Journal of Industrial Microbiology & Biotechnology (2002) 29, 149–154

www.nature.com/jim

REVIEW
A review of antifoam mechanisms in fermentation

R Pelton

McMaster Centre for Pulp and Paper Research, Department of Chemical Engineering, JHE-136, McMaster University, Hamilton, Ontario, Canada L8S 4L7

Antifoam (defoamer) chemicals are a crucial part of many commercial fermentation processes. Reviewed are the types of defoamers and their mode of operation. Also presented is a simple model, which simulates foam growth as functions of defoamer concentration, air hold-up, reactor volume and air flow rate.
Journal of Industrial Microbiology & Biotechnology (2002) **29,** 149–154 doi:10.1038/sj.jim.7000293

Keywords: defoamer; antifoam; formation foam control; defoamer modeling

Introduction

Many commercial fermentation processes depend upon antifoam addition to prevent excessive foam build-up. The goal of this paper is to review the scientific basis of antifoam technology. The types of commercial antifoams are surveyed with emphasis on current thinking on how antifoams function. Finally, discussed is a simple mathematical model for antifoam action, which may be useful for process models for design and/or control. The review is not exhaustive but instead highlights recent results and is biased towards our work. For more extensive reviews, see the book of Garrett [8], published in 1993. A much earlier review by Bryant [4] summarizes foam control issues in fermentation. Finally, mechanical foam breaking devices exist; however, these are not considered in this work.

Foam basics

Macroscopic characteristics

The physical chemistry of foams has fascinated physicists, chemists and children for generations. Although most modern texts on colloids and surface science [5] do a good job of describing foam fundamentals, the classic book by Boys [3], published first in 1911 and now available in a Dover edition, is worth reading. The major features of foam behavior are well understood; the very recent scientific literature deals with unresolved issues such as understanding what gives Champagne bubbles their unique characteristics [13] or what forces enable solid particles to attach to air bubbles [14].

In the context of fermentation, it is convenient to divide the fermentation reactor into two zones in which the dispersed air properties are very different. The heart of the fermentor is the *liquid zone* where the fermentation processes occur and in which dispersed air is present as individual air bubbles, providing a source of oxygen. Mixing causes bubble/bubble collisions. If during a collision, the thin film or *lamella* separating two bubbles ruptures, two bubbles become one. On the other hand, if the lamella does not rupture, the colliding bubbles will separate in flow.

The second zone is the *foam phase* which, like the head on a glass of beer, has a high volume fraction of air, is relatively stagnant and whose lamellae are long-lived. Such concentrated foams have been studied frequently. The key structural elements are thin films, called lamellae, separating the bubbles, and junction regions called Plateau borders where lamellas are joined (see Figure 1) [1]. Plateau identified the following two rules controlling foam geometry. The rules arise because foams attempt to minimize the total air/water interfacial area:

1. Along an edge in a foam structure, three and only three lamellae meet; the three lamellae are equally inclined to one another all along their edges to give a dihedral angle of 120°.
2. At a point four, only four edges meet; the four edges are equally inclined to one another in space; hence, the angle at which they meet is 109°.

Foams undergo two important processes — water drainage and bubble rupture or coalescence. Drainage is the flow of water from the foam phase and is driven by gravity and by curvature-induced pressure gradients (Laplace pressure). The literature contains many experimental and theoretical descriptions of foam drainage, which are beyond the scope of this review. The most important feature of foam drainage is that it is a slow process compared to the acceptable residence time of a foam bubble in a fermentation operation. In other words, we cannot wait for foams to drain in most fermentations.

Bubble rupture occurs when the lamellae separating two bubbles or a single bubble and the headspace rupture. Bubble/bubble coalescence leads to fewer, larger bubbles, whereas rupture to the headspace lowers the total foam volume. If the rate of bubble rupture to the headspace is slower than the rate of air injection into a fermentor, the foam phase volume increases with time. By contrast, if bubble rupture is fast relative to air injection, there will be little, if any, visible foam phase. The role of defoamers is to increase the rate of bubble coalescence, bubble rupture and release to the headspace.

Microscopic (chemical) properties of foams

Colloid science textbooks tend to treat foams as one-dimensional colloids since the thickness of foam lamellae are in the colloidal

Correspondence: Dr Robert Pelton, McMaster Centre for Pulp and Paper Research, Department of Chemical Engineering, JHE-136, McMaster University, Hamilton, Ontario, Canada L8S 4L7
Received 7 February 2002; accepted 14 May 2002

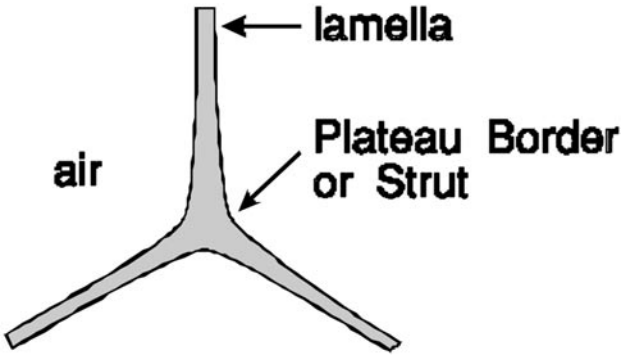

Figure 1 Intersection point of three bubbles in a foam phase.

(nano) size range. Indeed, many of the concepts of colloidal stabilization, such as the importance of double-layer, steric and van der Waals interaction, operate in foams. Electrically charged species at the lamella surface exert a repulsive force on the corresponding charged species on the opposite lamella surface — this effect opposes lamella drainage and thus is a foam-stabilizing effect. Similarly, hydrated polymeric species adsorbed on one lamella surface will repulse a similar layer on the opposite surface. Colloid scientists call this effect steric stabilization and, like electrostatic effects, it inhibits lamella thinning and thus promotes foam stability. By contrast, the ever-present van der Waals attractive forces tend to promote foam lamella thinning.

The phenomena described in the last paragraph are essentially static or equilibrium processes. In fact, foam stability is dominated by dynamic phenomena. For example, viscoelastic lamellae often obtained with adsorbed proteins are far more robust than inelastic lamellae obtained with simple adsorbed surfactants. Products formulated for high foam stability, such as dishwashing detergents, contain mixtures of surface active agents which give viscous, elastic lamellae.

Defoamers — what is in a name

The chemical technology and patent literature contain many references to both *antifoams* and *defoamers*. In some cases, the implication is that these are different chemicals doing different jobs in different ways. My view is that antifoams and defoamers are fundamentally the same. Perhaps the names reflect an application philosophy; defoamers are added when foam appears, whereas antifoams are added to the broth to prevent foam accumulation. Herein the terms antifoam and defoamer are used interchangeably.

Antifoams are found in nearly every water-based product and process including applications as diverse as soft drinks, antiacid pills and laundry detergents. The spectrum of antifoam suppliers is broad. Fortune 500 companies compete with very small formulators. Often small suppliers focus on specific markets, whereas major suppliers are active across the board.

Modern high-performance antifoams are formulated products containing many ingredients. When considering defoamer types, the major distinction is the solubility of the antifoam in water. Those that are soluble in cold (relative to the process or application temperature) water are sometimes called water-based or "cloud point" antifoams [2]. The latter name is a reference to their proposed mechanism of operation (see subsequent sections for mechanistic discussions).

Water-insoluble defoamer, herein called "oil-based," is the other major type. Oil-based antifoams are marketed as oil-in-water emulsions or as concentrates (sometimes called *compounds*) that are dispersed in the process stream, which is the broth in the case of fermentations. Mineral oil and/or silicone oil is the major component, whereas the foam-breaking active ingredient is a hydrophobic solid that may be surface-treated silica, wax particles, a silicone microgel or a combination. Also present are surfactants. The functions of the antifoam components are discussed in subsequent sections.

Selecting a defoamer for a given process or product is ultimately an exercise in trial and error. However, the choices can be limited by considering the active solids contents, and the cost and efficacy of commercial defoamers, which can span a broad range. The oil-based defoamers usually have the highest efficacy; however, oil-based defoamers ultimately contaminate processes and products because oil and hydrophobic particles are not compatible with water. By contrast, cloud point defoamers dissolve when the process temperature is lowered. On the other hand, cloud-point defoamers are not usually as effective. Requirements for food grade status decrease the choices; however, both oil-based and cloud point food grade products are available.

Antifoam mechanisms

The essential function of a defoamer is that it must enhance the rate of lamella rupture. Addition of an effective defoamer to a fermentor will increase the average bubble size in the liquid phase due to the increased bubble coalescence rate as well as decreasing the volume of the foam head. Although there is variety of defoamer types, all aqueous defoamers contain surface-active agents, contain or form water-insoluble phases and "wear out," often requiring some form of continuous addition. The following sections present a view of the defoaming mechanism.

Commercial defoamers are complicated formulated products containing surfactants, oil and one or more types of hydrophobic particles with an average particle size in the range 1–10 μm. For aqueous applications, the defoamers are either added as water-in-oil emulsions or as compounds that emulsify in the process. Defoamer emulsions are coarse with average emulsion droplet sizes in the range 5–50 μm.

The first step in the defoaming mechanism is the collision of an emulsion droplet with an air bubble resulting in the deposition of the defoamer onto the bubble surface (see Figure 2). Not every collision leads to the attachment of the defoamer emulsion droplet to the air bubble. The defoamer formulator must achieve a delicate balance when choosing surfactants for the defoamer. Surfactants are required to generate and colloidally stabilize the oil-in-water

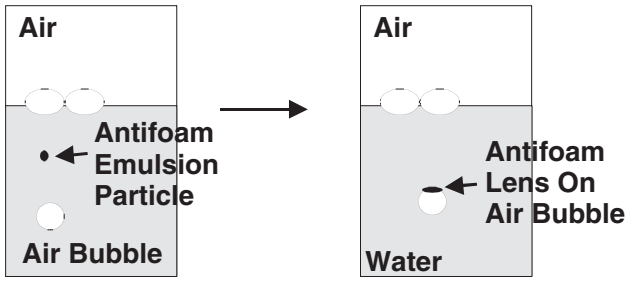

Figure 2 Step 1 — formation of a defoamer lens in the liquid phase.

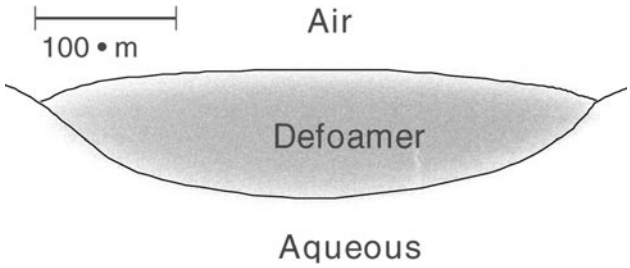

Figure 3 The cross-section of a defoamer lens sitting on gelled surfactant (adapted from Ref. [15]).

defoamer emulsion; however, if the surfactant is too effective at stabilizing the emulsion, the oil droplets will not adhere to the air bubbles.

Upon adhering to an air bubble, spherical emulsion droplets deform to give lenses on the water/air interface. Figure 3 shows the cross-section of a dyed defoamer lens measured by confocal laser scanning microscopy [15]. For these experiments, large (100 μm) defoamer oil droplets were placed on the top surface of gelled surfactant solution. This experimental configuration was a model for a lens on an air bubble. The gel immobilized the lens, permitting the imaging.

The shape of the lens (see Figure 3) reflects the balance of surface tension and gravitation forces. The lens has two interfaces (air/oil and water/oil) and a three-phase contact line where air, oil and water meet. Most mineral oil-based defoamers contain small amounts of free silicone oil introduced with the hydrophobic silica. Silicone oil is insoluble in water and mineral oil, so the lens shown in Figure 3 is likely to include a microscopic silicone oil phase, most probably near the air/mineral oil/water contact line. Therefore, a defoamer lens is a complex structure containing as many as four fluid phases (air, water, mineral oil, silicone) and a solid phase (silica or wax).

Since the hydrophobic particles are the active foam-breaking agents, the location of the particles in the defoamer lens is a crucial question. We used confocal microscopy to view the position of fluorescent labelled hydrophobic silica in the defoamer lens [15]. Figure 4 is an image looking down onto a defoamer lens on a gelled surfactant solution. The dark domains are the fluorescent silica particles. Optical sectioning of the lens with confocal microscopy showed that most of the hydrophobic silica were on the oil surface near the three-phase contact line. For foam breaking, it is crucial that the hydrophobic particles migrate to the oil surface. By changing or removing surfactants, it was possible to produce defoamer compositions in which the silica remained inside the oil phase — these compositions were ineffective defoamers [15].

The fundamental foam-breaking event occurs when two bubbles collide and coalesce because at lease one of the bubbles contains a defoamer lens. This is illustrated schematically in Figure 5, which shows three bubbles in a foam phase coalescing into one. Bubble/bubble coalescence can also occur in the liquid phase resulting in a larger average bubble size than would be present without defoamers. For a given volume fraction of dispersed air (hold-up), the larger the bubble size, the lower the air/water interfacial area and thus the lower the oxygen transport flux.

The microscopic details leading to lamella rupture have been the subject of many experimental and theoretical investigations [8].

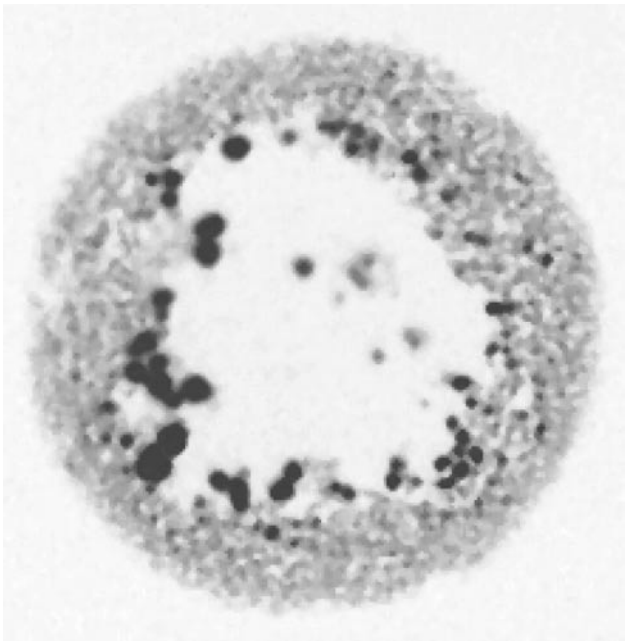

Figure 4 Top view of a defoamer lens sitting on gelled surfactant (not visible). The dark objects are fluorescently labeled hydrophobic silica sitting on the aqueous/oil interface [15].

There are a number of key experimental observations pertinent to the defoaming mechanism. These are as follows:

1. The shape of the hydrophobic particle is important — smooth particles are ineffective whereas particles with asperities and sharp edges break foams [6].
2. Hydrophobic particles are much more effective when suspended in mineral or silicone oil [7]. Presumably bare, unprotected hydrophobic particles rapidly adsorb components from the solution, which render them hydrophilic.
3. Effective defoamers spontaneously spread to cover the air/water interface with a very thin oil layer [9,11]. The remainder of the oil is present in the lens.
4. Hydrophobic particles smaller than 1 μm and larger than 10 μm are not very effective. Presumably the former are too small to have long, lamella-penetrating asperities, whereas very large particles are ineffective because it is not practical to have them present in sufficiently large numbers.

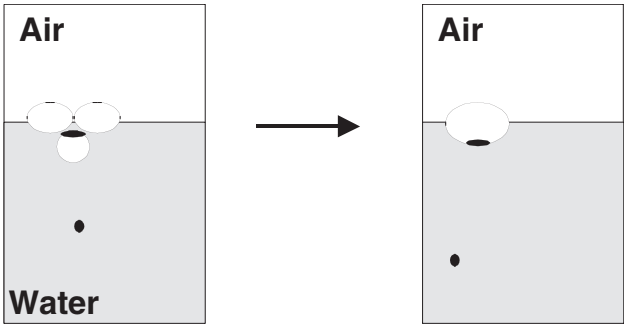

Figure 5 Bubble coalescence — the foam-breaking step.

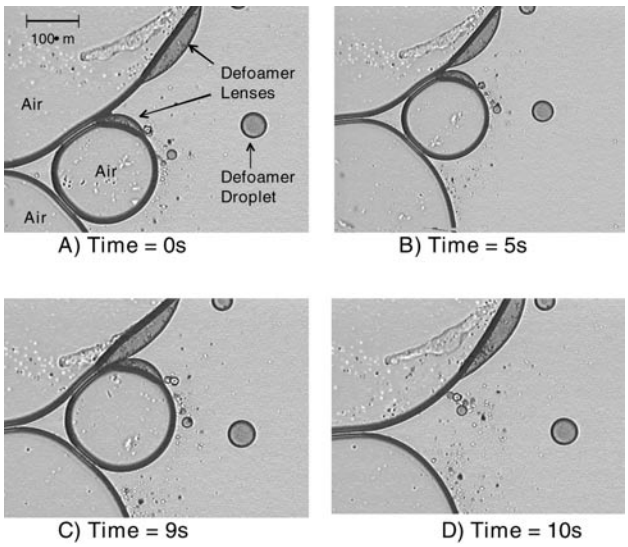

Figure 6 A sequence of captured video frames showing the migration of a defoamer lens into the lamella between two air bubbles causing their coalescence [15].

Any successful defoaming mechanism must explain these observations. Most of the early works concentrated on molecular mechanisms in the thinnest part of the lamella. These, however, failed to explain many of the observations. Ralston *et al* [14] proposed that defoamer lenses are too large to enter the lamella but instead function in the Plateau borders. In an effort to verify this mechanism, we conducted two-dimensional foam-breaking experiments in which a single layer of soap bubbles on the surface of a liquid was observed under a microscope [15]. Figure 6 shows some frames from a video. The defoamer emulsion contained an oil-soluble dye to enhance the observations. The first frame Figure 6A, shows three bubbles, two defoamer lenses and defoamer emulsion droplets in the liquid phase. With time, the two lenses moved together at the edge of the lamella in what would be the Plateau border [10]. Between the third Figure 6C, and fourth Figure 6D, pictures, the defoamer lens caused the small bubble to coalesce with the larger one. We can only guess at the key events that are submicroscopic. It seems reasonable to speculate that a lens with a surface covered with rugged hydrophobic particles bumps into the opposing lamella surface and, like a submerged iceberg hitting a ship's hull, the result is catastrophic rupture. This is illustrated in Figure 7.

The mechanisms by which cloud-point defoamers function are unknown [2]. One might speculate that a surfactant coacervate phase forms like an oil-based defoamer lens, which can rupture lamellae. On the other hand, there are no ragged hydrophobic surfaces in a coacervate. Perhaps they function at a molecular level by displacing the foam-stabilizing surfactants and polymers from the air/water interface.

Process models

Fermentations are particularly challenging applications for antifoams — airflow rates are high and many fermentation broths contain proteins and carbohydrates, which are excellent foam stabilizers. Obviously, the antifoam must not be toxic for micro-

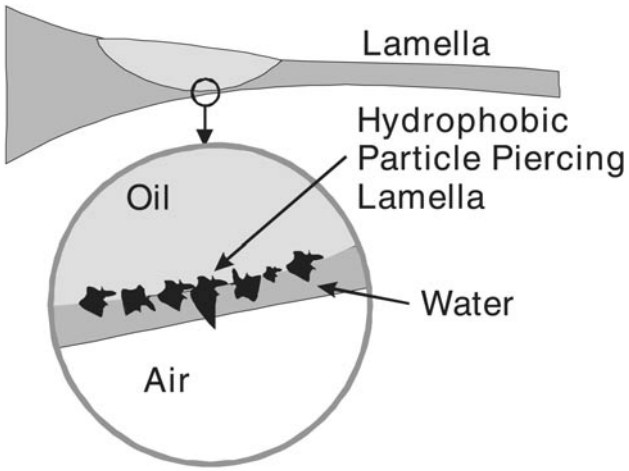

Figure 7 An illustration of defoamer-induced lamella rupture.

organisms. In some cases, there is a potential for antifoams to interfere with oxygen transport. Two obvious mechanisms for this are:

1. The average bubble size in the broth may increase and gas hold-up can decrease due to antifoam-induced bubble coalescence. The consequence is a lower total air/solution interfacial area, which in turn gives lower oxygen transport rates.
2. Oil or surfactants from the defoamer could be present as a spread film on the bubble surface inhibiting oxygen diffusion.

Strategies are needed for efficient defoamer addition. Simply adding excessive defoamer is not only expensive, it has the potential to inhibit productivity. Choice of the optimum defoamer addition strategy is an exercise in process optimization and process control — subjects beyond the scope of this review. However, it is relevant to consider simple, semiempirical models for defoaming, which could be incorporated into a fermentation process model.

Defoaming is a kinetic process requiring kinetic models. In particular, a realistic kinetic model must describe the slowest, rate-determining process. We developed a model that predicts foam volumes as functions of time. The key assumption is that the rate-determining step was the deposition of a defoamer emulsion droplet

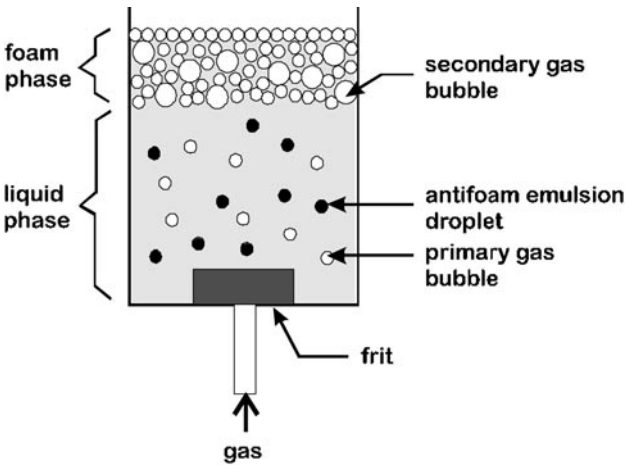

Figure 8 Schematic diagram illustrating the components of the model. Diagram adapted from Ref. [12].

onto a bubble to give a lens (Figure 2). The elements of the model are shown in Figure 8 [12]. Gas enters the liquid phase as "primary bubbles," which are assumed to have a radius, R_p. Also present in the liquid phase are antifoam emulsion droplets, which are assumed to be colloidally stable with respect to homocoagulation and monodisperse in terms of particle size. Each emulsion droplet is assumed to contain at least one hydrophobic particle capable of inducing lamella rupture.

It is assumed that the foam above the liquid phase contains two types of bubbles — primary bubbles from the liquid phase and secondary bubbles formed by coalescence of the primary bubbles.

The primary bubbles in the liquid phase are assumed to collect antifoam emulsion droplets by heterocoagulation. Upon entering the foam phase, those primary bubbles carrying at least one defoamer lens are then assumed to coalesce with neighboring primary bubbles yielding a secondary bubble with radius R_s. The secondary bubbles are assumed to be large enough to rise through the foam phase and rupture in the headspace. Thus, only primary bubbles that do not form secondary ones contribute to the volume of stable foam.

The mathematical formulation of the model is based on statistical arguments. For example, if the secondary bubbles consist of 50 primary bubbles, then the probability of a secondary bubble *not* forming is the probability that none of 50 primary bubbles collects a defoamer lens while traveling through the liquid phase.

The mathematical derivation has been published elsewhere [12] and the main equations are:

$$V(t) = \int_{t=0}^{t} R(t)dt \tag{1}$$

where $V(t)$ is the total volume of foam and $R(t)$ is the rate of foam rise (m^3/s) given by:

$$R(t) = r\left(1-\frac{1}{g}\right)^{\delta} \tag{2}$$

where r is rate of air flow into the fermentor (m^3/s); δ is number of defoamer droplets captured by an air bubble over a period of one bubble residence time (z seconds) of bubbles in the liquid phase;

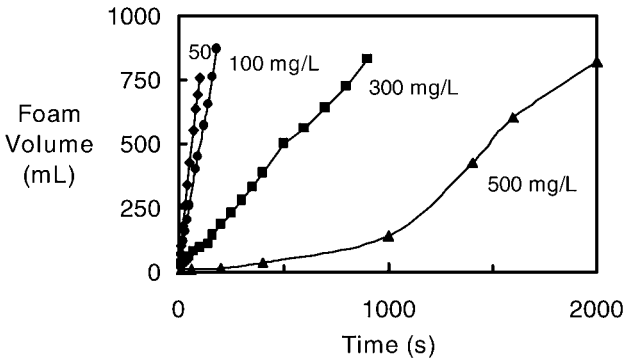

Figure 9 Foam volume *versus* gas flow time for 0.5 % Ivory Liquid™. The labels give the concentrations of SAG 1010 antifoam. The gas flow rate was 7 ml/s (adapted from Ref. [12]).

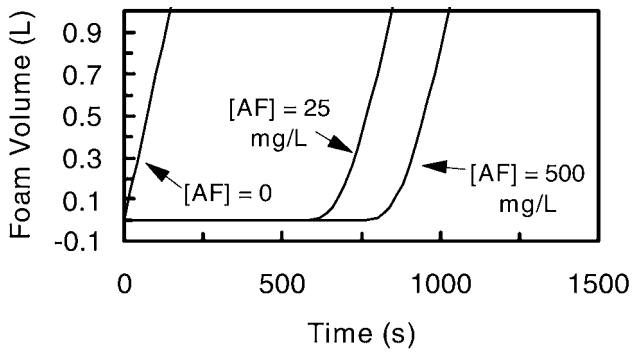

Figure 10 Simulated foam rise curves using Eqs. (1)–(4) varying only the antifoam concentration and time. Adapted from Ref. [12].

and g is the maximum number of secondary bubbles that could be created from the dispersed air in the liquid phase. δ is given by the following standard heterocoagulation kinetics theory where the constant K is the product of the concentration of primary bubbles and the coagulation rate constant. E_0 is the initial concentration of defoamer emulsion droplets and V_L is the total liquid volume:

$$\delta = (\exp(-K(t-z))-\exp(-Kt))E_0V_L. \tag{3}$$

The parameter g is given by the following where G is the volume fraction of air bubbles in the liquid phase (i.e., the hold-up).

$$g = \frac{V_L G}{\frac{4}{3}\pi R_s^3} \tag{4}$$

The model was evaluated by comparison with simple laboratory foam rise experiments in which foam volumes were measured as functions of time with a constant air flow rate. Figure 9 shows typical foam volume *versus* time curves for various defoamer concentrations. With low defoamer levels, the foam volume increased linearly whereas high defoamer concentrations gave little foam initially; however, the defoamer eventually was depleted and the foam growth accelerated.

The model contains only two unknown and thus adjustable parameters, K and R_s. However, these are independent of defoamer concentration so all of the curves in Figure 9 were fitted with a single value of these parameters. Figure 10 shows the simulated curves reflecting different values for E_0, the initial defoamer concentration. Most of the main features of the experimental curves were obtained, suggesting that our model may have some utility in process analysis.

Concluding remarks

Antifoam technology is sophisticated and evolving. The major mechanisms are understood; however, the detailed mechanistic contributions of some active ingredients remain elusive. Simple but important issues such as the average number of bubbles ruptured per emulsion droplet are not known. For example, consider the experiments summarized in Figure 9; to have low foam after 500 s required 500 mg/l defoamer in 250 ml of surfactant solution. Let

us assume that the average air bubble diameter was 2 mm and the defoamer emulsion diameter was 10 μm. The corresponding number of defoamer emulsion drops in the experiment was 2.4×10^8 (assuming specific gravity of 1) and the number of air bubbles was 8.4×10^5. Thus, in this example, 286 antifoam emulsion droplets were needed for every air bubble. In theory, one antifoam emulsion droplet can cause at least two air bubbles to coalesce. It seems to me that in this case and in perhaps all cases, there is scope for great improvements in defoamer efficacy.

References

1 Bikerman JJ. 1973. Foams. Springer-Verlag, New York.
2 Blease TG, JG Evans, L Hughes and P Loll. 1996. The mode of action of antifoams. In: Garrett PR (Ed), Defoaming Theory and Applications. Marcel Dekker, New York, pp. 299–324.
3 Boys CV. 1958. Soap Bubbles Their Colors and Forces Which Mold Them. Dover, New York.
4 Bryant J. 1970. Anti-foam agents. *Methods in Microbiology* vol. 2. Academic Press, New York, pp. 187–203.
5 Evans DF and H Wennerström. 1999. The Colloidal Domain. Wiley-VCH, New York, pp. 591–597.
6 Frye GC and J Berg. 1989. Antifoam action by solid particles. *J Colloid Interface Sci* 127: 222–238.
7 Frye GC and J Berg. 1989. Mechanisms for the synergistic antifoam action by hydrophobic solid particles in insoluble liquids. *J Colloid Interface Sci* 130: 54–59.
8 Garrett PR. 1993. The mode of action of antifoams. In: Garrett PR (Ed), Defoaming Theory and Applications. Marcel Dekker, New York, pp. 1–118.
9 Jha BK, SP Christiano and DO Shaw. 2000. Silicone antifoam performance: correlation with spreading and surfactant monolayer packing. *Langmuir* 16: 9947–9954.
10 Koczo K, JK Koczone and DT Wasan. 1994. Mechanisms for antifoaming action in aqueous systems by hydrophobic particles and insoluble liquids. *J Colloid Interface Sci* 166: 225–238.
11 Kulkarni RD, ED Goddard and B Kanner. 1977. Mechanism of antifoaming action. *J Colloid Interface Sci* 59: 469–476.
12 Pelton R. 1996. A model of foam growth in the presence of antifoam emulsion. *Chem Eng Sci* 51: 4437–4442.
13 Peron N, A Cagna, M Valade, C Bliard, V Aguie-Beghin and R Douillard. 2001. Layers of macromolecules at the champagne/air interface and the stability of champagne bubbles. *Macromolecules* 17: 791–797.
14 Ralston J, D Fornasiero and N Mishchuk. 2001. The hydrophobic force in flotation — a critique. *Colloids Surf A* 192: 39–51.
15 Wang G, R Pelton, A Hrymak, N Shawafaty and YM Heng. 1999. On the role of hydrophobic particles and surfactants in defoaming. *Langmuir* 15: 2202–2208.