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Régimen de colapso pulsante de espumas

Pulsating foam decay regime

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Resumen

El comportamiento dinámico de espumas producidas con soluciones de surfactantes no iónicos es estudiado mediante un método neumático. Según el valor de variables como el caudal de gas, la concentración de surfactante o la viscosidad, se encontraron dos regímenes: el primero en el cual la espuma aumenta de volumen hasta alcanzar un estado estacionario, y el otro que se caracteriza por una alternancia de crecimiento y colapso de tipo avalancha, que se llama régimen pulsante. En este régimen el decaimiento no puede describirse como una función continua del tiempo, sino discontínua, contrariamente al comportamiento llamado de Bikerman. Se deben cumplir dos condiciones para que se desarrolle este régimen. Primero, el surfactante debe proporcionar una espuma abundante y suficientemente estable para alcanzar el estado de espuma seca, y segundo, el drenaje del líquido de la espuma debe producirse a cierta velocidad para formar películas delgadas capaces de romperse cuando se produce una onda de choque. De acuerdo a los resultados no hay correlación entre avalanchas sucesivas.

Palabras claves: Espumabilidad; estabilidad de espuma; surfactante no iónico.

Abstract

The dynamic behavior of foams produced from non-ionic surfactant solutions has been studied by a pneumatic method. Depending upon variables such as gas flow rate, surfactant concentration and liquid bulk viscosity, two behaviors were found: one in which the foam grows until a steady-state height is reached and the other in which there is a succession of linear increases of foam height followed by avalanche-like collapses, which was called pulsating regime. In this regime, the decay rate cannot be described as a continuous but as a discontinuous function of time, contrary to Bikerman-type behavior. Two conditions should be fulfilled for the appearance of the pulsating decay. First, the surfactant should have enough foaming ability and stability to form expanded dry foam, and second, the foam drainage should occur at a certain rate, so that the films are thin and the burst propagates along the foam column. Judging from the experimental results, it seems that there is no correlation between avalanches.

Key words: Foamability; foam stability; non-ionic surfactant.

1 Introducción

The understanding of the foaming behavior of surfactants solutions is important in many applications such as in enhanced oil recovery, fire fighting, or paper processing, but in other processes the production of foam is often an undesirable outcome. Therefore, a vast number of studies are dedicated to understand the foam formation and destruction.

Foams are nonequilibrium collections of polydisperse gas bubbles packed in a small amount of a liquid containing surfactants or other surface-active agents (Durian and Weitz, 1994). Because foams are not thermodynamically stable, their equilibrium properties cannot be measured; consequently, foam characterization has to be carried out by measurements under conditions in which foam decays, or when the formation and destruction of the foam occur at the same time. Several methods have been proposed to study foam behavior, among them, the Bikerman's method (Bikerman, 1973) is widely used. In this method, the height of a foam column formed by continuous injection of gas into the foaming solution, reaches a steady-state value, which is a measure of both the system foamability and the foam stability.

Several stages can be identified in the life of liquid foams: initially, a dispersion of spherical gas bubbles is formed. Then, liquid drainage from the lamellas takes place and bubbles form polyhedral structures, the foam films become thinner and the foam dries. At the same time, the gas diffuses from small to large bubbles because of the Laplace's pressure difference. As a consequence, the shapes and sizes of the bubbles change with time (Gopal and Durian, 1995). A large number of studies have dealt with the decay of bulk foams when they exhibit a slow destruction pattern (Gopal and Durian, 1995; Prud'homme and Khan, 1996). However, there are a variety of systems in which bubbles can break in a collective mode, showing cascades of bubbles ruptures or avalanches (Vandewalle et al., 2001; Rodriguez et al., 1994). In this perspective, we present a report on unusual, avalanche-like dynamic behavior of foams produced by a conventional pneumatic method.

2 Experimental conditions

2.1. Materials

Solutions of tributyl phenol ethoxylates, symbolized in the following as TBPEON, where EON is approximately the average number of ethylene oxide groups per surfactant molecule) in bi-distilled water were used to produce foams. Some properties of the surfactants, trade name Sapogenat T080 (TBP08) and T180 (TBP18) from Clariant GmbH, are shown in Table 1. Carboxy methyl cellulose (technical grade) from Sigma was used to increase the bulk viscosity of foaming solutions

Table 1: Properties of surfactants

Surfactant	CMC (wt%) at 23 °C	EON	HLB
TBP08	0.005	8	11
TBP18	0.015	18	16
TBP08	0.005	8	11

2.2. Methods

Foams were prepared according to the so-called pneumatic method. Nitrogen (pre-saturatePd with water by bubbling in an Erlenmeyer) was injected at a constant flow rate through a nozzle (0.5 mm ID) located at the bottom of a glass column (5 cm OD, 120 cm height) containing the surfactant solution. The experimental setup is shown in Fig. 1. This method generates a foam with a fairly monodisperse bubble size. Experiments were carried out at 23 ± 1 °C and 640 mmHg (atmospheric pressure). In some experiments, a second injection nozzle was added aside the first one, in order to double the gas flow rate without altering the bubble diameter.

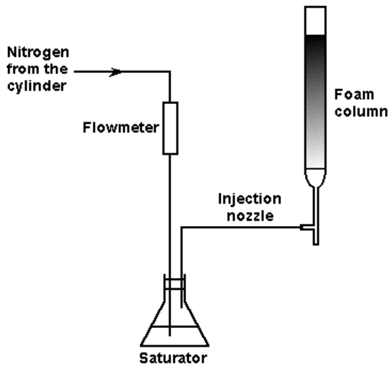

Fig. 1. Schematic view of the experimental setup.

3 Results

Fig. 2 and 3 show the dynamic behavior of foams in the systems under study, i. e, the foam column height (H) as a function of time (t) from the start of the bubbling. In the case of TBP18, the data exhibits the typical Bikerman's test features. The foam column height monotonously increases with time as shown in Fig. 2, and after some period its rising slows down and reaches an almost constant (steady-state) value. On the other hand, the TBP08 system behaves in a very different way. At first, the foam rising takes place according to a straight-line variation, i.e., a steady rate increase, as shown in Fig. 3. At a certain time, most of the foam column suddenly collapses in a so-called avalanche instability (Müller and di Meglio, 1999). After the collapse, the foam column rises again at the same constant rate. This phenomenon, which takes place repeatedly, was originally called pulsating decay (Rodriguez et al., 1994) and referred to later as cyclical regime because of the periodicity of the phenomenon (Cheah and Cilliers, 2005).3.1

As seen in Fig. 3, the maximum height reached just before the collapse tends to increase from the first to the second peak and so forth, at least in the first 3-4 cycles. The heights of the residual foam column just after successive collapses seem to be roughly the same, even for different experimental conditions.

It has been found that this pulsating behavior is not characteristic of the surfactant species, but rather depends on the experimental conditions such as gas input flow rate

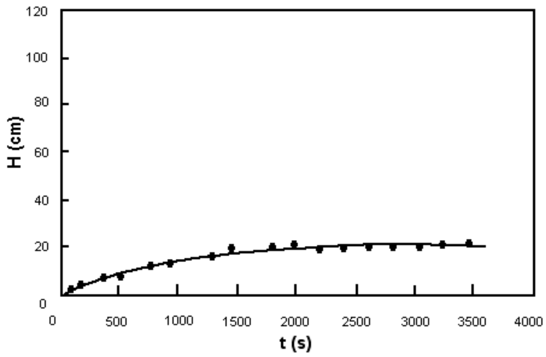

Fig. 2. Dynamic behavior of TBP18 foams. TBP18 concentration is 0.02 wt%, and incoming gas flow rate is Qe = 0.3 mL/s. The line shows the best fit to Eq. 3 for ε = 0.99.

and surfactant concentration. Fig. 4 shows a change in regime when the TBP08 concentration is increased. The pulsating decay which takes place at 0.02 wt% surfactant (dashed line), is no longer observed when its concentration is multiplied ten-fold (continuous line)

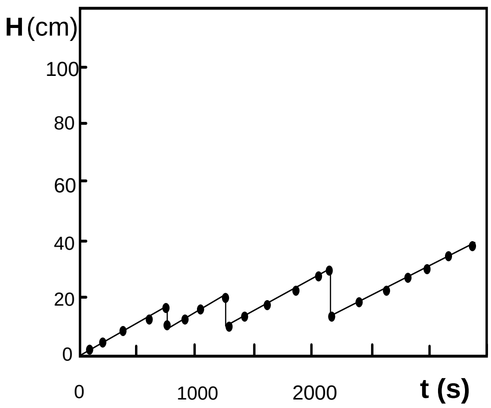

Fig. 3. Dynamic behavior of TBP08 foams. The TBP08 concentration is 0.02 wt%, and the incoming gas flow rate is Qe= 0.3 mL/s.

It is worth noting that the high concentration case (continuous line) exhibits a much lower foamability, close to the the post-collapse level. Namely, at high concentration, expanded dry foam is never generated, and this is probably why avalanches do not take place. Fig. 5 shows another effect in the foaming behavior of TBP08 systems. i.e., the pulsating decay disappears when the liquid viscosity increases, with the foam behavior returning to the typical Bikerman's type.

On the other hand, Fig. 6 shows that an increase in gas flow rate (at constant bubble size) increases the frequency of avalanches, even though the foam height still increases linearly with time between successive avalanches.

The dynamic behavior of foams produced under the conditions mentioned in the experimental section, i.e., the variation of the foam height (H) with time (t), can be described by a mass balance for the gas phase present in the foam:

$$\rho_e Q_e - \rho_o Q_o = \rho \varepsilon A \frac{dH}{dt} \tag{1}$$

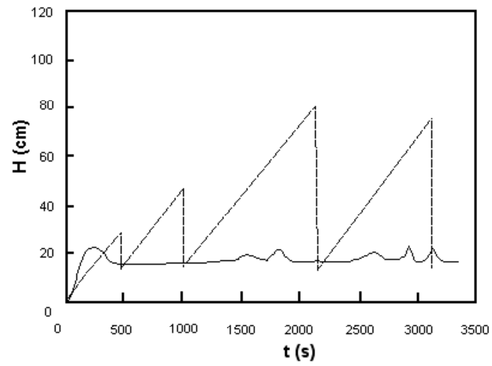

Fig. 4. Effect of concentration on the dynamic behavior of TBP08 foams 0.02 wt % (dashed line); 0.2 wt % (continuous line). The incoming gas flow rate is Qe = 1.0 mL/s. Only the lines joining the experimental points are shown.

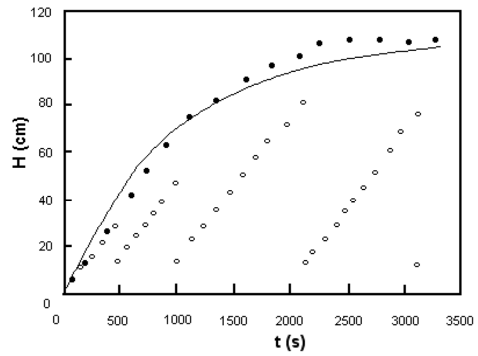

Fig.5. Effect of the liquid bulk viscosity on the dynamic behavior of TBP08 foams: 1 mPa·s (open circles); 10 mPa·s (filled circles). The incoming gas flow rate is Qe = 1.0 mL/s and the TBP08 concentration is 0.02 wt%. The line shows the best fit to Eq. 3 for ε = 0.99

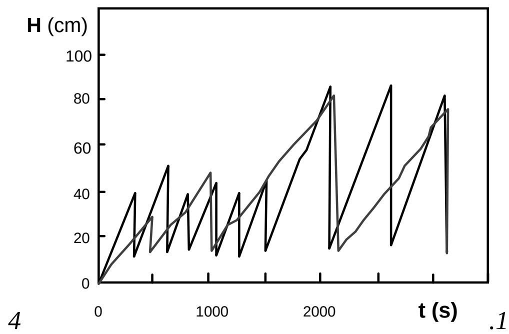

Fig. 6: Dynamic foam behavior of TBP08 foams for different Qe: 1.0 mL/s (dashed line); 1.7 mL/s (continuous line). In both cases the bubble diameter is 3.5 mm and the TBP08 concentration is 0.02 wt%. Only the lines joining the experimental points are shown.

where Qe and Qo are the entering and outgoing gas volume flow rates, respectively, ρ_e and ρ_o are the entering and outgoing gas densities, respectively, ρ is the average gas density , ε is the volumetric fraction of gas in the foam, and A is the cross-sectional area of the foam column. Qe and Qo can be related to the foam formation and decay rates. Neglecting density changes, Eq. 1 can be rewritten as (Jeelani et al., 1990):

$$Q_e - Q_o = \varepsilon A \frac{dH}{dt} \quad (2)$$

At steady-state, dH/dt = 0 and therefore, from Eq. 2, Qe = Qo, which is the condition that corresponds to the constant height regime, i.e. the plateau, in Bikerman's experiment. The way the system approaches this dynamic equilibrium (if ever reached) depends mainly on Qo, since in our experiments, Q_e is constant. Qo is determined by several phenomena, such as drainage, interbubble gas diffusion, evaporation, mechanical or thermal perturbations, and others (Durian and Weitz 1994). One intuitive and simple approach is to express Qo as a linear function of H, namely, Qo = k H, where k would be a decay rate constant. Solving Eq. 2 for this expression for Qo with the initial condition H(0) = 0, an exponential approach to the steady state value is attained so that :

$$H(t) = Hs\,(\,1 - \exp(-t/\tau)\,) \quad (3)$$

where Hs is the foam height at the steady state ($t \rightarrow \infty$) and □is a time constant, given by $\tau = k/(\varepsilon A)$. As seen in Figs. 2 and 5, Eq. 3 gives a relatively good fit to the experimental data for Bikerman-type behavior.

However, in the case of Fig. 3, it is evident that Q_o cannot be described as a continuous but as a discrete (discontinuous) function (Pilon et al., 2002). In fact, H changes linearly with t in the periods between sudden collapses, i.e. dH/dt is practically constant and Qo ≈ 0 from experimental evidence. Accordingly, as can be seen in Fig. 7, the plot of dH/dt versus Q_e/A, gives a straight line passing through the origin, with a slope 1/ε = 1. Hence, the volumetric fraction of gas in the foam is very high (ε = 0.99), and therefore, most of the foam can be considered as a structure of polyhedral cells with thin elastic walls that can be broken by any faint perturbation. Hence, the bubbles are likely to break in a collective mode. Accordingly, the pulsating regime can be described as a succession of dry foam expansions followed by avalanches triggered by a single rupture event.

From Eq. 2 (assuming ε = 0.99 the height of the foam at the time of the avalanche is given by (Qe/A)(t-Δt*(n-1)) where Δt is the time interval between events and n = 1, 2, 3… is the counter for the events. If it is considered that the amplitude of the avalanche is E = H(ta)-Hf, where H(ta) is the foam height just before the avalanche and Hf is the height of the foam column right after the avalanche, then, the pulsating decay may be expressed as a sum of Dirac functions Δ(t):

$$Q_o = -AH_f\delta(t-\Delta t) + A\sum_n (Q_e/A)(t-\Delta t(n-1))\delta(t-\Delta tn) \quad (4)$$

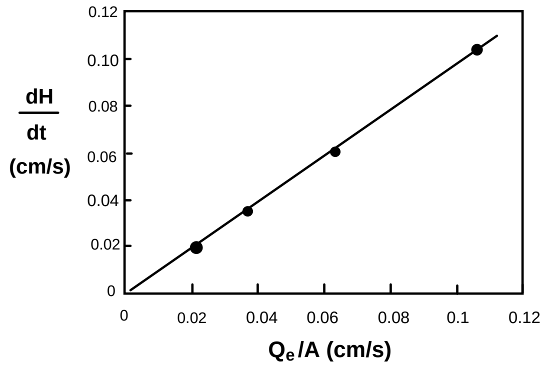

Fig. 7. Slope of H vs t plot during the foaming-up process as a function of Qe for 0.02 wt % TBP08 solutions. The line is the best fit to experimental points.

Introducing Eq. 4 in Eq. 2 and solving for constant values of □t and Hf, a saw tooth sequence is obtained as shown in Fig. 8 plot.

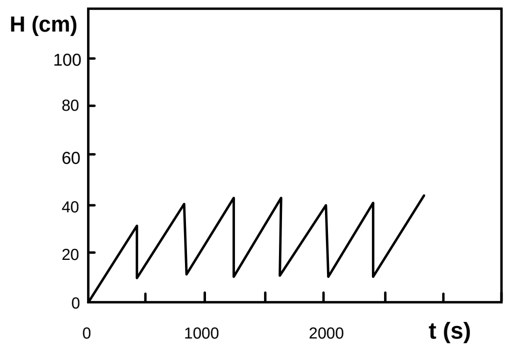

Fig. 8. Simulation of the pulsating decay using Eqs. 1-2 (Qe= 1.0 mL/s, Hf = 10 cm, Δt = 400 s)

Although there is a qualitative agreement with the experimental results, it is evident from Fig. 3 that the actual pulsating decay regime is not exactly periodic, and therefore Δt is not constant. Catastrophic events are usually associated with the attainment of some critical value, such as the critical bubble film thickness or the volume fraction of dispersed phase (in a way similar to emulsion inversion), but the lack of periodicity in Δt makes it difficult to support such a view in the present case.

It is reasonable to assume that the contribution of Q_o term is mainly determined by the rate of collapse of the bubbles at the top of the column, N_o. Previous studies showed that N_o might be related to avalanche-like collapse of foam bubbles (Müller and di Meglio, 1999; Vandewalle and Lentz, 2001), the time duration between avalanches being

ing statistically distributed according to a power law (Vandewalle and Lentz, 2001). Avalanche-like rearrangements in foams induced by small strains have also been studied both experimentally and theoretically (Gopal and Durian, 1995; Prud'homme and Khan, 1996; Okuzono and Kawasaki, 1995).

The amplitude of the avalanche depends on the bubble diameter, interbubble film thickness and mechanical strength. Small bubbles with high Laplace pressure are more likely to generate a pressure wave (detonation) which propagates through the foam. If the foam column is dry enough, i.e., if bubble walls are sufficiently thin, the breaking of a few bubbles will cause others to burst almost simultaneously in a chain reaction. Due to a fast liquid drainage, the dynamic foam generated in the experiments displays a strong vertical gradient of liquid content, i.e., bubbles exhibit thin walls and polyhedral shape at the top, and thick walls and spherical shape at the bottom. This observation was confirmed by measuring the electrical conductivity along the foam column. These features, together with moderate bubble size and gas flow rate, make the foam prone to collapse in a discrete fashion as discussed previously. The avalanche stops in the lower part of the foam column where thicker films are able to resist the mechanical perturbation wave. Viscosity also tends to slow down the wave propagation effect due to viscous dissipation, which explains the absence of pulsating decay in Fig. 5, whose 10 mPa.s solution contains a viscosity enhancing agent. On the other hand, high surface tensions increase the energy released when the bubbles burst, therefore the pulsating decay would be favored at low surfactant concentrations (below the critical micelle concentration).

As a first approximation, the pulsating decay may be visualized as a stochastic renewal process describing the sequence of events occurring at intervals Δt. For uncorrelated (random) events, the number of events in a time interval would be expected to exhibit a Poisson distribution, and Δt should be exponentially distributed according to

$$f = \exp(-t_1/\theta) - \exp(-t_2/\theta) \qquad (5)$$

where f is the relative frequency of events in the interval Δt = t1-t2 and θ is the mean of the intervals between events.

In order to carry out a preliminary statistical analysis, the foaming experiment was repeated while keeping the same conditions for pulsating decay (number of events > 100), and the results are shown in Fig. 9. The data show a relatively good fit to an exponential distribution (Eq. 5), indicating low correlation between events, namely, there is no memory in the system and the foaming properties are likely to be preserved after each avalanche.

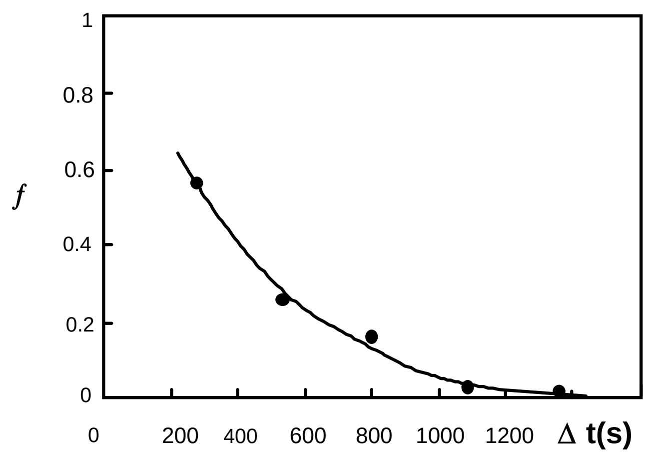

Fig. 9. Distribution of avalanches in TBP08 foams. The incoming gas flow rate is Qe = 1.0 mL/s and the TBP08 concentration is 0.02 wt%. The line represents the exponential distribution calculated from Eq. 4. f is the relative frequency of avalanches and Δt is the interval of time in which the avalanches occur.

5 Conclusions

Two kinds of dynamic behavior were found in the studied systems as the response to continuous gas flow input. One is the classical Bikerman-type, in which the foam decay rate can be described as a continuous function, so that the foam height reaches a steady state value after some ti me. In the other, so-called pulsating decay regime, the foam height is a discontinuous function of time. This second regime is found to take place when two conditions are fulfilled. First, the surfactant should have enough foaming ability and stability to form expanded dry foam, which is related to the film elasticity. Second, the foam drainage should occur at a certain rate, so that the films are thin enough and the burst wave could propagate along the foam column. It seems that there is no correlation between avalanches in the systems examined. The pulsating decay phenomenon could have potential implications in foaming control such as decontamination of large scale plants as nuclear installations, and could also provide a model to study dynamic collective phenomena (Müller and di Meglio, 1999; Bak et al., 1998).

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