Influence of Anionic Concentration and Water Hardness on Foaming Properties of a Linear Alkylbenzene Sulfonate

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Foam height and foam stability of solutions of a linear alkylbenzene sulfonate (LAS) were measured according to the Ross-Miles test to establish their relationship with ionic concentrations in the solution. The anionic concentration and water hardness were varied alternatively. The results obtained show different behavior for both parameters depending on the concentration of LAS and calcium. However, the results are in line with the proposed theoretical model based on the LAS-calcium precipitation boundary diagram. These tests were aimed at providing a scientific explanation to the complex foaming phenomena. Also, these tests emphasize how essential it is to know the position of the points tested within the LAS-calcium solubility diagram when evaluating the foam properties of an anionic surfactant.

KEY WORDS: Anionic surfactant, foam height, foam stability, LAS, water hardness.

Surfactant ingredients used today in the detergent industry belong to two large groups as far as foaming properties are concerned: high-foaming (basically anionics) or low-foaming (nonionics, soaps).

Where handwashing is concerned, foam has a great psychological effect, although it does not necessarily imply a direct relationship with detergency performance.

Foaming is a complex phenomenon. For this study, we have chosen the most popular foaming agent in the anionic group of surfactants, linear alkylbenzene sulfonate (LAS).

Neither the literature nor the existing theories on foam formation, its stability and the parameters on which it depends (1) show any work where an existing relationship between foaming properties and water hardness is established.

The aim of this work is to present a qualitative explanation concerning foam properties of a commercial-grade LAS over a wide range of surfactant and calcium ion levels. For this purpose, an LAS-calcium solubility diagram has been used.

EXPERIMENTAL PROCEDURES

One commercial linear alkylbenzene (LAB) sample (Petrelab-550, Petroquimica Española, S.A., San Roque (Cadiz), Spain) obtained through a hydrofluoric acid (HF) alkylation process and an industrial sulfonic acid (Petresul-550, Petroquimica Española, S.A.) have been used for this study. The chainlength distribution of LAB is the following: <phenyl C10, 0.4 wt%; phenyl C10, 8.5 wt%; phenyl C11, 36.5 wt%; phenyl C12, 30.8 wt%; phenyl C13, 23.1 wt%; phenyl C14, 1.0 wt%. The molecular weight was 241.6.

The sulfonic acid composition was: active ingredient, 96.8 wt%; free oil, 1.5 wt%; free sulfuric acid, 1.3 wt%.

The foam height determination has been carried out according to the Ross-Miles Test (ASTM-D-1173-53) at 49°C and an LAS concentration of 0.5 g/L. It is the volume of foam obtained after running 200 mL of an LAS solution from a height of 90 cm onto a liquid surface of the same solution.

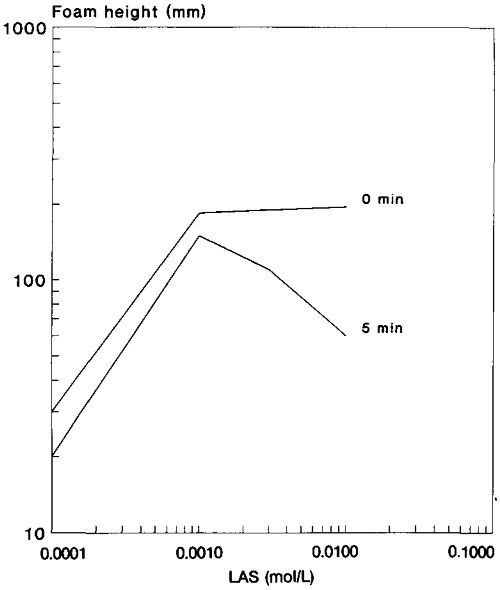

FIG. 1. Ross-Miles test. Initial water hardness: 300 ppm $CaCO_3$.

The foam stability index is given by the difference between foam heights measured at t = 0 and t = 5 min, respectively.

The LAS-calcium boundary diagram has been obtained (Fig. 1) by visual observation of the turbidity of LAS-calcium solutions prepared in 1-L glass bottles. The turbidity observation and the foam tests were both conducted 24 h after preparation of solutions.

This diagram is essentially a phase diagram drawn on a log-log plot. The precipitation boundary is the graphical representation of points at which the onset of precipitation is observed. The diagram is divided into areas where only monomers or micelles, or both exist. A more detailed description is given elsewhere (2).

RESULTS AND DISCUSSION

Foam height vs. *LAS concentration.* For water hardness of 0 ppm, the experimental results are plotted in Figure 2. Foam height (t = 0 min) increases with an increase in surfactant concentration and reaches a maximum in the neighborhood of the critical micelle concentration (CMC) (LAS = 10^{-3} M). Beyond the CMC, the foam height remains constant, regardless of LAS concentration.

The explanation for this is based on the Marangoni effect, which is maximum for concentrations around the CMC (1). The Marangoni effect refers to different viscosity and mechanical phenomena taking place in the surface solution due to the surface tension differences in various points of the liquid surface.

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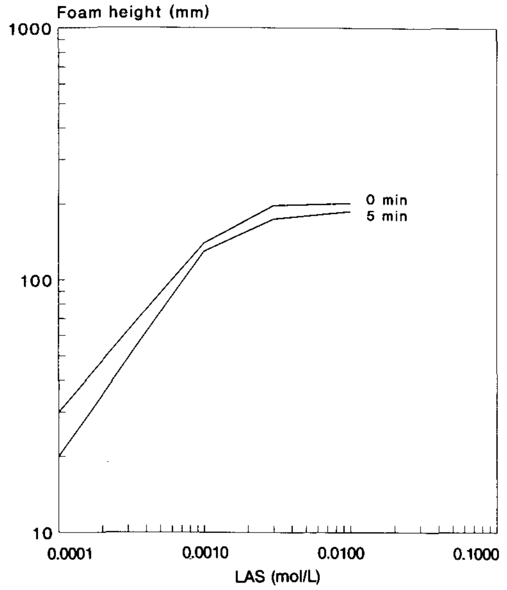


FIG. 2. Ross-Miles test. Initial water hardness: 100 ppm $CaCO_3$.

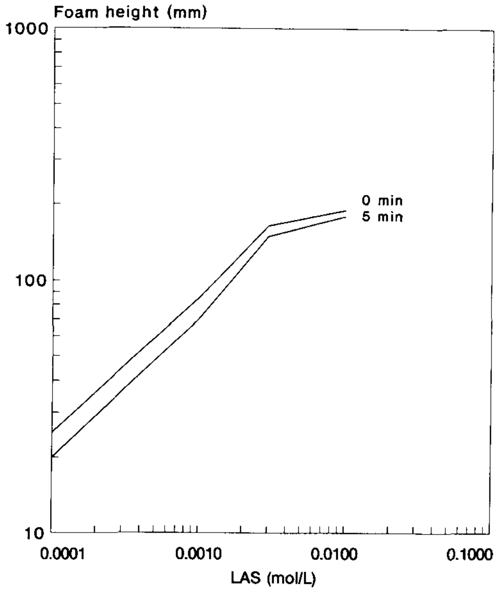


FIG. 3. Ross-Miles test. Initial water hardness: 300 ppm $CaCO_3$.

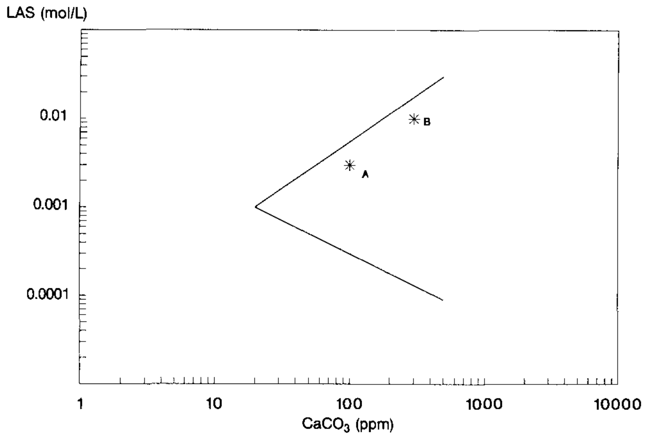


FIG. 4. Linear alkylbenzene sulfonate (LAS)/calcium precipitation boundary diagram.

Foam stability (t = 5 min) reaches a maximum around the CMC. Beyond the CMC there is a dramatic decrease of foam stability with an increase in surfactant concentration. Foam stability is defined as the difference between foam heights at t = 0 and t = 5 min, thus the lower this difference, the higher the foam stability.

It is apparent from Figure 2 that when neither calcium nor magnesium ions are present in the solution, the sodium micelles are less stable than monomers and the surface collapses with time.

Water hardness: 100 and 300 ppm. The experimental results are plotted in Figures 2 and 3, and the following conclusions can be drawn from the data: Foam height reaches a maximum at an LAS concentration above the CMC. This LAS concentration increases with an increase in water hardness (LAS = 3.10^{-3} M for 100 ppm and LAS = 10^{-2} for 300 ppm).

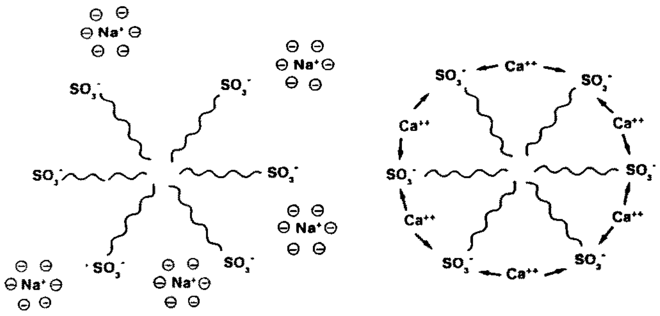
The LAS-calcium precipitation boundary diagram in Figure 4 helps explain these results. Points A and B in Figure 4 represent the initial LAS and calcium concentrations corresponding to the maximum in foam height obtained, *i.e.* 3.10^{-3} M at 100 ppm and 10^{-2} M at 300 ppm, respectively.

Points A and B have initial LAS concentrations higher than the CMC (10^{-3} M). However, as $Ca(LAS)_2$ begins to precipitate out, dissolved LAS and free calcium ions at these points will decrease with time until equilibrium conditions are reached. The commercial LAS sample used is a complex mixture of homologs and isomers; thus, the first homologs to precipitate are the heavier ones, and therefore, the dissolved LAS remaining in solution will correspond to the lighter ones.

It is well-known that the lower the molecular weight of the hydrophobic group, the higher the corresponding CMC. Because the CMC increases as the number of carbon atoms in the hydrophobic group decreases, the CMC of LAS dissolved at 100 and 300 ppm water hardness will be somewhat higher than the CMC of the starting LAS. Accordingly, at equilibrium conditions, concentration values will be close to the CMC of dissolved LAS. Thus two observations can be made: (i) In the presence of calcium and magnesium ions, at equilibrium conditions both the composition and the concentration of dissolved LAS are significantly different from the initial ones. (ii) For LAS-calcium solutions, the maximum foam height is always reached in the neighborhood of the CMC of the dissolved LAS.

Foam stability does not decrease beyond the surfactant CMC. According to Rosen (3), this phenomenon can be explained because of the greater cohesiveness of anionic surface films in the presence of calcium. Ca^{++} helps to increase the surface excess adsorption of LAS at the air/water interface. This improves foam performance.

Binding of the counter ion to the micelle in aqueous solution appears to increase with an increase in the polarizability and charge of the ion because of the stronger interaction with the anionic part of the molecule. This



Sodium Micelle
(unstable)

Calcium Micelle
(stable)

FIG. 5. Schematic representation of linear alkylbenzene sulfonate sodium and calcium micelles.

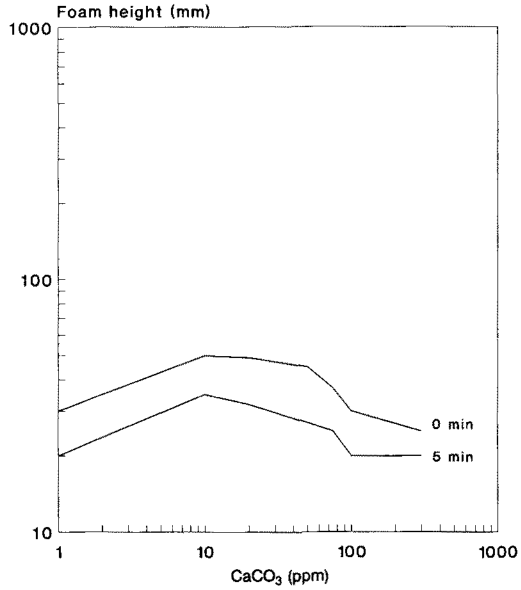


FIG. 6. Ross-Miles test. Initial linear alkylbenzene sulfonate concentration: 0.0001 M.

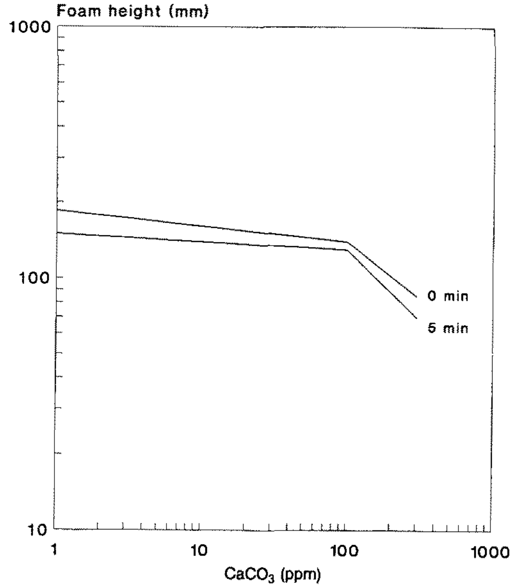


FIG. 7. Ross-Miles test. Initial linear alkylbenzene sulfonate concentration: 0.001 M.

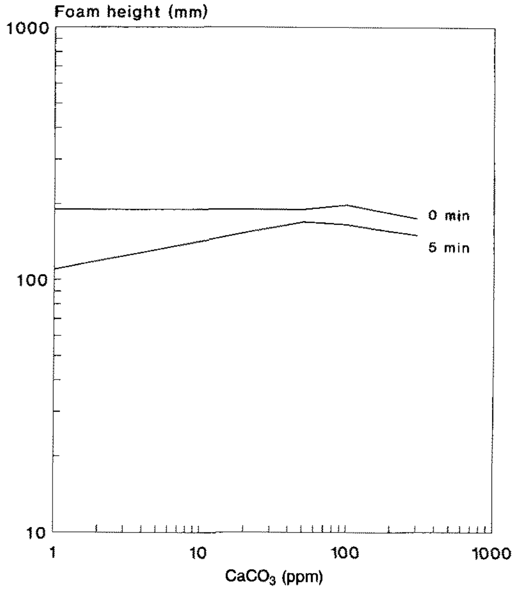


FIG. 8. Ross-Miles test. Initial linear alkylbenzene sulfonate concentration: 0.003 M.

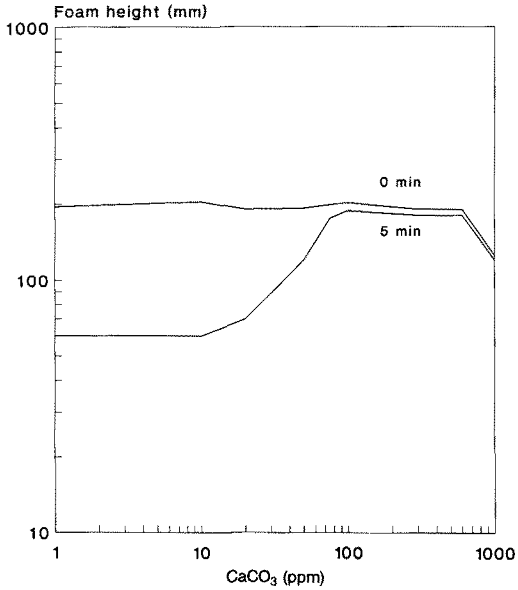


FIG. 9. Ross-Miles test. Initial linear alkylbenzene sulfonate concentration: 0.01 M.

creates a more stable micelle structure for calcium than for sodium. This is shown in Figure 5.

Foam height vs. *calcium concentration.* The results are plotted in Figures 6 through 9. It is worthwhile to highlight the following two observations: (i) Foam height is almost independent of calcium concentration until a "critical" calcium concentration is reached, where the amount of precipitated LAS is substantial, and therefore, there is a dramatic decrease of foam height. As expected, the critical calcium concentration increases with LAS concentration increase. (ii) Foam stability depends on the initial LAS concentration zone. In the premicellar zone (around 10^{-3} M), foam stability is independent of calcium concentration, whereas in the postmicellar zone, the higher the calcium concentration, the higher the foam stability, until a calcium concentration is reached where foam stability remains constant. Again, the calcium concentration increases with the LAS concentration increase. This phenomenon can be explained by the fact that, as the CMC of the dissolved LAS increases, a higher calcium ion concentration becomes necessary to stabilize micelles.

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