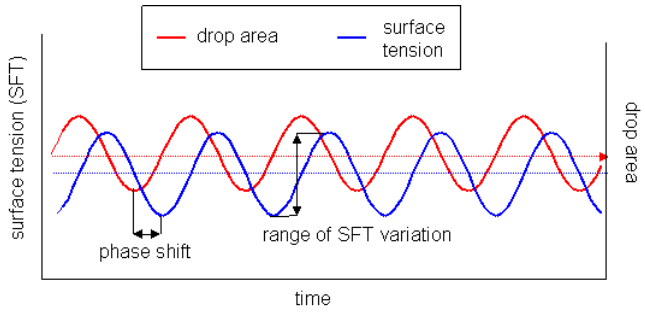

Fig. 3: Drop area change and surface tension vs. time

There is a phase shift between the area change of the drop and the change of surface tension. This yields from the fact that the surface active compounds in the bulk of the liquid and at the interface need some time to react to the changing environmental conditions. During the increase of the drop size, the concentration of surfactants per square unit in the interface will decrease due to the increasing surface area. This causes an increase of the surface tension of the drop. The diffusion speed of the surface active compound from the bulk to the surface determines then the time for the system to get back to the initial surface tension value. During a decrease of the drop size procedures are opposite way round. The decrease of the surface area of the drop increases the surfactant concentration per square unit and forces the compounds to diffuse from the surface into the bulk liquid of the drop.

From the information about the phase shift (between the area change and the surface tension) and the magnitude of the relative area change, the elastic and viscous modulus can be calculated after Lucassen & van den Tempel [3, 4]. Phase shift as well as range of surface tension variation depend on (1) the incident frequency, (2) the relative area change during one oscillation, (3) the concentration of surface active compounds in the liquid phase, and (4) the characteristic behavior of this surfactants (in terms of diffusion velocity). To compare the properties of different systems the frequency range (point 1) and the deformation (i.e. the relative change of the area, point 2) have to be the same.

The results of two measurements each of the two formulations are summarized in table 3.

Results

As shown above, the numbers of E´ and E´´ can be easily obtained with the EDM/ODM measurement. But how do the values now compare to the stability of the related foams?

Pure liquids without surface active compounds do not show any elastic modulus, the surface behaves totally viscous. Compared to our experimental setup this would mean that the surface tension of a pure liquid remains constant over the course of oscillation. Only by the addition of surface active compounds the surface can show an elastic modulus. We found the following relation between stability of foam and its rheological parameters: An increase of the ratio of elastic modulus vs. viscous modulus results in increased foam stability.

	Sample1	Sample1	Sample2	Sample2
Volume* [µl]	10.46	10.02	9.93	9.53
Surface area* [µm2]	21.39	20.62	20.30	19.70
Surface Tension Mean value [mN/m]	27.99	27.52	30.10	28.45
Time shift [s]	-0.59	-0.60	-0.41	-0.45
Elastic modulus E` [mN/m]	7.68	6.99	15.92	13.61
Visc. modulus E´´ [mN/m]	6.95	6.50	9.01	8.70
Ratio E´/E´´	1.11	1.08	1.77	1.56

Table 3: Results of measurements; *mean values from image analysis

Our measurements lead to E´/E´´ ratios of 1.11 and 1.08 for the (unstable) sample 1 and 1.77 and 1.56 for the (stable) sample 2. Even if the difference in foam stability between the two formulations is not too large (70% foam remaining after 10 minutes at sample 2, 60% remaining at sample 1, see fig. 1), the results differ significantly telling us that foaming of sample 2 will lead to a more stable foam than foaming of sample 1.

Summary

The characterization of surfactant solutions with the EDM/ODM module of the DSA100 allows a fast and sound prediction of the stability of a foam. In the chosen measurement mode, the EDM/ODM module creates an oscillating drop and thereby an oscillating liquid/air interface. The change of surface tension during the course of oscillation is observed with the pendant drop method. From the phase shift between the area change of the drop surface and the related change of surface tension, and from the magnitude of the relative area change, the elastic (E´) and viscous (E``) moduli of the surface are calculated. The higher the ratio of E´/E´´, the more stable a foam liquid will be.

Literature

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