



## A new method to estimate the stability of short-life foams<sup>☆</sup>

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### Abstract

In classical foam stability studies, foam height variation is monitored versus time. The decay pattern depends, however, upon the foam structure at the start of the decay; in many instances this structure changes significantly during the first few minutes, and it is difficult to select a proper "zero time" of decay. We have found that the decay behavior is very well defined when the original state of the foam is taken as the equilibrium state of the classical Bikerman's experiment, i.e. when the foam formation by bubbling (at the bottom of the column) exactly compensates the foam collapse (at the top).

It is found that under such starting conditions, short life foam decay exhibits a linear variation in the foam column height with the logarithm of the elapsed time. A dimensionless  $H$  vs.  $\log t$  plot exhibits the same features for different systems; thus, both a characteristic height and a characteristic time can be extracted from the experimental data, the latter being readily related to the foam stability.

These parameters are used to quantify the effect of additives on the decay of several foam systems containing nonionic and anionic surfactants.

*Keywords:* Foam; stability; Short-life foam.

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### 1. Introduction

Foams are dispersed systems of great practical importance, either in their capacity as low density media, or because they must be suppressed owing to their unfavorable effects. The statement in the title of a recent paper "foams, friend and foe" [1] is quite significant, since it emphasizes that a foam can be either the savior or the culprit depending on the process considered [2-4]. Therefore, an attempt must be made to understand the phenomenology as a whole.

Surfactants are responsible for the very existence of foams, as well as their desirable or troublesome persistence. In a broader approach, the whole

Physicochemical formulation is to be related to the foam properties. Formulation variables include not only the surfactant(s) [5,6], but also the solvent nature, dissolved substances such as electrolytes and polymers, and temperature and pressure [7,8]. This approach has been successful in describing the relationship between the formulation, and the emulsified system properties. The research constituting the Enhanced Oil Recovery projects in the seventies provided the physicochemical framework for accurately describing the phase behavior and interfacial properties of surfactant-oil-water systems at equilibrium [8-10]. It was found that a strong relationship exists between the well studied equilibrium situations and the

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emulsion properties, at least in many cases of interest [11- 14].

Since the approach was successful for emulsions it was also applied to foams, by considering that a foam is similar in nature to a high internal phase ratio emulsion. In fact, this analogy was found to work reasonably well in the case of an emulsion that could be considered as a blueprint of a foam, i.e. in the O/W case with a fairly hydrophilic surfactant [15,16]. In such a situation, it was argued that the dispersed system stability was controlled by the thinning of the interbubble or interdrop film in a similar way, whatever the nature of the dispersed phase.

Although the apparent complexity of the situation could simply be due to ignorance, it seems that the phenomena involved in foam formation and decay are both more numerous and more intricate than in the emulsion case. There are several reasons for this. First, it is well known that the early stabilization of the formed bubbles, which determines the very existence of the foam, depends upon unsteady state phenomena that are always more difficult to handle than equilibrium situations.

Second, in most cases, foams contain a very high amount of internal phase; as a consequence, they would be expected to exhibit similar behavior to emulsions with 98 or 99% of internal phase, an extreme case which has not been studied to a significant extent; the current known phenomenology [17] concerns emulsions with up to 70-75% of internal phase, a situation that is actually quite different.

Third, the presence of a gas phase brings some additional phenomena, such as interbubble gas diffusion, compressibility, and evaporation, that have no relevant equivalent in the emulsion case.

The very concept of stability seems more complex to handle with foams than with emulsions. In the early stage of foam formation, the so-called Gibbs and Marangoni non-equilibrium effects are responsible for the accumulation of bubbles that make up the foams. Thus, the interbubble film stability is in this case more linked with the concept of foamability than with actual stability. After a foam is made (by any process), there is a period of rest during which there is no apparent change before the onset of the decaying process is

indicated by some visible occurrence such as a volume variation, a bubble collapse, or a change in the bubble size or the general aspect of the foam.

The concept of stability generally refers to this third stage in which the foam volume or aspect is altering slowly as time elapses. The faster the change, the less stable the foam. A good stability criterion will thus be a measure of the time scale for some event to occur (for instance, half or total collapse), or a measure of the amount of change (for instance, foam height) after a specific time. However, it should be noted that such an approach applies only to systems with smooth decay, excluding situations such as catastrophic collapse [18] or interbubble diffusion without breaking which should be studied by means other than foam volume monitoring [19].

The present work deals with short life foams, i.e. foams whose decay occurs by drainage and/or film breaking, and whose time scale is too short for interbubble diffusion to become significant. This typically applies to foams persisting for less than one hour.

## 2. Discussion on Bikerman's dynamic method

The simplest method for estimating the stability of a foam is to follow its change in volume with time. After the foam is made by whichever means, it is poured into a graduated cylinder and the foam column height is monitored versus time. For instance, in the popular Ross-Miles method, the foam is made by letting a standard volume of liquid fall on top of another volume of liquid located in a graduated cylinder (D 1173 ASTM norm slightly modified).

Depending on the way the foam is made and/or poured into the cylinder, a shorter or longer initial stage takes place, in which the bubbles rearrange themselves in the column, according to basic physical phenomena such as the gravity pull (the bigger bubbles rise to the top), the resistance to displacement (linked to liquid and foam viscosity), and the capillary action, as well as geometrical parameters such as the column dimensions.

As a consequence, the actual state of the foam at this stage is very likely to depend much more upon circumstantial situations or geometry, than upon

some intrinsic property of the foam. This is indeed very unfortunate, since a well defined situation is sought after as the decay zero time. It has been found convenient to let the foam reach the end of the initial stage to attain a better defined state. In effect, at the end of this stage, the drained liquid attains an essentially constant level; the bubbles are no longer moving or spherical, and hopefully they have not started to break yet.

If such a state can be attained, the decay zero time can be taken as the point at which the first bubble breaking occurs. At this time, the foam column exhibits a variation from top to bottom; the foam located at the top has reached the breaking condition, while the aging of the foam at the bottom is not well defined, since some time has elapsed during the initial rearrangement and drainage. This lack of definition is annoying, and should be avoided.

The next step is therefore to find a zero time at which the states of the foam are well defined both at the top and bottom of the column. In Bikerman's classical method, a certain amount of liquid is poured into a graduated column and gas is bubbled at a constant flow rate in the liquid through some dispersing device. The foam starts forming at the bottom and accumulates in the column. The plugflow-like displacement of the foam results in segregation by age, the oldest foam settling at the top and the youngest at the bottom, with very little rearrangement by size. The liquid drains downwards so that the quality of the foam varies with height; the top foam contains the lesser amount of liquid, is the oldest and is the most likely to break. At some moment the top foam reaches the breaking condition and the top layer collapses. The higher the column, the older the top foam layer, and the more likely it is to collapse; as a consequence, dynamic equilibrium is finally attained and the column height remains constant with time, when the rate of foam breakage at the top exactly compensates the rate of foam formation at the bottom. This dynamic equilibrium is attained in most cases after a few minutes and it is rather stable in many instances. In such a situation the state of the foam is perfectly defined both at the bottom and top of the column, since these extremes correspond to the birth and death conditions of the foam. For this reason, the Bikerman's experiment equilibrium

is taken as the original state or zero time of the decay experiments to be carried out in the present study.

Before proceeding further, it is worth noting that the problem in interpreting Bikerman's experiment data is that the foam column height depends on both the decay rate, i.e. a parameter related to the concept of stability, and upon the formation rate, i.e. a parameter related to foamability. As a consequence, this type of method cannot separate the two concepts, and actually gives combined information on foamability and stability.

### 3. Experimental procedures

Some of the foaming solutions to be tested contain a commercial ethoxylated nonyl phenol surfactant provided by Gaf Chemical Corporation Chemical Products (Igepal-CO series), symbolized by NP + XEO, where X stands for the average number of ethylene oxide groups per molecule. It is used as a 0.02 wt.% solution in distilled water, a concentration substantially higher than its critical micelle concentration (CMC around 0.002 wt.%). Some solutions additionally contain 1 wt.% reagent grade alcohol from Merck. A trace (0.03 wt.%) of n-heptane (symbolized C7) is also added to some of the alcoholic solutions, in which it found to be completely solubilized. Other tested foaming solutions contain sodium lauryl sulfate (99% from Merck) at a 0.23 wt.% concentration in pure water, or in sodium chloride (p.a. from Merck) solution.

The foam decay experiments are carried out in a graduated borosilicate glass column (typically 5 cm W., 150 cm height). A 50 ml sample of the foaming solution is introduced into the column, and a pre-humidified nitrogen flow is bubbled from the bottom through a hypodermic needle #20 (1.5 mm diameter), at a constant flow rate of 140 ml min<sup>-1</sup> (at P = 1 atm and 22°C) unless stated otherwise. The experiment is carried out at ambient temperature (22 ± 2°C). Under the given conditions the foam column height typically reaches the Bikerman's experiment equilibrium after 10 min.

When dynamic equilibrium is reached, i.e. when the foam column height attains a stable value, the

gas input is closed and the foam column height is monitored versus time. The initial draining stage is found to be very short in general, often a very few minutes, which is an insignificant time lag with respect to the decay time scale in most cases.

#### 4. Decay with dynamic equilibrium as initial condition

The foam column height is found to change with time according to a decay pattern illustrated in Fig. 1, indicating two typical situations labeled "nice

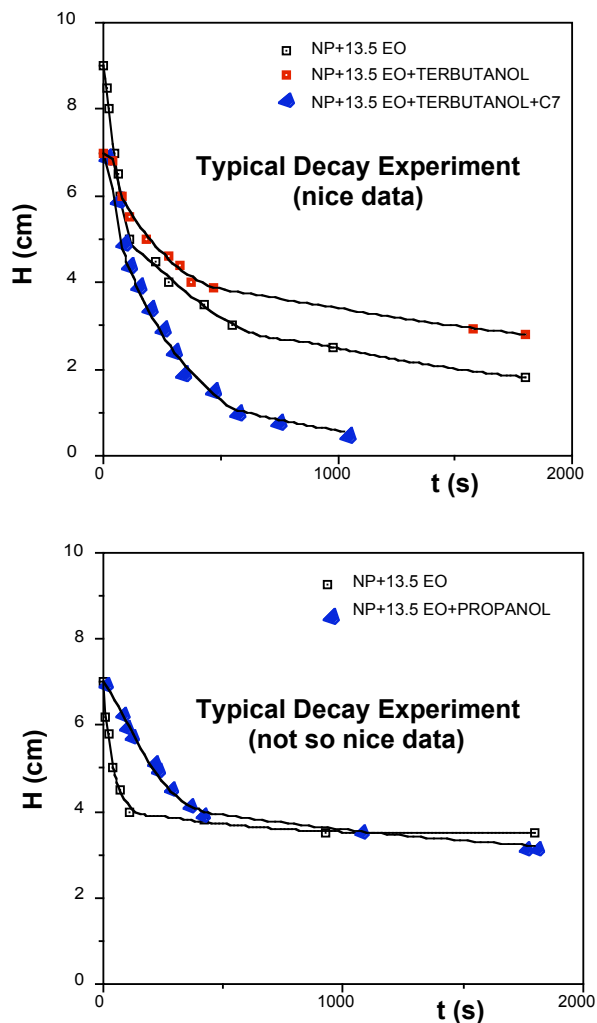


Fig. 1. Typical foam decay of foam column height vs. time. Zero time is taken as Bikerman's experiment equilibrium.

data" and "not-so-nice data". In the first case, the decay curves from different experiments are well ranked and it is easy to conclude which one has a higher or lower stability. However, the representation is not appropriate for deciding whether a given foam is two or three time more stable than another.

In the "not-so-nice" data case, the situation is even worse because there is obviously a difference in the early decay, after which the difference seems to vanish and the two decays proceed at the same pace. It is somewhat arbitrary to form conclusions about the relative stability of the foams, since the answer depends upon the time at which the comparison is made.

Fig. 2 illustrates a data processing method to attain a significant numerical value for the foam stability concept. First, the "nice"  $H$  vs.  $t$  data from the previous Figure are plotted on a semi-log graph, i.e.  $H$  vs.  $\log t$ . In the case of short life foams, we found that the decay is represented on such a plot by a straight line over a wide time range, say from 20 to 80% of the foam decay. The three different experiments represented in Fig. 2 exhibit different straight lines which are easier to handle than the curves in the previous case. The slope is probably linked to the variation in height with time, and thus might be a candidate for estimating the stability. The height at a specific time or the time required to reach a given degree of decay might be alternative candidates. The trouble is that all these characteristics can switch their relative positions (and alter the corresponding conclusions) since the lines can eventually cross over. It is thus necessary to process the information further to eliminate this ambiguity.

Before doing so, let us consider the significance of the  $H$  vs.  $\log t$  straight line variation, which can be written as

$$H = \square a \log t + b$$

from which the rate of height change is calculated as

$$\frac{dH}{dt} = \square \frac{k}{t}$$

From this equation, it can be seen that the rate of

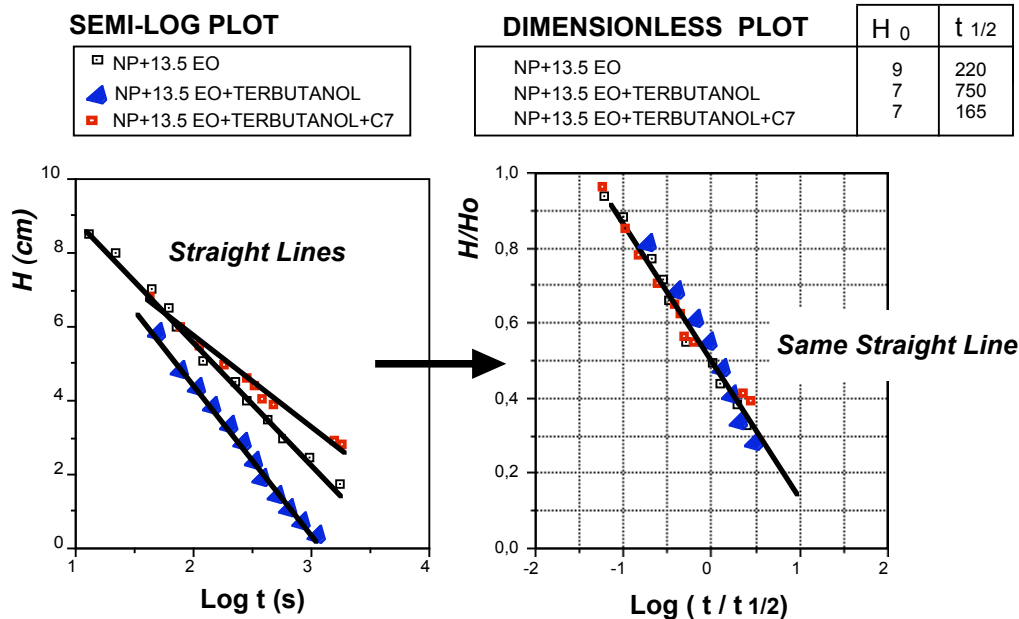


Fig. 2. Data processing into a dimensionless plot and calculation of characteristic parameters at half decay.

change of the column height, i.e. the thickness of the foam layer that collapses at a certain age, over an interval of time, is inversely proportional to its age.

Since the original time ( $t = 0$ ) cannot be represented on the logarithmic scale, the differential equation is integrated with respect to some reference state  $H_{\text{ref}}-t_{\text{ref}}$ , optimally selected according to the following discussion.

On the one hand, the initial situation is not very well defined because of the short initial drainage time, as mentioned previously. On the other hand, the last bubble to burst may be out of line with the other data. As a consequence, it is convenient to select a reference in the most secure part of the linear variation, i.e. in the decay mid-range. Let us therefore take the half decay situation as the reference. Since the zero time is not well defined, it is better to base the half decay on the height value. Thus the reference is taken as the time  $t_{1/2}$  at which the column height  $H_{1/2}$  is half the original height  $H_0$  reached by the Bikerman's method dynamic equilibrium. The data are then replotted in a dimensionless form as  $H/H_0$  vs.  $\log(t/t_{1/2})$ ; it is expected that all the straight lines would pass through the central point of the diagram, i.e.  $H/H_0 =$

$1/2$  and  $\log(t/t_{1/2}) = 0$ . An unexpected and fortunate result is that all the straight lines do coincide, as indicated in Fig. 2. The general equation for this line is

$$H/H_0 = 1/2 - \square \log(t/t_{1/2})$$

where  $\square$  is about 0.3-0.4, apart from a few cases with greater or smaller values. This means that the differences between the three situations illustrated in this Figure are translated to the  $H_0$  and  $t_{1/2}$  values, which become the characteristic parameters for each case. As seen from  $H_0$  data, the original foam height is not very much affected by the addition of alcohol or a trace of hydrocarbon. However, the half decay time is very significantly affected, changing from 220 s for the pure nonyl-phenol ethoxylate surfactant alone, up to 750 s when 1% ter-butanol is added, and going down to 165 s in the presence of a trace of heptane. Since the original height is essentially the same in the three cases, the change in  $t_{1/2}$  appears to be due to the foam stability.

Since the three data are represented by the same dimensionless line, a multiplicative factor can be calculated not only to rank the effects but also to quantify the change. For instance, it can be said that the addition of 1% ter-butanol increases the foam

stability by a factor of 3.4 (750/220), and that the addition of a trace of heptane to a system containing 1% alcohol causes the stability to drop by a factor of 4.5 (750/165).

### 5. Some examples of applications of the method

The method is carried out to determine the effect of several additives on foam stability. Fig. 3 shows the same kind of data for systems containing ethanol and propanol, with and without traces of oil. The analysis of the data indicates that the presence of water soluble alcohols enhances the foam stability at the expense of a decrease in  $H_0$ , which probably means that the foamability decreases significantly, since the increased stability would rather tend to increase  $H_0$  at constant foamability. It is worth noting that the clear-cut conclusion that the best stability enhancement is attained with propanol was not obvious from the "not-so-nice" data plotted in Fig. 1.

When a trace of heptane is added, the stability drops considerably in all cases, sometimes over-

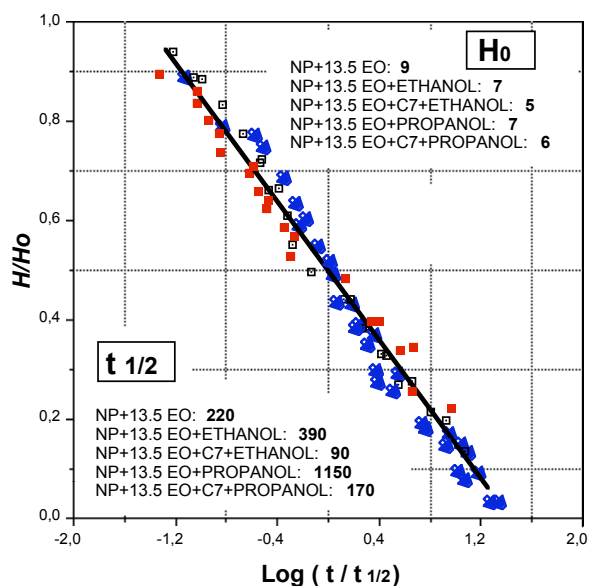


Fig. 3. Dimensionless plot and characteristic parameter values showing the effect of alcohol and a trace of heptane on the foaming of ethoxylated nonylphenol solutions.

taking the improvement due to the alcohol. It is interesting to note that the quantification of the effect allows a better comparison. For instance, the numbers indicate that the strongest drop occurs for the system containing ethanol, i.e. the system in which the oil phase is less soluble, and most likely to produce small droplets in the stretched films when the surfactant concentration drops below the CMC with the eventual release of oil solubilized in the micelles.

The value of the  $\square$  slope is found to be constant for a given surfactant type and concentration; it is not known for sure whether, and if so, how it depends upon the surfactant nature, absolute concentration or relative concentration. Some preliminary results seem to indicate that it does vary, although not very much, with the surfactant type and concentration [20], but further work is required to clarify this point.

The method is also used to study the influence of the electrolyte on the stability of the foam formed with sodium lauryl sulfate, a surfactant commonly found in shampoos. Fig. 4 indicates the dimensionless  $H$  vs.  $\log t$  plot for three cases:

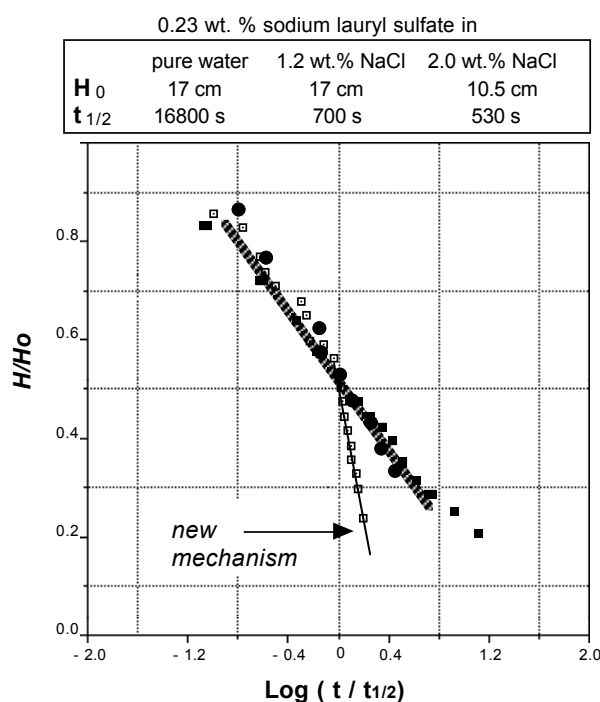


Fig. 4. Effect of salinity on the foam parameters.

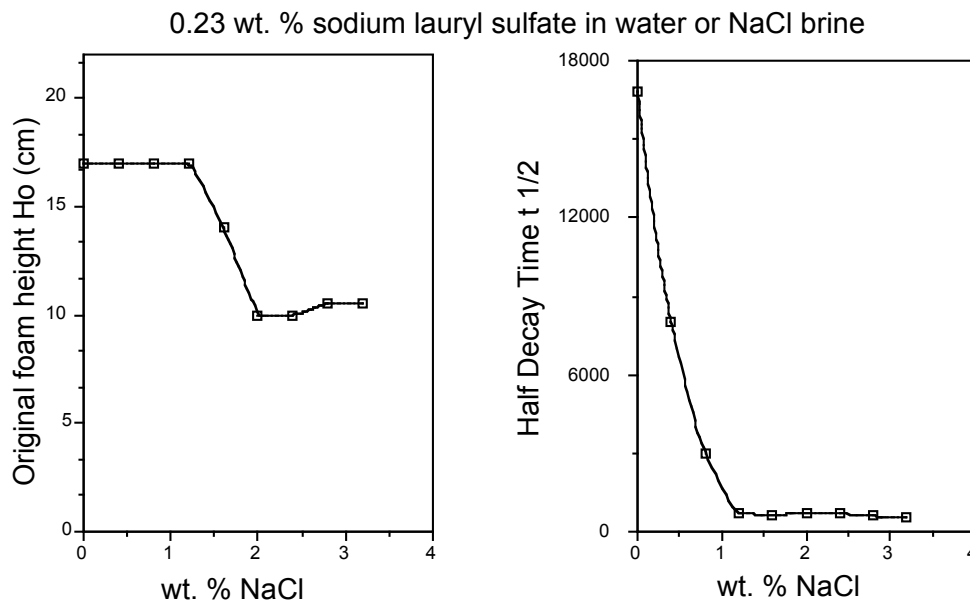


Fig. 5. Effect of salinity on the foam characteristic parameters. Sodium lauryl sulfate (0.23 wt.%) in water or NaCl brine.

surfactant solution (0.23 wt.%) in pure water, or in 1.2 and 2.0 wt.% NaCl solution. As far as the pure surfactant solution case is concerned, the half decay time considerably exceeds the range of short life foams; it is interesting to note that the straight line variation follows the previous trend approximately up to half decay; the trend then changes slope, indicating a faster decay rate, probably a hint that another mechanism is taking over after several hours (diffusion, evaporation, change in room temperature). It is, however, interesting to note that the new decay rate also follows a straight line variation on the dimensionless plot.

The characteristic parameter values indicate that the presence of electrolyte produces a significant decrease in foam stability, as could be expected from DLVO theory and other well known phenomena. Fig. 5 sums up the variation in the two characteristic parameters versus electrolyte concentration. It is seen that the stability is significantly affected by the electrolyte content up to 1 wt.% NaCl, and that there is no further change above this value. As far as the  $H_o$  value is concerned, the changes occur in a different way. At first there is essentially no variation in foam height, although the stability drops very significantly. This means that there is probably an increase in

foamability, due to a decrease in CMC for instance. A second plateau is then attained, with both a lower stability and a lower foamability.

## 6. Conclusions

The proposed experimental method and data processing techniques allow the monitoring of two characteristic parameters of a foam. One of these is the half decay time ( $t_{1/2}$ ), an estimate of the foam stability in the sense that it provides a reliable measurement of the foam decay rate. This parameter is accurate enough to give a numerical estimation of the stability change. The other parameter ( $H_o$ ) gives an estimate of the conjugated influence of both the stability and foamability, so that information on foamability alone can be extracted, although with some caution.

The method can be used to estimate the effect of different additives on foam stability.

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