



# Mechanistic understanding of the modes of action of foam control agents



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## ABSTRACT

In this paper we present briefly our current understanding of the modes of action of foam control agents (often termed “defoamers” or “antifoams”). After summarizing the background knowledge, reviewed in previous articles, the focus of the presentation is shifted to the antifoam studies from the last decade. The new experimental results, obtained by various research groups, are reviewed briefly to reveal the main mechanisms of antifoam action and the related key factors, governing the efficiency of the foam control agents. The role of the entry, spreading and bridging coefficients, of the entry barrier of the antifoam entities, and of the dynamics of surfactant adsorption is specifically discussed.

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## 1. Introduction

Foam control is needed in various technological processes and consumer products. Well known industrial examples are the pulp and paper production, fermentation, oil and gas recovery, froth flotation, wastewater treatment, textile dyeing, phosphoric acid production, food and beverages production, and chemical processing (agitation, distillation) [1–5]. Consumer and industrial products which are heavily relying on foam control during application are the machine detergents (washing powders, dish washing liquids), some pharmaceutical products

(e.g., antifatulence drugs for humans and cattle), paints and coatings, inks, metal working fluids, adhesives and sealants [5–11].

In most cases, the most efficient foam control is realized by adding a small fraction of chemical additives (typically, between 0.01 and 0.5 wt.%) whose main role is to prevent or reduce the formation of undesired foam [12–14]. These additives are usually termed “antifoams”. In some cases, one needs additional control realized by spraying (sprinkling) such substances over an already formed foam – in such a case, these additives are usually called “defoamers” [12,13]. In recent years, several consumer products benefitted from a limited amount of foam which has a desired lifetime, e.g. of the order of 0.5 to several minutes [5,13]. Illustrative examples are the machine washing detergents (certain amount of foam in the machine appears to the consumer as a clue for active detergent) and floor cleaning liquids

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(voluminous foam with short lifetime is best accepted by consumers) [5,6,11]. In this last type of applications, the most appropriate term for the used additives is “foam control agents”. Similar foam control is needed in froth flotation to achieve an efficient separation of the ore components [15,16].

Wide range of chemical substances has been used as antifoams, defoamers, and/or foam control agents. These include various oils (silicone, mineral, triglycerides, fluorocarbons), solid particles (silica, calcium soaps, plastic beads), mixtures of oils and particles (so-called antifoam “compounds”), various amphiphilic molecules (alcohols, fatty acids, fatty esters), or specific polymers with partial solubility in water (e.g., polymers, based on oxyethylene, oxypropylene and oxybutylene units) [1–14].

The mechanistic studies showed that in most cases, similar substances can be used for all three functions, as described above – antifoams, defoamers, and foam control agents. However, some subtle effects have been reported [13,14,17–20] – a substance that is a good defoamer could be a poor antifoam, etc. The reasons for these subtle effects have been clarified in several cases, by analyzing the mechanisms of action of the substances and the main controlling factors. Therefore, for brevity, in the following presentation we will use the word “antifoam” as a generic term (*viz.* as a synonym to defoamer and foam control agent) for all substances leading to reduced foaming, or used for foam suppression and control. Only if the specific function of the substance is important, the respective term is used to emphasize this specificity.

The rich chemistry of the agents, used for foam suppression or control, and their use in very wide range of applications, have created a lot of difficulties in the initial stages of understanding the mechanisms of antifoam action and the related optimization of the antifoam efficiency. The classification by chemical composition turned out to be not always helpful, because it remained unclear why some agent could be very efficient in a range of applications, while being very inefficient in others.

Starting from the pioneering works of S. Ross [21,22], and followed by the studies of Kulkarni et al. [23,24], Garrett [12,17], Wasan and collaborators [14,25–27], Aveyard et al. [28–31], Bergeron and Radke [32,33], and several others [34–39], it became clear that the physico-chemical analysis of the mode of antifoam action could be rather a useful approach toward understanding and rationalizing these complex systems. The main advantage of this physico-chemical approach is that the bewildering variety of compositions converges into a limited number of possible mechanistic scenarios, typically involving several subsequent steps in the foam destruction process. Most importantly, if the mechanism of antifoam action is defined, one can rationalize the efforts to optimize the antifoam by varying systematically only those critical physico-chemical parameters (contact angles, interfacial tensions, rheological properties, size of antifoam globules, etc.) which control the main steps in the mechanism.

The initial stage of this “physico-chemical” period of analysis was full of clever ideas and many speculations about the possible mechanisms of antifoam action. In 1980–1990s, mainly due to the studies of Garrett et al. [12,17], Wasan et al. [14,25–27], and Aveyard et al. [28–31], new experimental methods have been involved and some specific mechanisms have emerged as most probably explaining the experimental data. Still, the picture was rather fragmented and often the explanations proposed by the various authors were not compatible. With few exceptions, the proposed mechanisms remained at the level of very reasonable hypotheses, without discarding other possible scenarios.

By combining systematic measurements of the so-called “entry barrier” with the results from several other complementary methods, incl. optical observations of the behavior of the antifoam entities in the foam films and Plateau borders, Denkov et al. [13,18–20,40–54] succeeded in the late 1990s and beginning of 2000s to reveal unambiguously the mechanisms of action of silicone oil-based antifoams and, on this basis, to explain the most important trends observed experimentally in these systems. These studies, along with the essence from the

previous studies on the mechanisms of antifoam action, were summarized in two detailed reviews [13,19].

The main conclusions from these earlier studies will be briefly presented in Section 2 to provide the background for the more recent studies from the last decade, presented and discussed in Section 3. The final Section 4 summarizes the main conclusions from the recent antifoam studies.

Complementary information on some of these topics could be found in the recent reviews [5,55–57], each having a specific strength in the presentation. The paper by Hilberer and Chao [5] gives a detailed overview of the various industrial applications of antifoams and the specific requirements for each of these applications. The review by Miller [55] summarizes in a very clear and concise way the main results and conclusions from several important recent studies, especially those related to the in-situ formation of solid particles (calcium oleate and  $\text{CaCO}_3$ ) in foaming solutions, relevant to detergent applications. The review paper by Junker [56] is focused on the substances used for foam mitigation in fermentation systems and on the related processes. The review by Karakashev [57] makes an interesting historical retrospective of the development of the science about antifoams. Unfortunately, the latter review contains several imprecise explanations about the mechanisms of antifoam action (e.g., about the interpretation of  $E$ ,  $S$ , and  $B$  coefficients) and, therefore, should not be considered as a reliable source of information in this aspect.

## 2. Main modes of action of foam control agents

The main results and conclusions from the studies on the mechanisms of antifoam action, performed till ca. ten years ago, could be summarized as described below. More detailed discussion of these mechanisms, along with the description of the experimental results which clarified these mechanisms, could be found in Refs. [12,13,19,29].

### 2.1. Types of antifoam entities

Depending on the specific foaming agents (surfactants, proteins, or soluble polymers) one can realize an efficient foam control by using appropriate hydrophobic solid particles, oil drops or oil–solid compounds. In all these cases, the antifoam entities are dispersed as a separate phase in the foaming solution and, therefore, these antifoams are called “heterogeneous” antifoams [12–14,16,19,25]. The practical experience and the theoretical analysis of the experimental trends show that the surface of the dispersed particles (drops) should be sufficiently hydrophobic for effective antifoam action – therefore, these antifoams are sometimes called “hydrophobic” antifoams [5]. Usually, most efficient are the mixed oil–solid compounds, for reasons which are explained in Section 2.5.

In some specific cases, molecularly dissolved species (surfactant or polymer molecules) could also act as foam suppression agents – these are called “homogeneous” [5,11,16,58–60], “molecular” [5] or “amphiphilic” [11] antifoams. Usually, these substances are less efficient compared to the heterogeneous antifoams, but might have other important advantages – lower cost, no residual stains on the final product, food compatibility, etc. The effect on foaming of these substances is very system-dependent and difficult to predict. Therefore, the following discussion is focused mostly on the heterogeneous antifoams, except for Section 3.3 where we discuss the transition from homogeneous to heterogeneous mechanisms of antifoam action for the partially soluble antifoam substances (e.g., fatty alcohols and esters, and nonionic copolymers).

### 2.2. Fast and slow antifoams; role of entry barrier

The particular mode of foam destruction depends on the type of antifoam used (liquid, solid or mixture of both). From mechanistic viewpoint, it is appropriate to classify the antifoams into two large

groups, depending on the location where the antifoam entities enter the air–water surface and begin the foam destruction process, see Fig. 1 [13,18,19,45,46].

Thus, one can define (for a third group of antifoams, defined in the current review, see Section 3.1 below):

- Fast antifoams, which destroy the foam films within seconds, in the early stages of the film thinning process. These fast antifoams significantly reduce the foaminess of the surfactant solutions and destroy completely the quiescent foams in less than 1 min after stopping the foam generation. Therefore, these antifoams are preferred when the foam should be completely suppressed.
- Slow antifoams, which destroy the foam only after the antifoam globules are first entrapped and compressed by the shrinking walls of the Plateau borders and nodes in the processes of foam drainage. Several distinct stages are observed in the foam evolution, under the action of slow antifoams [13,18,19,45]. Some of these stages may continue for minutes or hours, and residual long-standing foam remains in the last stage of the foam decay process. One should emphasize that the slow antifoams are very appropriate if a specific foam evolution is required – e.g., formation of voluminous flash foam with limited lifetime.

The key factor for determining whether a given antifoam would act as fast or slow is the entry barrier, which characterizes how difficult it is for pre-dispersed antifoam globules to enter the foam film surfaces [12,13,46,54]. The entry barrier was quantified by the Film Trapping Technique [13,46,54], and a threshold value of  $\approx 15$  Pa was established (in terms of critical capillary pressure leading to drop entry) which separates the fast from slow antifoams. The antifoam globules with entry barrier lower than 15 Pa are able to break the foam films soon after their formation (viz. to act as fast antifoams), whereas the globules with higher entry barrier are expelled from the foam films into neighboring Plateau borders (viz. they may act as slow antifoams).

The drop entry barrier depends on various factors, such as the presence of co-surfactants, electrolytes and solid particles; size of oil drops; and the chemical nature of the oil [12,13,17,20,46,48,54]. All these factors can be used for control of the antifoam effect to achieve a desired result – fast foam destruction or pre-defined control of foam decay. Any of the heterogeneous antifoam entities (particles, drops, or compounds) could act as fast or slow, depending on the specific conditions and the related entry barrier of these entities.

### 2.3. Modes of antifoam action of solid particles

It is well established now [12,15,28,37] that the solid particles destroy the foam films by the bridging–dewetting mechanism, which consists of two main stages: (i) the solid particle comes into contact with

the two opposite surfaces of the foam film, making a solid bridge between them, and (ii) the liquid dewets the particle surface and the foam film gets perforated at the three-phase contact line on the particle surface (see Fig. 2).

The efficiency of solid particles as antifoam entities depends mainly on their hydrophobicity, shape and size [12,15,28,37]. Particle hydrophobicity could be varied in wide range by chemical grafting or by physical adsorption of surfactant and/or polymer molecules [61,62]. For complete dewetting of solid particles with smooth convex surface (spheres, ellipsoids), the three phase contact angle air–water–solid should be larger than  $90^\circ$  [12,13,15,30,31,63]. Particles with sharp edges (cubes, prisms, star-shaped and irregularly shaped particles) can destroy the foam films even when their contact angles are lower, ca.  $30\text{--}40^\circ$ , if the particles are properly oriented inside the foam film [15,37,63]. In addition, the presence of sharp edges strongly facilitates the particle entry and bridge formation [13,15]. The size of the solid particles becomes an important issue for their antifoam action only if the particles become too small (with radius smaller than ca.  $1\ \mu\text{m}$ ) [12,13,42]. In fact, at given weight concentration of particles, an optimal size of the antifoam entities exists, in the range of several micrometers, because the smaller size corresponds to higher number concentration of particles, that is, to higher probability for particle entrapment in the foam films and to subsequent film rupture.

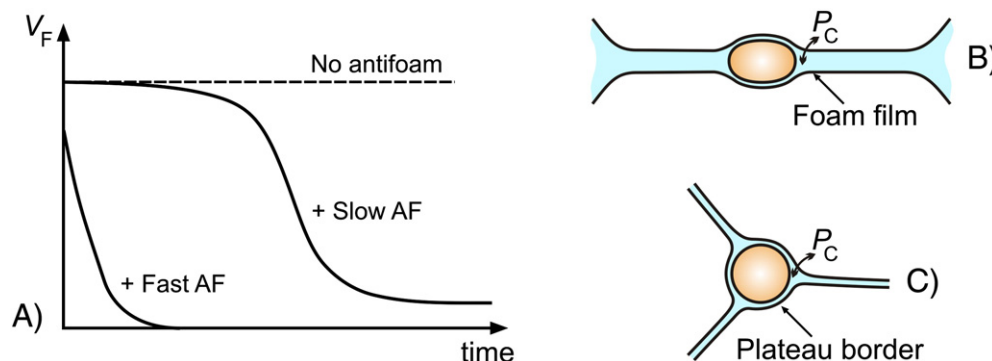
If solid particles are able to enter and bridge the film surfaces, but are too hydrophilic to act as antifoam entities, these particles can strongly enhance the foam stability by several mechanisms, e.g. stabilizing thick equilibrium foam films (Pickering stabilization) [62,64–69] decelerating the water drainage from the foam by plugging Plateau borders [14,27,68,69], or arresting the bubble coarsening through gas diffusion across the foam films (blocking Ostwald ripening of the bubbles) [69,70].

### 2.4. Modes of antifoam action of oil droplets; role of entry, spreading and bridging coefficients

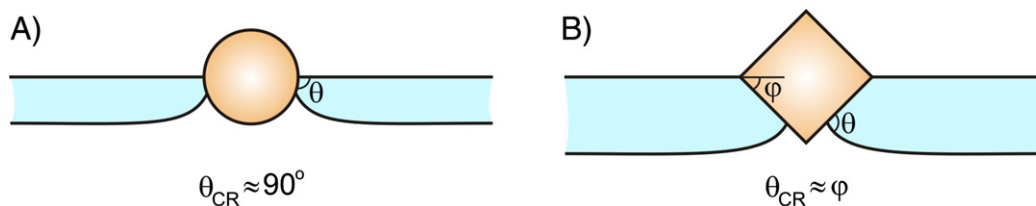
Oil drops were shown to destroy foams by various mechanisms: bridging–stretching [40], bridging–dewetting [12], and several mechanisms related to oil spreading [13,18,48,51].

In any of the bridging mechanisms, the oil drop first connects the two film surfaces, that is, makes a “bridge” between them (Fig. 3). Next, two different scenarios for film destabilization are possible:

In the bridging–stretching mechanism (Fig. 3C–D), the oil bridge deforms, driven by the requirements of the laws of capillarity – curvature of the various interfaces which ensures balance of the capillary pressures (Laplace law), and appropriate three-phase contact angles satisfying the vectorial balance of the interfacial tensions at the three-phase contact lines (Neumann triangle). As shown theoretically in Ref. [41], if the bridging coefficient  $B > 0$  (see Eq. (2) below for the definition of  $B$ ), the laws of capillarity could not be satisfied for such oil bridge and



**Fig. 1.** Comparison of the fast and slow antifoams with respect to (A) foam evolution after foaming, (B, C) structural foam element where the antifoam globules enter the solution surface and break the foam films (see also Table 1). The capillary pressure  $P_C$  expresses the compression exerted on the antifoam globule by the solution surfaces – depending on the critical compression pressure, needed to induce globule entry on the solution surface (i.e. on the so-called “entry barrier”), the antifoam may behave as fast or slow.



**Fig. 2.** Schematic presentation of the bridging of foam film surfaces by a solid particle. (A) For spherical particle the dewetting and film rupture occur when the contact angle,  $\theta$ , measured through the liquid phase, is larger than  $\theta_{CR} \approx 90^\circ$ . (B) Cubic or cone-shaped particle with slope angle,  $\varphi$ , of the particle wall (with respect to the plane of the foam film) can be dewetted if the contact angle,  $\theta$ , is larger than  $\theta_{CR} \approx \varphi$ .

the latter extends in radial direction until it ruptures in the bridge center.

Alternatively, in the bridging–dewetting mechanism (Fig. 3E–F) the bridge has no time to deform and the surfaces of the foam film dewet the oil drop surface, thus leading to film rupture at the periphery of the oil bridge.

As proven theoretically by Garrett [12,71,72], the requirement for rupture of the foam films by deformable oily droplets is  $B > 0$  for either of the bridging–dewetting or bridging–stretching mechanisms. If  $B < 0$  stable oil bridge is formed in the foam film, without causing film rupture, Fig. 3G–H.

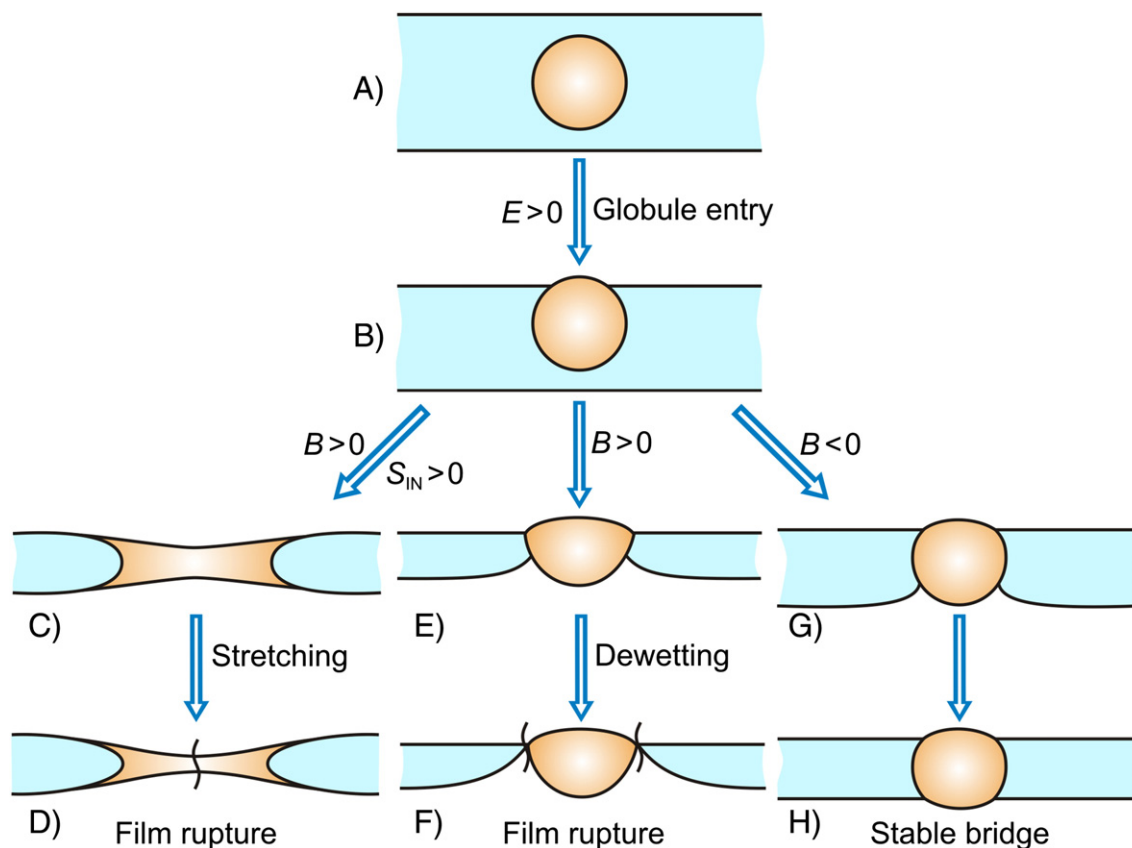
The silicone oils and silicone-oil based compounds, known to spread well on the surface of the foaming solutions, were found to break the foam films via the bridging–stretching mechanism [40]. In contrast, some compounds based on non-spreading mineral oils, were observed to break the foam films via bridging–dewetting mechanism (unpublished results). It is still unclear whether this trend is general, or it reflects only the specific properties of the oils, used in these studies.

In any of these mechanisms, the antifoam globules should first enter the solution surface (Fig. 3A–B). Two different types of factors, thermodynamic and kinetic ones, determine the possibility for realization of drop entry. The kinetic aspect is usually discussed in terms of the drop entry barrier [12,13,34,46,48] whereas the thermodynamic aspect is discussed in terms of the oil entry coefficient [12,30,71]:

$$E = \sigma_{AW} + \sigma_{OW} - \sigma_{OA} \quad (1)$$

where  $\sigma_{AW}$ ,  $\sigma_{OW}$ , and  $\sigma_{OA}$  are the interfacial tensions of the air–water, oil–water and oil–air interfaces, respectively, see Fig. 4.

The value of  $E$  depends on variety of factors, such as the used oil, and the type and concentration of surfactants, electrolytes, and co-surfactants. Negative values of  $E$  correspond to complete wetting of the oil drop by the aqueous phase. Therefore, pre-emulsified oil drops with  $E < 0$  remain immersed inside the aqueous phase and cannot form oil bridges between the surfaces of the foam films or Plateau borders. Even if an oil phase has appeared on the solution surface (e.g., as a result of oil deposition



**Fig. 3.** Schematic presentation of the entry (A → B) of an oily globule at the foam film surface, at positive entry coefficient,  $E > 0$ , and sufficiently low entry barrier. Bridging of the foam film surfaces may occur at  $E > 0$  for both positive and negative values of the bridging coefficient,  $B$ . At positive bridging coefficient,  $B > 0$ , the foam film is unstable and may rupture by bridging–stretching (C → D) or bridging–dewetting mechanism (E → F). If the bridging coefficient is negative,  $B < 0$ , the oil bridge is stable and the foam film does not rupture.



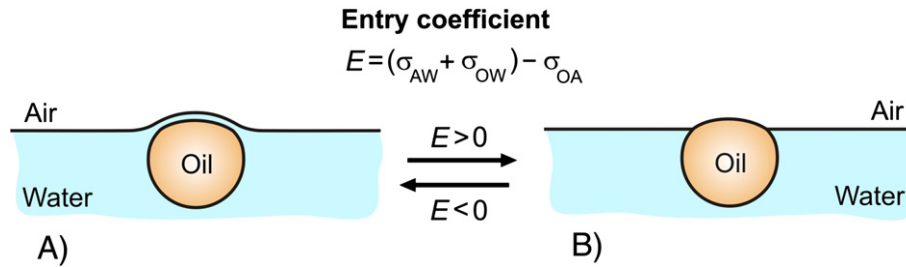


Fig. 4. Schematic presentation of the physical meaning of the entry coefficient,  $E$ .

from the air phase in the case of defoamer application), this phase would spontaneously immerse into the aqueous phase, because this is the thermodynamically favored configuration. Note that, due to the definitions of the three coefficients, negative value  $E < 0$  implies that the other two coefficients are also negative,  $S < 0$  and  $B < 0$ . As a result, oils with negative  $E$  are certainly inactive as antifoams [12,30,71]. In contrast, positive values of  $E$  correspond to well defined equilibrium position of the oil drop/lens at the air–water interface. Hence, when the oil has positive  $E$  and the entry barrier is not-too-high, stable or unstable oil bridges can be formed in the foam films [12,13,16,30,71]. On the other hand, positive value of  $E$  does not guarantee appearance of the oil droplet on the solution surface, because the entry barrier is equally important – high entry barrier could prevent the drop entry process even for highly positive entry coefficients.

It is worth emphasizing that positive values of  $E$  are needed for the formation of an oil bridge between the two foam film surfaces, because this process is equivalent to the entry of a globule on the two opposite surfaces of the foam film. Therefore, the thermodynamic condition for the formation of an oil bridge is equivalent to the condition for globule entry,  $E > 0$ . On the other hand, the mechanical stability of the formed bridges depends on the value of the bridging coefficient, introduced by Garrett [72] (see Fig. 5)

$$B \equiv \sigma_{AW}^2 + \sigma_{OW}^2 - \sigma_{OA}^2. \quad (2)$$

As proven theoretically by Garrett [12,72] an oil bridge cannot acquire a mechanically stable configuration in the foam film if  $B > 0$ . In a later study Denkov deepened this analysis for the bridging–stretching mechanism [13,41] and found an additional effect of the oil bridge size. One can show theoretically that positive values of  $B$  necessarily imply positive entry coefficient,  $E$ , while the reverse statement is not always true [71]. Concluding, oils with  $B > 0$  form unstable bridges, while

oils with  $B < 0$  could form stable bridges (if  $E > 0$ ) or might be unable to form bridges (if  $E < 0$ ).

For oils with appropriate bridging coefficient, the antifoam efficiency of the oil drops correlates well with the drop entry barrier [13,19,46]. In the following discussion we use the term “entry barrier” as defined in Refs. [13,46], namely, the entry barrier is quantified as the capillary pressure of the air–water interfaces, which compress the antifoam globule (in the foam film or in the Plateau border, see Fig. 1B, C), in the moment of drop entry. The main advantages of this definition are that it can be measured directly with real antifoam globules of micrometer size, e.g. by the Film Trapping Technique [46,54], and that it could be directly linked to the actual capillary pressures in real foams [13,46,48].

As explained in Section 2.2., the oil drops behave as fast antifoams and break the foam films by the bridging mechanisms if the entry barrier is below the threshold value of  $\approx 15$  Pa. If the entry barrier is higher, the oil drops destroy the foam as slow antifoams by bridging or spreading mechanisms, after drop entry in the Plateau borders. In typical surfactant solutions with concentration higher than the critical micelle concentration (CMC), the oil drops usually behave as slow antifoams because their entry barrier is higher than 15 Pa. The most efficient way of reducing the entry barrier of oil drops was found to be the introduction of properly hydrophobized solid particles in the oily phase (Section 2.5).

Let us discuss briefly the effect of oil spreading on the antifoam action. It has been known for years that the spreading oils are usually more active as antifoams than the non-spreading ones [21,25,34,39]. To discuss in quantitative terms the spreading affinity of the oils, their spreading coefficients are used [12,29–31,71,72], see Fig. 6:

$$S = \sigma_{AW} - \sigma_{OW} - \sigma_{OA}. \quad (3)$$

One should distinguish between the initial spreading coefficient,  $S_{IN}$  (defined by using  $\sigma_{AW}$  in the absence of spread oil on the solution

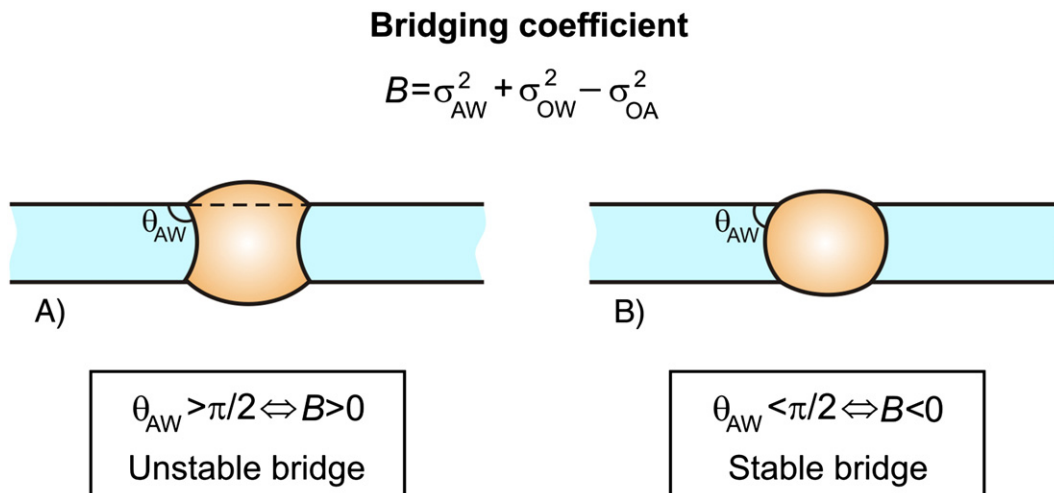


Fig. 5. Schematic presentation of the physical meaning of the bridging coefficient,  $B$ .

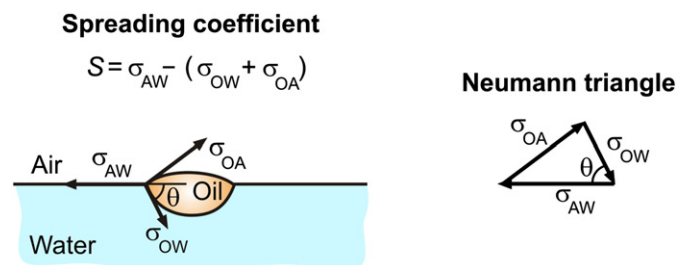


Fig. 6. Schematic presentation of the physical meaning of the spreading coefficient,  $S$ .

surface) and the equilibrium spreading coefficient,  $S_{EQ}$  ( $\sigma_{AW}$  in the presence of spread oil) [12,30,72]. Rigorous thermodynamic analysis shows that  $S_{EQ} \leq 0$ , while  $S_{IN}$  might have an arbitrary sign [12,30,72]. Note that  $S_{EQ} \leq S_{IN}$ , because  $\sigma_{AW}$  decreases upon oil spreading. The initial spreading affinity, when the oil is first deposited on the solution surface, is characterized by  $S_{IN}$ . Negative value of  $S_{IN}$  means that the oil does not spread on the surface. Positive  $S_{IN}$  means that the oil would spread as thin or thick layer. On its turn,  $S_{EQ}$  brings information about the thickness of the equilibrium spread layer: if  $\sigma_{AW} = \sigma_{OW} + \sigma_{OA}$  (i.e.  $S_{EQ} = 0$ ), the oil spreads as a thick layer, whereas negative  $S_{EQ}$  and positive  $S_{IN}$  imply the appearance of a thin equilibrium layer, possibly co-existing with oil lenses. The comparison of Eqs. (1) and (3) shows that positive  $S > 0$  necessarily corresponds to positive entry coefficient,  $E > 0$ , because  $\sigma_{OW}$  is positive.

The critical analysis of the available experimental results showed that positive initial spreading coefficient,  $S_{IN}$ , and high spreading rate could enhance significantly the antifoam activity, without being a necessary pre-requisite for antifoam action [13,19]. Several mechanisms were proposed (and proven in several cases) to explain this positive effect of spreading for the antifoam action of oils. For example, it was firmly established that the oil spreading may: facilitate the antifoam dispersion inside the foaming solution, thus increasing the number concentration of the antifoam globules [51]; reduce the entry barriers of the emulsified antifoam globules [51]; and facilitate the oil bridge rupture [41]. In addition, oil spreading could directly induce foam film rupture, as shown in Refs. [13,18,45]. The optical observations in these studies showed that the spreading oil induces capillary waves of large amplitude on the surface of the foam films. These waves often led to foam film rupture within several seconds, even at relatively large average film thickness  $h_{AV} \approx 1 \mu\text{m}$ . As discussed in Ref. [13], the spreading oil probably “sweeps” some of the surfactant adsorbed on the foam film surface, which results in film destabilization.

Summarizing the explanations in this section, positive bridging coefficient (which implies positive entry coefficient as well) is a necessary condition for realization of the bridging mechanisms by oily antifoams, whereas positive initial spreading coefficient could be an important factor for enhancing antifoam activity (without being a pre-requisite for antifoam action [17]). Negative entry coefficient definitely leads to absence of antifoam action.

Two additional comments are important in this context. First, the role of entry barrier is equally important to that of the  $E$ ,  $S$ , and  $B$  coefficients – high entry barrier leads to very low (if any) antifoam activity, even for oils with highly positive coefficients [13,18,34,45,46]. Second, the equilibrium values of the interfacial tensions are usually inappropriate for calculating the values of  $E$ ,  $S$ , and  $B$  in dynamic foams (e.g., during foaming). Instead, the dynamic interfacial tensions should be used to explain the antifoam effect in dynamic foams [20,59]. This is particularly important in the context of foam control. These dynamic effects on the antifoam efficiency are addressed in Section 3.1.

### 2.5. Specific features of the antifoam action of mixed solid–oil compounds

The typical oil–solid compounds with large excess of oil destroy the foam by the same mechanisms as the oil drops. The main difference

between compounds and oil drops is that the compound globules usually exhibit much lower entry barrier (due to the pin effect of the solid particles, Fig. 7), which allows them to act as fast antifoams even in solutions of high surfactant concentration [13,19,46].

The strong synergistic effect between oil and solid particles in the antifoam compounds is due to the complementary roles of the two components. The main role of the solid particles is to destabilize the asymmetric oil–water–air films, facilitating in this way the oil drop entry. The main role of the oil is to ensure deformability of the compound globules and to spread on the solution surface. The globule deformability is an important pre-requisite for the foam film rupture by the bridging–stretching mechanism [40,41]. Furthermore, as discussed by Garrett [12] and Denkov [41] in most cases the spherical oil drops should first deform and make a flattened lens on one of the foam film surfaces to make possible the bridging–dewetting mechanism. Thus we see that the globule deformability is usually needed in both bridging mechanisms. On its turn, the oil spreading facilitates the entry of the antifoam globules and the foam film rupture. In some systems related to mineral flotation (when the solid particles are in excess and no strong surfactants are used), the oil can coat the particle surface rendering it more hydrophobic [37].

As shown in Refs. [19,42,53], the observed process of exhaustion (deactivation) of the oil–solid compounds, in the course of foam destruction, is due mainly to the gradual segregation of the oil and solid particles into two inactive populations of globules: particle-free and particle-enriched. The particle-free globules are unable to enter the foam film surfaces due to their high entry barrier, whereas the particle-enriched globules are non-deformable and, hence, cannot break the foam films.

### 3. Recent progress in the mechanistic understanding of foam control agents

Generally said, the original studies in the area of antifoams from the last decade have confirmed the conclusions from the previous studies. Furthermore, they showed how the various elements of the antifoam mechanisms, discussed above, could appear in rather complex combinations, when considering the variety of antifoam chemistry used in the practical applications. Below we summarize the main general patterns which have emerged from these recent studies. The focus is again on the general physico-chemical processes and phenomena which have been observed with the various antifoam substances.

#### 3.1. Role of foam dynamics for the antifoam activity

Very often, the addition of oils to foaming solutions leads to a significant reduction of the foam volume while agitating the system (e.g. during foaming), while the effect of the same oil on the still foam, formed after the agitation cycle, is either very limited or very slow, see Fig. 8 and Table 1. This typical case is very important in the context of foam control, because it ensures a desired amount of foam, without leading to gradual

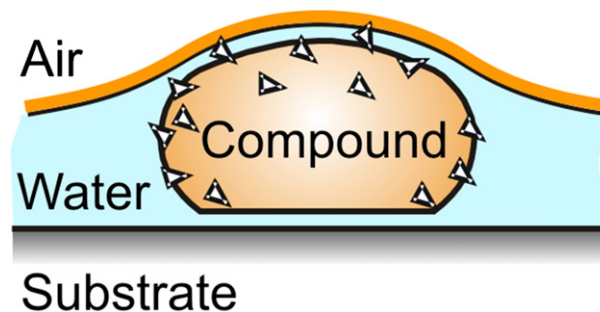
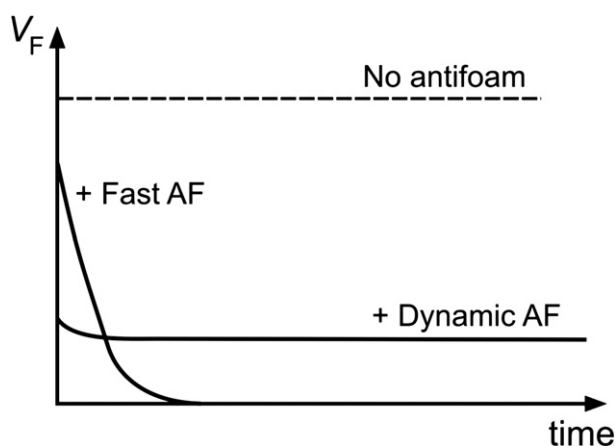


Fig. 7. Schematic presentation of the “pin effect” of hydrophobic solid particles in mixed oil–solid antifoam compounds, leading to reduced entry barrier of the antifoam globules.



**Fig. 8.** Comparison of the fast and dynamic antifoams with respect to foam evolution after foaming. The dynamic antifoams are active during foam agitation only, when the bubble surfaces are not covered with equilibrium adsorption layers. Once the foam agitation is stopped, the surfactant forms complete adsorption layers which preclude the further antifoam action. Therefore, these antifoams strongly reduce the initial foam volume without reducing significantly the foam stability of still foam.

excessive foam accumulation which might be a serious problem, e.g. in washing machines and during paper production [5,6].

The analysis of the experimental results shows that during foaming, the antifoam entities are able to destroy the foam films (thus resembling the fast antifoams) whereas after ceasing the agitation, the same entities are accumulated in the Plateau borders and act as slow antifoams. Therefore, from the viewpoint of the mechanisms of antifoam action, this situation does not fit directly either the concept of slow antifoams or the concept of fast antifoams, as described in Section 2.2. This behavior is very typical for slowly adsorbing foam stabilizers, such as nonionic surfactants, proteins and synthetic polymers. To emphasize the fact that the antifoams in these systems are active exclusively during foam agitation, under dynamic conditions, we specify them as “dynamic antifoams”, see Table 1 and Fig. 8.

The reasons for this peculiar behavior are clear now. During agitation, the surfactant adsorption layers are not completed in these systems. As a result, the surface tension of the foaming solution, and the related to it entry barrier and  $E$ ,  $S$  and  $B$  coefficients (Eqs. (1)–(3)) have very different values, as compared to those corresponding to the completed equilibrium adsorption layers (unpublished results). This situation is very difficult for quantitative mechanistic and theoretical analysis, because there are no straightforward procedures which would allow one to measure the non-equilibrium values of these key parameters, related to the antifoam activity. The main problem is that the measurements used to determine these quantities (interfacial tension measurements, Film Trapping Technique, observations of foam films) can be realized only with surfaces which are aged for much longer time (typically tens of seconds or minutes), when the interfacial properties are very close to equilibrium.

The best strategy, proposed so far to study such dynamic antifoams is the following. By using maximum bubble pressure method, one can measure the dynamic surface tension of the foaming solutions at surface age, representative for the bubble formation process during foaming. Usually, the surface age of 0.1–1 s is considered as representative for the typical foaming process. This dynamic surface tension reflects the density and composition of the dynamic adsorption layer, formed during foaming. To mimic the interaction of the antifoam with such dynamic surface layer, one can do the following (unpublished results):

First, one can introduce the dynamic surface tension  $\sigma_{AW}(0.1\text{ s})$  in Eqs. ((1)–(3)) and to calculate the dynamic  $E$ ,  $S$  and  $B$  coefficients, which represent much better the interaction of the antifoam oil with the dynamic solution surface, realized during foaming. Very often, highly positive values of  $E$ ,  $S$  and  $B$  coefficients are determined with the dynamic surface tension, whereas these coefficients might be

**Table 1**

Comparison of the main characteristics of the fast, slow and dynamic antifoams. “Reference” here means the same foaming solutions without any antifoam added.  $\tau_{1/2}$  denotes the time needed for destruction of half of the initial foam column, after stopping the foam generation process.

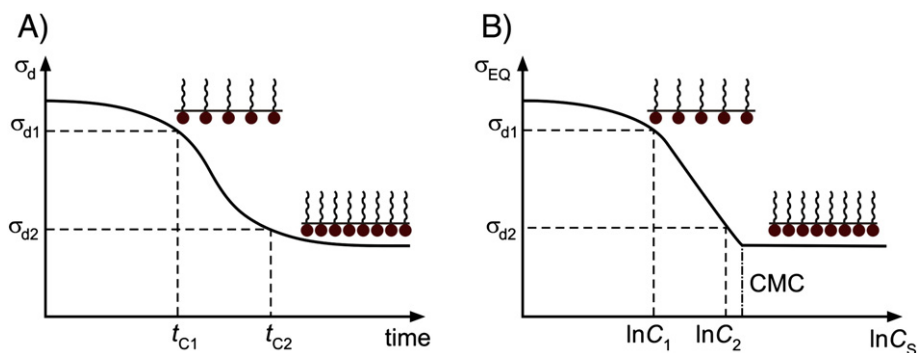
| Type of antifoam | Foaminess   | Foam stability               | Other features                    |
|------------------|---|------------------------------|-----------------------------------|
| Fast             | $\leq$ reference  | $\tau_{1/2} \approx$ seconds | No residual foam                  |
| Slow             | $\approx$ reference (could be slightly higher or lower) | $\tau_{1/2} \approx$ minutes | Residual foam                     |
| Dynamic          | $<$ reference   | $\tau_{1/2} \approx$ hours   | AF active during agitation mostly |

negative or equal to zero for the equilibrated solution surfaces, because  $\sigma_{AW}(0.1\text{ s}) > \sigma_{AW}(\text{equil})$ .

Second, one can perform model experiments, aimed to analyze the interaction of the antifoam globules with the foam films by using diluted model surfactant solutions, having equilibrium surface tension, similar to the dynamic surface tension of the actual foaming solutions – see Fig. 9. Note that this implies one to use surfactant solutions which are below the CMC in these model experiments, because only these solutions have high equilibrium surface tension which can mimic the dynamic surface tension of the actual foaming solution. Thus one can determine an entry barrier and observe microscopically the entry of the antifoam globules in the foam films, for surfaces which are covered with uncompleted adsorption layers, representing much better the conditions during foaming. The experiments showed that much lower entry barriers are measured with such uncompleted adsorption layers, compared to the equilibrium adsorption layers (unpublished results). In agreement, the globules may easily break the foam films, formed from these model (diluted) surfactant solutions, whereas the same globules escape from the foam films and accumulate in the Plateau border when the foam films are formed from the original foaming solutions with  $C_S > \text{CMC}$ .

Using the above procedures, one could explain quantitatively or semi-quantitatively a variety of experimental data about the activity of antifoams during foaming, which cannot be explained even qualitatively by using the values, measured with equilibrated interfaces. One should note that the experimental procedure described above has one drawback – the reduced surfactant concentration in the model solutions leads to different oil–water interfacial properties, compared to those in the original foaming solutions. This deficiency of the procedure seems to have smaller impact to the experimental results (viz. this effect can be neglected in most cases), because the values of the solution surface tension,  $\sigma_{AW}$ , are usually much higher than those of the oil–water interfacial tension,  $\sigma_{OW}$ , and, therefore, the changes in the surface tensions are more important for the observed trends.

One important consequence of this type of analysis is the possibility to explain the observed strong effect (in some systems) of the hydrodynamic conditions during foaming on the activity of dispersed antifoams. For example, given antifoam could be very active in the highly dynamic Ross–Miles test and completely inactive (in the time scale of minutes) in the bubbling method (unpublished results). The analysis of the experimental data showed that this different activity of the antifoams in the same foaming solution is related to the different characteristic times between the moment of bubble (surface) formation and the moment of bubble–bubble collision, which depends on the method of foaming. In the Ross–Miles test, the bubbles collide with each other very soon after their formation and this characteristic time is of the order of 0.1–0.2 s. Therefore, in the moment of bubble collision, the dynamic adsorption layers are incomplete, so that the antifoam globule entry and the related bubble–bubble coalescence are realized easily (the experiments showed that, in the absence of antifoams, the bubbles are protected from coalescence by such incomplete adsorption layers). In contrast, in the bubbling method (release of bubbles through pores from the bottom of the foaming container) the bubbles float in the surfactant solutions for one



**Fig. 9.** Choice of surfactant concentrations in model experiments, aimed to mimic the dynamic bubble surfaces during foaming. From measured dynamic surface tension  $\sigma_d(t)$  and the characteristic time of the foaming method, viz the typical time before two newly created bubbles collide with each other,  $t_c$ , one could determine the characteristic dynamic surface tension,  $\sigma_d$ , for the used foaming method. In (A) two characteristic times,  $t_{c1}$  and  $t_{c2}$ , are shown to illustrate that the shorter characteristic time corresponds to higher  $\sigma_d$ . For example,  $t_c$  for the Bartsch method is estimated to be 0.1–0.2 s, whereas  $t_c$  for the bubbling (sparging or Bikerman) test could be as long as 1–2 s. Next, one could take a surfactant solution with concentration below the critical micelle concentration (CMC) to obtain equilibrium adsorption and equilibrium surface tension, equal to  $\sigma_d$  in the foaming test. Working at this lower surfactant concentration, allows one to make experiments (e.g., measuring entry barrier or characterizing foam film stability) at reduced surfactant adsorption, corresponding to that on the dynamic bubble surfaces during foaming.

to several seconds, driven by gravity, before reaching the foam accumulated on top of the foaming solutions. This long floating time of the bubbles allows the formation of (almost) complete adsorption layers, which are able to protect much better the bubbles against entry of the antifoam globules and the related bubble–bubble coalescence.

An additional dynamic aspect of the antifoam action by solid particles was studied by Joshi et al. [73]. Using insoluble fatty alcohol particles with micrometer size and a two-colliding-bubbles technique, these authors observed a re-entrapment of the antifoam particles in the zone of contact of the colliding bubbles, viz. the particles were seen to move from the periphery toward the center of the bubble contact zone. This re-entrapment is a non-trivial phenomenon, because it is opposed by the strong hydrodynamic forces (generated by the flowing liquid, squeezed from the contact area) which push the antifoam particles away from the contact zone. The authors attributed this phenomenon to Marangoni effects, i.e. to appearing gradient in the surface tension on the bubble surface, created by the nonionic surfactant used to stabilize the antifoam suspension. The main role of this re-entrapment is in facilitating the bridging of the bubble surfaces by the antifoam particles, with subsequent coalescence of the colliding bubbles by, presumably, bridging–dewetting mechanism.

### 3.2. In-situ formation of solid particles with antifoam activity

In several studies [74–76], it was demonstrated that solid particles with significant antifoam activity could be formed directly in the foaming solution, if calcium ions are present in the aqueous phase, which is usually the case when these solutions are prepared with potable or industrial water. These solid particles could be precipitated calcium soaps if the surfactant mixture or the oily antifoam phase contains fatty acids, or  $\text{CaCO}_3$  if carbonate buffer is used in the detergent formulation.

The antifoam activity of these particles depends mostly on two factors – the hydrophobicity of the particle surface and the presence of oily droplets in the foaming solution. The particles of calcium soaps are naturally rather hydrophobic, due to the incorporation of the soap hydrocarbon tails in the particle structure. In contrast, the genuine  $\text{CaCO}_3$  particles are rather hydrophilic and their surface is positively charged at neutral and high pH. However, the anionic and/or nonionic surfactants and polymers, present in the foaming formulations, tend to adsorb on the surface of  $\text{CaCO}_3$  particles, thus covering them with hydrophobic adsorption layer. Therefore, both types of particles, calcium soaps and  $\text{CaCO}_3$ , were found to exhibit antifoam activity in foaming solutions. This activity is strongly enhanced in the presence of oily drops, when the hydrophobic particles combine with these drops, thus forming oil–solid antifoam compounds.

Various studies showed that this scenario could be realized with vegetable oils [77], mineral oils [74–76], or co-polymers with balanced hydrophobicity [59]. Therefore, this scenario is rather general and reflects the already discussed strong synergy between hydrophobic solid particles and various oils in the antifoam compounds (Section 2.5). Additional support of this general trend can be found in the observations that the addition of various types of solid particles (e.g. hydrophobized silica) to various types of oils (vegetable, mineral, silicone, etc.) results in a strong boost of the antifoam effect of these oils, provided that the particles and oil are compatible and combine together in the foaming solution [12,13,25,26].

This method of in-situ particle formation is of definite practical interest, because relatively cheap materials are needed and the specific problem of the particle segregation in the genuine oil–particle compounds (due to gravity-driven particle sedimentation) is avoided. However, the size, shape, and surface properties of the in-situ formed particles may depend significantly on the specific conditions during foaming (temperature, stirring, calcium concentration, etc.) which would affect the antifoam efficiency. Further systematic studies would be very helpful to clarify the relations between all these complex processes in order to obtain robust and efficient antifoam performance.

As shown by Zhang et al. [76], the effect of the oily drops in the presence of precipitated particles could be overcome by using appropriate cosurfactants which reduce the values of the  $E$ ,  $S$ , and  $B$  coefficient. For oily globules composed of hexadecane and oleic acid, lauryl alcohol was very efficient as cosurfactant. This study complements in a nice way the previous studies by Basheva et al. [18,45] where it was shown that appropriately chosen cosurfactants could suppress the antifoam effect of silicone oils by increasing the entry barrier for the silicone oil globules.

### 3.3. Interplay between homogeneous and heterogeneous mechanisms for surfactant-based and polymer-based molecular antifoams

As shown by Kruglyakov and Koretskaya forty years ago [78], linear alkanols may affect the foam stability of solutions, containing typical anionic and nonionic surfactants. These authors found that the effect of the alkanols depends strongly on their chain length and concentration. Medium-chain alkanols ( $n$ -hexanol to  $n$ -octanol) were found to be most efficient at high surfactant concentrations, however, only if the alkanol concentration in the foaming solution is higher than the solubility limit which leads to the formation of oily droplets enriched in alkanol. Therefore, the alkanols were found to reduce the foam stability in these systems only when they can act as heterogeneous antifoams



(the effect of alkanols on the solution foaminess was not reported in these studies).

In subsequent studies, similar conclusions were reached by several independent research groups, who studied different polar oils with limited solubility in water. For example, the well known antifoam effect of the ethoxylated nonionic surfactants, above their cloud point, was shown also to rely exclusively on the phase separation of surfactant-enriched globules which act as oily antifoam entities [79–83]. Arnaudov et al. [47] reported similar trends with branched alkanol (2-butyloctanol) and branched ester (isohexyl-neopentanoate). In more recent works, Joshi et al. [73] and Marinova et al. [59] demonstrated similar effects with nonionic block copolymers.

What remained as less-discussed effect in many of these studies, was the fact that the adsorbed molecules of the studied antifoam substances may have a significant foam boosting or foam suppressing effect, depending on the specific conditions. For example, Arnaudov et al. [47] showed clearly that the initial volume of the foam, produced from solutions of sodium dodecylbenzenesulfonate (anionic surfactant), was higher in the presence of *n*-heptanol, 2-butyloctanol or isohexylneopentanoate, when these substances were added at concentrations below their solubility limit. At concentrations higher than the solubility limit of these additives, this foam boosting effect of the molecularly dissolved species was masked by the heterogeneous antifoam action of the oily drops of the same substance. Therefore, the molecularly dissolved or solubilized species were shown to act as foam boosters with respect to the initially produced foam, while the long-term foam stability was reduced both below and above the solubility limit of the used additives.

In the study by Marinova et al. [59], similar foam boosting effect was observed in Na-caseinate solutions (as main foaming agent) with Pluronic L61 copolymer, when it was used below its solubility limit. In contrast, for other Pluronic copolymers of different molecular architecture, antifoam activity was observed both below and above their solubility limit, which evidenced for combined homogeneous and heterogeneous mechanisms of antifoaming by these polymers.

As reviewed by Ross [84], the observed complex effects of the partially soluble substances could be considered as a manifestation of two more general phenomena: (1) Lundelius rule which relates the reduced solubility of a given substance (as a result of increased temperature, changing solvent properties, or varied molecular structure) to increased surface activity and adsorption of the same substance, (2) the so-called “Ross-Nishioka effect” which states that the foam stability has a maximum around the precipitation boundary of such substances, due to the interplay of the increased surface activity of the adsorbing species (which has a foam boosting effect) and the antifoam effect of the droplets of the separated phase, formed above the solubility limit. Interesting examples of the Ross-Nishioka effect are presented in [84], such as the sharp drop in bubble stability in whiskey samples when the alcohol concentration increases above 50 vol.%, and the effect of silicone oil viscosity variation (related to changes in oil solubility) for aviation lubricants, where these silicone oils are used as antifoams.

Summarizing all this information, we can conclude that the activity of antifoam substances with partial molecular solubility (nonionic surfactants and block copolymers) may exhibit very complex dependence on their concentration. The reason is that these substances may act either as foam boosters or as foam inhibitors at concentrations lower than their solubility limit, whereas they are often very efficient foam suppressors at higher concentrations, especially in the presence of solid particles. Therefore, a systematic study of the concentration and temperature dependences of the activity of these substances is needed to define the optimal conditions for their applications.

#### 3.4. Studies focused on specific applications of antifoams

The literature review shows that the studies focused on the mechanisms of antifoam action are relatively scarce during the last years

[3,5,59,73]. Instead, more studies have been published with focus on specific antifoam applications or on the substitution of more expensive antifoams (e.g., silicone-based) by less expensive antifoams with comparable efficiency. Besides the higher price, the silicone antifoams have been shown to exhibit some non-desirable and even damaging impact in several applications. For example, in 2011 the Renewable Fuels Association issued a notice to fuel ethanol manufacturers, recommending avoidance of the silicone-based antifoams in the manufacturing process due to damaging effect found for car engines [85].

Several important trends, reported in these recent studies, are briefly summarized below. We start with several studies that have reported successful substitution of silicone-based antifoams by other substances in specific applications:

Kirby et al. [86] showed that a combination of fatty acid salts, chelating agents and a polyacid polymer had excellent foam reduction for water dispersible granule formulations, where silicone and other common defoamer types were used with a limited success.

Rocker et al. [87] reported successful application of dioctyl sodium sulfosuccinate instead of silicone antifoam in oil/gas separators.

Wylde [88] presented data for successful application of phosphate-based products, ethoxylated and propoxylated esters, polyethylene glycol esters and oleates, alcohols, fatty alcohols, and ethoxylated and propoxylated alcohols, in order to avoid the poor environmental and asphalt manufacture damaging impact of the silicone-based antifoams.

Wu et al. [89,90] compared the antifoaming performance of various polysiloxanes, modified with fluoroalkyls and/or polyethers in oil-based systems, since the silicone antifoams have been shown to give not satisfactory results in some applications. The authors analyzed and compared the surface tension and solubility properties trying to explain the foam inhibiting effect and the observed exhaustion of the antifoams.

The main processes of foam formation and mitigation in fermentation systems are reviewed and analyzed by Junker [56]. The role of specific operating conditions in the fermentation systems, of the biological cells and their metabolite products, solution sterilization and other factors are considered. The specific advantages and disadvantages of the various types of antifoams used (based on silicone oils, polyalkylene glycols, fatty acids and esters, polyesters, animal and vegetable oils) are critically reviewed. The general trends in the antifoam applications are summarized and the specific difficulties in the up-scaling of the laboratory observations into the real plant applications are analyzed.

The role of oil in foam destabilization, in the context of enhanced oil recovery by injecting foam in the porous oil reservoirs, was discussed in the review by Farajzadeh et al. [3]. The effect of oil on foam stability was analyzed from the viewpoint of the various mechanisms and factors controlling the foam film destabilization and stabilization. The available theoretical models for foam modeling in porous media are critically analyzed and several possible approaches for improving the foam stability in the presence of oil are described.

The effect of latex particles on the foam behavior of surfactant solutions in general and on the antifoams efficiency in particular, was investigated in details by Garrett et al. [91] in relation to water-borne coatings. The authors demonstrated that the latex particles could stabilize the foam films via oscillatory structure forces. On the other hand, the surfactants present in the coating formulations adsorb on the surface of the latex particles which results in reduced foamability and foam stability. These two opposite effects lead to a complex dependence of the foaming properties of these systems on their composition.

#### 3.5. General trends from the viewpoint of antifoam and surfactant chemistry

The search for specific antifoam formulations is still performed mainly via a process of “trials and errors”. Nevertheless, the accumulated mechanistic understanding has explained many of the general trends, observed with the various systems, and has become a source of general guidelines on how the antifoams should be selected for specific

applications. These general trends are briefly outlined below, without entering into the wide domain of detailed requirements for specific applications (fermentation, paper production, oil processing, etc.).

The requirement for positive bridging and (preferably) spreading coefficients, see Section 2.4, explains why silicone and fluorinated oils have very high antifoam activity in many foaming solutions. The main reason is that the lower surface tension of these oils,  $\sigma_{OA}$ , allows one to have positive  $E$ ,  $S$  and  $B$  coefficients in most foaming solutions, thus favoring the oil antifoam activity. However, even at positive values of all these coefficients, the antifoam could be inactive if high entry barrier for the antifoam globules is present [46,48]. This barrier depends on the surface forces in the asymmetric oil–water–air film and is, thus, not related directly to the interfacial tensions determining the values of  $E$ ,  $S$  and  $B$  coefficients. Therefore, the factors controlling the  $E$ ,  $S$  and  $B$  coefficients, on one side, and the factors controlling the entry barrier, on the other side, are different. The latter fact allows one to suppress the antifoam effect of silicone oil droplets in various applications, despite the highly positive values of the respective  $E$ ,  $S$  and  $B$  coefficients (e.g., in conditioners and shampoos, containing silicones).

In the case of polar oils with limited solubility in water, see Section 3.3, the chemical structure is essential also for defining the solubility limit of the antifoam. Thus one could choose oils with more hydrophobic structure if the heterogeneous mechanism of antifoam action is to be enhanced (the latter mechanism is more efficient than the homogeneous one). In contrast, if the oil has to ensure more subtle foam control, one could use polar oils with higher solubility, because these oils could increase the foaminess of the solutions, acting as a cosurfactant during foaming, or could have other functions in the formulations. For example, the low foaming nonionic surfactants have dual role in dish washing formulations – to clean (which requires some solubility of these surfactants) and to reduce foaming (which is best done via the heterogeneous mechanisms) [59].

In several studies, the branching and the length of the molecules of the added antifoam substances (oily droplets of low-molecular mass molecules with limited solubility) were shown to be very important for the observed effect on the foaminess and the foam stability. In general, the branching of the antifoam molecules and the use of medium-chain molecules lead to looser surfactant layers and reduced long-term foam stability, though the foaminess of the solutions could be improved. Examples for this type of behavior are the medium chain fatty alcohols, 2-butyl-octanol and iso-hexylneopentanoate [47,78]. In contrast, the addition of longer chain straight molecules (e.g. of lauryl alcohol or lauric acid) may lead to reduced foaminess of the solutions, but to significantly higher long-term foam stability [45,92]. Furthermore, the addition of such molecules as cosurfactants to the main surfactants in the formulation could suppress the antifoam effect of mineral, vegetable or silicone oils, via formation of condensed mixed surfactant–cosurfactant layers which ensure high entry barriers and (possibly) reduced or even negative  $E$ ,  $S$  and  $B$  coefficients for the oil [45,46].

Similar type of consideration could be very useful in each specific domain of antifoam application. However, it would require much more extended analysis of the available experimental data and this demanding task goes well beyond the scope of the current study.

#### 4. Conclusions

The systematic studies performed in the last decades have identified clearly the basic elements which compose the main mechanisms of antifoam action. Despite the variety of chemical compositions involved in the antifoam formulations, the actual mechanistic scenarios are very limited in number – see Section 2 and Figs. 2–3.

The current difficulties in the mechanistic analysis of the antifoam action originate mainly from two obstacles: (1) the dynamic character of the foaming process, which often makes irrelevant the equilibrium surface properties, usually invoked to analyze the antifoam performance;

and (2) the lack of convenient experimental methods for studying the actual processes occurring in the dynamic foam films during foaming. In the former days, these deficiencies were compensated by using various hypotheses to explain the experimental results. Many of these hypotheses were very clever, but still remained at the level of reasonable speculations.

In more recent years, the systematic use of optical observations to characterize the interaction of the antifoam entities with the foam films and Plateau borders, and their spreading on the solution surface; the quantitative characterization of the entry barrier by the Film Trapping Technique; and the comparative studies of various antifoam systems allowed the researchers in this area to overcome the stage of the speculative hypotheses and to define unambiguously the actual mechanisms of antifoam action in many of the studied systems. As discussed in Section 3, the variety of complex phenomena observed in the various systems could be rationalized by accounting for the dynamic effects during foaming and several additional processes (such as solid particle precipitation and the limited solubility of polar oils) which interfere with the main antifoam mechanisms. This is a remarkable achievement, having in mind the rich variety of chemicals used in the antifoam formulations. In addition, the developed methodology, including several complementary techniques, appears as a valuable toolbox for analysis of any new specific system of interest.

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