

Role of Oil Spreading for the Efficiency of Mixed Oil–Solid Antifoams

Nikolai D. Denkov,* Slavka Tcholakova, Krastanka G. Marinova, and Asen Hadjiiski

Laboratory of Chemical Physics Engineering, Faculty of Chemistry, Sofia University, 1 James Bourchier Avenue, 1164 Sofia, Bulgaria

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The role of oil spreading in the process of foam destruction by oil-based antifoams (oils or mixed oil–solid compounds) has been the subject of a long debate in the literature. To clarify some aspects of this problem, we compare the entry barriers of antifoam globules in the presence and in the absence of a prespread layer of oil on the surface of the surfactant solution. The film trapping technique is employed to measure precisely the critical capillary pressure, at which the entry of the antifoam globules on the solution surface occurs. The experimental results show that the prespread oil layer reduces by several times the entry barrier for mixed oil–silica antifoams, as compared to the barrier in the absence of spread oil. Thus, the oil spreading facilitates the entry of mixed antifoam globules and the subsequent bridging and rupture of the foam films. A simple mechanistic explanation of this effect is given, taking into account the main role of the solid particles in mixed antifoams, namely, to pierce the asymmetric oil–water–air film, formed when an antifoam globule approaches the solution surface. This explanation is expressed in terms of the three-phase contact angles solid–water–oil and solid–water–air, when spherical solid particles are considered.

1. Introduction

Nonsoluble oils (such as hydrocarbons or silicone oils) and their mixtures with hydrophobic solid particles (e.g., a few percent of hydrophobized silica) are often used to destroy undesirable foam. Leviton and Leighton¹ were the first who suggested that there is a qualitative correlation between the spreading behavior of oils and their antifoam activity. Ross² put this idea in quantitative terms by comparing the sign of the spreading coefficient, S (introduced by Harkins³),

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

of various oils with their foam-breaking efficiency. The subscripts AW, OW, and OA in eq 1 refer to air–water, oil–water, and oil–air interfaces, and σ is the respective interfacial tension. On the basis of the data available at that time, Ross² revealed a certain correlation, in the sense that most of the oils with antifoam activity had positive spreading coefficients. Several exceptions, however, were noticed in the same study. Since that time, there has been an ongoing debate in the literature about the role of oil spreading for the antifoam activity.^{4–28} Periodically, papers

appear in which the relation between the spreading behavior of the oils and their antifoam activity is reiterated in one form or another,^{4–8,19,23–25,28} whereas this relation is opposed as a general rule in other papers.^{10–12,16–18,20–27}

The discussions on the role of oil spreading were usually made in the context of the assumed mechanism of antifoam action. Ross² speculated that the oil should first connect the two foam film surfaces and that the subsequent spreading as a thick oil layer would lead to a replacement of a portion of the aqueous foam film (presumably stable) with an unstable oil bridge; this bridge is the “weak point”, where the foam film ruptures.

* To whom correspondence should be addressed. Assoc. Prof. Nikolai D. Denkov, Laboratory of Chemical Physics Engineering, Faculty of Chemistry, Sofia University, 1 James Bourchier Ave., 1164 Sofia, Bulgaria. Phone: (+359) 2-962 5310. Fax: (+359) 2-962 5643. E-mail: ND@LCPE.UNI-SOFIA.BG.

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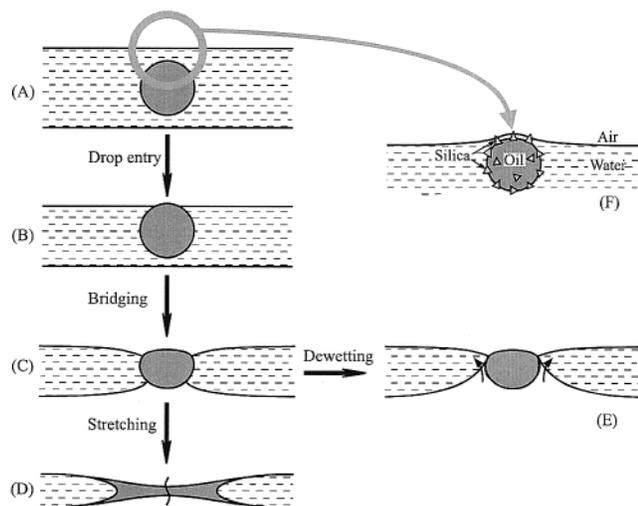


Figure 1. Bridging–stretching (A–D) and bridging–dewetting (A–C–E) mechanisms of foam film rupture by antifoam globules. An antifoam globule approaching the foam film surface is schematically presented in (F); the main role of the solid particles is to aid the emergence of the antifoam globules on the foam film surface.

Later on, the so-called “spreading-fluid entrainment” mechanism was proposed.⁴ According to this mechanism, a bridging of the two foam film surfaces by oil drops is not necessary. Once an oil drop enters either of the film surfaces, the oil would spread from the formed oil lens, if S is positive. The oil spreading is assumed to drag water in the foam film away from the oil lens, inducing in this way a rapid local thinning and a subsequent rupture of the foam film. A respective theoretical model was suggested,⁵ and the rate of oil spreading was discussed in several studies^{5,19,28} as one of the important factors for the antifoam activity.

In the mechanism proposed by Kulkarni et al.,^{7,8} the spreading is deemed important for another reason. These authors assume that the oil acts only as a carrier fluid (and a coat) for the solid particles, which are considered as the actual foam-breaking entities. The oil spreading, after a mixed antifoam globule has entered the foam film surface, leaves the surface of the solid particles uncovered, and a rapid surfactant adsorption on the particles' surface is assumed to occur. The authors suggest that this event leads to a local depletion of surfactant and to foam film destabilization. This mechanism, however, contradicts some later observations by other authors^{17,23,25} and remains unproven.

On the other side, it was found in many studies^{10–12,16–18,20–27} that there is no correlation between the magnitude of the spreading coefficient for a given oil and its antifoam activity. This result was explained by the important role of the repulsive forces, which prevent the emergence of the predispersed oil drops on the foam film surface. Indeed, any of the mechanisms of foam destruction by emulsified oil drops or by globules of mixed oil–solid antifoams include the stage of drop (globule) entry, which precedes the subsequent stages of dewetting, spreading-fluid entrainment, and so forth; see Figure 1. That is why drops of oils that have positive spreading coefficients can remain arrested in the surfactant solution upon foam formation, without being able to emerge on the solution surface and to rupture the foam film.^{11,26} A good quantitative correlation was found in several studies between the magnitude of the entry barrier, as measured by the film trapping technique (FTT),^{29,30} and the activity of

various antifoams.^{26,27,29,31} Furthermore, by selecting an appropriate oil–surfactant system, Garrett et al.¹⁷ were able to show that nonspreading oils still have antifoam activity. These results can be explained by assuming that the foam destruction in these systems occurs through the so-called “bridging–dewetting”¹⁶ or “bridging–stretching”^{23,24} mechanism (Figure 1), which does not require one to invoke the oil spreading for the foam rupture event. An important result of these studies was the conclusion¹⁶ that the main role of the solid particles in mixed oil–solid antifoams is to facilitate the oil drop entry. The latter effect was explained¹⁶ by piercing the asymmetric oil–water–air films (formed upon the approach of the antifoam globules toward the solution surface) by the sharp tips of the particles; see Figure 1F.

The major aim of the present study is to clarify how the oil spreading affects the entry barrier for globules of mixed oil–silica antifoams. Direct measurements of the entry barriers by FTT showed that the presence of a prespread oil layer (even of nanometer thickness) on the solution surface leads to significantly lower entry barriers, as compared to those in the absence of a spread oil. This result is explained by considering the wettability of the solid particles by the oil and water phases (and the respective three-phase contact angles) and seems rather general. Thus, a new explanation for the role of oil spreading in the action mode of mixed oil–solid antifoams has emerged.

2. Experimental Details

2.1. Materials. Two surfactants were used as received: anionic sodium dioctyl-sulfosuccinate ($C_{20}H_{37}O_7SNa$, Sigma catalog no. D-0885; named hereafter AOT); and nonionic octylphenol decethylene glycol ether (Triton X-100, product of Merck). The experiments were performed with aqueous solutions of concentrations 10 mM for AOT (approximately $3.6 \times \text{cmc}$ (critical micelle concentration)) and 1 mM for Triton X-100 (approximately $6 \times \text{cmc}$). Deionized water from a Milli-Q purification system (Millipore, USA) was used for preparing the surfactant solutions.

Three antifoams were studied:

(a) Poly(dimethylsiloxane) oil (PDMS) of dynamic viscosity 1000 mPa s, produced by Rhodia Silicones Europe (Saint Fons, France) under the commercial name 47V1000SH.

(b) Compound A (CA), which is a mixture of PDMS oil and 4.2 wt % silica particles R974 of pyrogenic origin (Degussa AG,³² Germany). In this compound, the silica particles assemble, forming fractal agglomerates of a broad size distribution (from 0.1 to 5 μm).

(c) Emulsion A (EA) is a stable 10 wt % oil-in-water emulsion of compound A. It is further diluted to the desired final concentration in the surfactant solution. The stock emulsion is stabilized by two nonionic surfactants: sorbitan monostearate (Span 60) and ethoxylate of stearic acid with 40 ethoxy groups (stearyl-EO₄₀, Mirj 52), both products of ICI Specialty Chemicals Ltd., U.K. Span 60 is a solid substance at room temperature, which means that two different types of solid particles (fumed silica and Span 60) are present in EA.^{25,31} Microscope observations show that this emulsion is polydisperse with drop diameters ranging from ca. 1 to 10 μm .

The antifoam concentration in the working surfactant solutions is 0.01 wt %.

All glassware is carefully cleaned by immersion in ethanol solution of KOH (at least for 12 h), followed by copious rinsing with deionized water.

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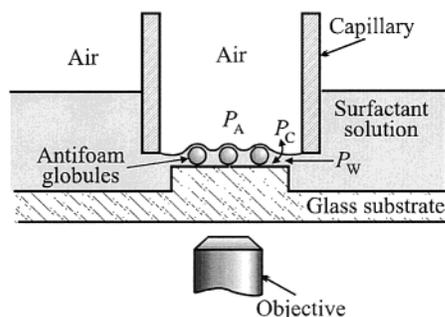


Figure 2. Schematic presentation of the basic principle of the film trapping technique, which is used for measuring the critical capillary pressure, P_C^{CR} , leading to entry of the antifoam globules (refs 29 and 30).

2.2. Methods. 2.2.1. Foam Tests. To compare the activity of the studied antifoams (PDMS, EA, and CA), we used a simple hand-shake test, Bartsch method. A 100 mL quantity of the surfactant solution is poured in a 300 mL glass cylinder (4 cm in diameter). The antifoam (10 μ L) is then added by using a micropipet M800 (Nichiryo Co., Tokyo, Japan). The cylinder is tightly plugged by a bung, and the foam is generated by 10 up-and-down hand shakes. The kinetics of foam destruction is afterward monitored for 15 min. At least three independent experiments are made with each system to check for the reproducibility of the data. To exclude the effect of water drainage from the final results, the foam volumes quoted below are actually the volumes of the entrapped air, calculated as a difference between the entire volume of the system (foam plus surfactant solution) and the volume of the used solution.

As discussed in refs 23 and 25, the surface of the AOT solutions in the presence of silicone-silica antifoams is typically covered by a thin layer of spread silicone oil (2–3 nm in thickness), which is in equilibrium with oil lenses, floating on the surface. We found by ellipsometry and by optical microscopy that similar layer of spread silicone oil (2–3 nm) and oil lenses are present on the surface of the used Triton solutions, as well (unpublished results). To illustrate the effect of the prespread oil on the foam destruction, we used a standard shake machine Agitest (Bioblock) for foam generation. The respective foaming solutions were prepared in the following way: EA (0.03 vol %) was first dispersed in a 10 mM AOT solution in a cylinder. In parallel, two glass bottles for the shake test were charged with 75 mL of pure AOT solution (no antifoam). Afterward, 25 mL portions of the solution, containing EA, were transferred into the bottles by using the so-called “two-tips procedure” (TTP),^{23,25,31} which ensured a solution surface free of spread oil. For this purpose, the solution was gently passed through the narrow orifice of a pipet tip, so that no direct contact was made between the surface of the original solution (which was covered by a spread layer of oil from the antifoam) and the solution surface in the shake-test bottles. If the procedure was successful (which was not always the case, because the globules of these relatively active antifoams easily emerged on the solution surface), the foam bubbles generated during pouring the surfactant solution remained intact. In this way, we prepared 100 mL of AOT solution containing 0.0075% of EA in the bottles for the shake test. One of these bottles was plugged and attached to the shake machine, whereas the other bottle was beforehand mildly hand-shaken several times (without generating new foam bubbles) until globules of the antifoam entered the solution surface and created a layer of spread oil. The appearance of spread oil was evidenced by surface tension measurements (see Table 2 below and refs 23, 25, and 31), as well as by the immediate collapse of the bubbles in this bottle. The two bottles were afterward agitated in a series of shake cycles on the machine (frequency, 360 min^{-1} ; amplitude, 2 cm). After each cycle of agitation for 2 s, the time for appearance of a clean water-air interface without bubbles (defoaming time, τ_D) was measured by a chronometer. In this way, we were able to evaluate the effect of the spread oil on τ_D ; see section 3.1 for further explanations.

2.2.2. Film Trapping Technique. The entry barriers are measured by the FTT;^{29,30} see Figure 2. A vertical glass capillary,

partially filled with the working solution, is placed in a close vicinity above a glass substrate. The capillary is connected to a pressure control system, which allows one to vary and to determine the difference, $P_C = (P_A - P_W)$, between the air pressure in the capillary, P_A , and the pressure in the aqueous phase, P_W . When P_A is increased, the air-water meniscus in the capillary is pushed against the glass and a wetting film is formed, which traps some of the oil drops (antifoam globules) dispersed in the working solution. The drops are observed from below, through the glass substrate, by means of an inverted optical microscope (Jenavert, Carl Zeiss, Germany). The entrapped drops enter the air-water interface around a certain critical capillary pressure, P_C^{CR} . The moment of drop entry, which is accompanied by a significant local change in the shape of the air-water interface, is clearly seen in the microscope. Higher values of P_C^{CR} correspond to more difficult entry and vice versa. For brevity, we term P_C^{CR} “the entry barrier”.

Two pressure sensors are used for determination of P_C , depending on the range of the measured pressures: PX274-01DI (range, ± 125 Pa) and PX163-005BD5V (range, ± 1250 Pa), both products of Omega Engineering, Inc., Stamford, USA. The data acquisition equipment includes also a digital multimeter Metex M-4660A (Metex Instruments) connected to a PC. Further details about the experimental setup and procedures are presented in refs 29 and 30. The so-called FTT-gentle version of the equipment³⁰ is used when $P_C^{CR} < 20$ Pa; otherwise, the conventional version of FTT was applied.

Micrometer droplets of the studied antifoams are obtained by preliminary emulsification in the tested surfactant solutions. The emulsification is performed by applying three standard shaking cycles of 10 s on the Agitest shake machine.²⁵ Afterward, the samples are poured in the experimental vessel for FTT experiments directly or by using the TTP,^{23,25} depending on whether or not we want to have spread oil on the solution surface.

In a typical FTT experiment,^{29,30} one observes many drop entry events, which certainly result in spreading on the solution surface of oil, which has been initially captured in the emulsion drops. Therefore, in the experiments aimed to measure the entry barrier in the absence of spread oil, special measures are undertaken: The solution is poured in the experimental vessel by the TTP and only the entry barrier of the first 1–2 drops is taken into consideration, because the subsequent entry events take place with a solution surface, which is not entirely deprived of oil.

2.2.3. Contact Angle Measurements. The effect of the spread oil on the three-phase contact angle of solid particles was studied with glass spheres of diameter ≈ 500 μm (Sigma, catalog no. G-9268). These spheres were cleaned by soaking in sulfochromic acid for 5 h, abundant rinsing with deionized water for 4 h, soaking in 10 mM NaOH for 10 h, rinsing with deionized water for 8 h until a neutral pH of the water is measured, and drying for 8 h at 80 $^\circ\text{C}$.

The glass beads, pre-cleaned as explained above, were first partially hydrophobized by hexamethyl-disilazane (HMDS). For this purpose, the particles were kept for 2 h in an atmosphere saturated with HMDS vapors. This treatment leads to chemical grafting of CH_3 -groups to the glass surface. Afterward, the glass beads were immersed in PDMS oil for 4 weeks, to ensure their subsequent hydrophobization by adsorption of PDMS molecules on the particle surface. Similar procedures are used for hydrophobization of the silica particles in commercial PDMS-silica antifoams.^{16,32,33} Finally, the glass beads were carefully washed by hexane to remove the excess of nonreacted PDMS.

When placed on the surface of AOT or Triton solutions, the hydrophobized glass beads acquired an equilibrium position, and the respective three-phase contact angle air-water-glass, θ_A , was measured by a goniometric method. Independent measurements showed that the placement of the hydrophobized beads on the solution surface did not affect the surface tension, which means that no PDMS was released from the surface of the washed particles. In some of the measurements, a layer of oil was spread over the solution surface by touching the latter with a glass tip, soaked by PDMS; in this way, the effect of the spread oil on the equilibrium position of the particle on the solution surface was

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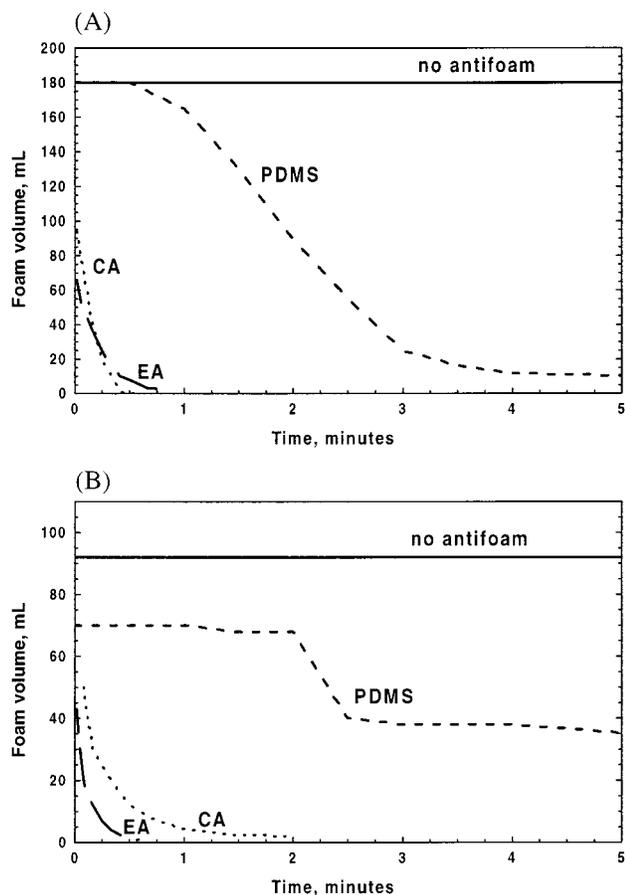


Figure 3. Foam volume as a function of time in a shake test (Bartsch method, section 2.2.1) for surfactant solutions containing 0.01% emulsion A, compound A, or PDMS: (A) 10 mM AOT; (B) 1 mM Triton. For comparison, the foam volume in the absence of antifoam is also shown.

studied. For comparison, the three-phase contact angles oil–water–glass, θ_0 , were also measured (without washing the glass particles with heptane).

2.2.4. Surface Tension Measurements. The equilibrium surface tension of the aqueous solutions is measured by the Wilhelmy plate method on a Krüss K10T tensiometer. The used platinum plate was cleaned before each measurement by immersion in hydrofluoric acid and heating in a flame.

3. Experimental Results and Discussion

3.1. Foam Tests: Fast and Slow Antifoams; Effect of Spread Oil. The antifoam activity of pure silicone oil, PDMS, is much lower than the activity of mixed oil–silica antifoams, CA and EA. As seen from Figure 3, the mixed antifoams completely destroy the foams obtained from AOT and Triton solutions in less than a minute (in the automatic shake test the defoaming time is typically 3 to 5 s; see Figure 4 below and ref 25), whereas PDMS destroys these foams in a much longer time scale and only partially (a residual foam, which is stable for many hours, usually remains). This large difference in the activity of pure oils and mixed antifoams is rather typical and is observed with various surfactant–antifoam pairs.²⁹ The terms “fast” and “slow” antifoams are used^{29,34} to distinguish these different modes of antifoaming.

As revealed in several recent studies,^{23–27,29–31,34} the different time scales are related to different mechanisms

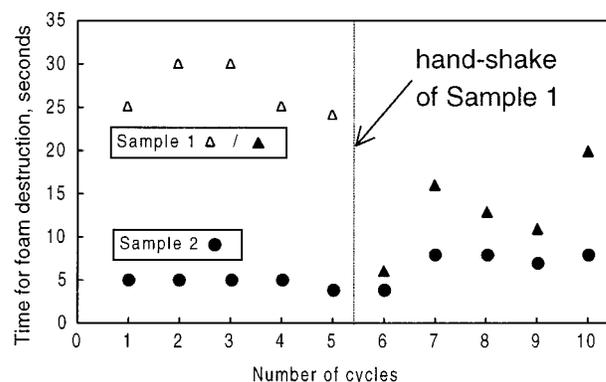


Figure 4. Defoaming time for 10 mM AOT solutions containing 0.0075 vol % of EA (foam test in the automatic shake machine). Sample 1 (triangles) is prepared in a way that prevents the appearance of a spread layer of silicone oil on the solution surface, whereas a spread oil is present in sample 2 (circles). A hand shake of sample 1 after the fifth cycle (the vertical line) induces the appearance of spread oil in sample 1; as a result, the defoaming time decreases about 2 times (see sections 2.2.1 and 3.1 for details).

of foam destruction by the fast and slow antifoams. The globules of the fast antifoams are able to enter the surfaces of the foam films almost immediately after these films are formed.²³ As a result, the foam films and the entire foam column are destroyed very rapidly via the bridging–stretching mechanism (Figure 1). On the contrary, the globules of the slow antifoams are unable to enter the surfaces of the foam films, because their entry barrier is higher.^{26,27} When the thickness of the foam films becomes smaller than the diameter of the antifoam globules, the latter are expelled into the neighboring Plateau borders (PBs).¹² It takes some time, on the order of minutes, until the globules are strongly compressed by the shrinking walls of the PB (due to the water drainage from the foam) and the drop entry is eventuated.²⁷ Precise measurements by FTT showed^{29,34} that whether a given antifoam would act as fast or slow depends primarily on the entry barrier of its globules. If the entry barrier is below ca. 15 Pa, the antifoam rapidly destroys the foam films (i.e., it acts as a fast antifoam), and vice versa.

To illustrate the effect of oil spreading on the foam stability, we prepared two samples, with and without a prespread layer of oil, as explained in section 2.2.1. For simplicity, we term the sample without a prespread oil layer as sample 1 and the other one as sample 2. The defoaming time, τ_D , of these samples was compared by using an automatic shake machine. As seen from Figure 4, the defoaming time for sample 1 was about 5 times longer (≈ 27 s), as compared to that of sample 2 (≈ 5 s). Note that the total concentration of antifoam was the same in both samples and the only difference between them was the absence of a prespread oil layer in sample 1. In fact, the machine shakes of these samples led to the emergence of some oil on the solution surface due to entry of antifoam globules. However, as explained in the discussion section of ref 25, the foam destruction was related to re-emulsification of the spread oil, so that a dynamic “equilibrium” between the processes of oil emergence and emulsification was established; as a result, sample 1 remained with a deficiency of spread oil during the first five cycles. After the fifth cycle, we removed sample 1 from the shake machine, mildly shook it several times to induce emergence of antifoam globules on the solution surface (without generating foam), and another series of shake cycles was accomplished; see Figure 4. We observed an immediate reduction of the defoaming time of sample

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Table 1. Entry Barriers, P_C^{CR} , of Different Antifoams in 10 mM AOT and 1 mM Triton Solutions in the Presence and in the Absence of a Prespread Layer of Silicone Oil

antifoam	spread layer	P_C^{CR} , Pa	
		AOT	Triton
silicone oil	no	28 ± 1	>200
	yes	19 ± 2	>200
compound A	no	8 ± 1	30 ± 1
	yes	3 ± 2	5 ± 2
emulsion A	no	20 ± 5	22 ± 1
	yes	4 ± 1	7 ± 1

1 by about 2 times; τ_D became much closer to, though still somewhat longer (6–16 s) than, that for sample 2 (6–8 s). In this way, we demonstrate that the presence of a prespread oil layer has an important effect on the activity of the antifoam. For further explanations on the process of oil emergence on the solution surface during foam generation and on the related process of emulsification of the spread oil layer during foam destruction, see ref 25.

For most mixed silica–silicone antifoams, which are rather active, such an experiment is impossible, because a spread layer of oil is always formed during sample preparation (due to the very easy coalescence of the antifoam globules with the solution surface). For example, we were unable to reproduce this experiment with CA and higher concentrations of EA, because always a fraction of the antifoam emerged on the solution surface after the TTP, and it was impossible to prepare an initial surfactant solution with the surface deprived of spread oil.

3.2. Results for the Entry Barriers. The measured critical capillary pressures to antifoam globule entry, in the presence and in the absence of a prespread layer of silicone oil, are presented in Table 1. First, we consider the results obtained with a prespread layer of oil, because this is typically the case in the respective foaming systems.^{23,25,31} As expected, the introduction of hydrophobic solid particles into the antifoam results in reduced entry barriers, as compared to those for pure oil: for pure silicone oil in AOT solutions $P_C^{\text{CR}} = 19 \pm 2$ Pa, whereas for CA and EA the values are 3 ± 2 and 4 ± 1 Pa, respectively. For Triton solutions, this difference is even larger: the entry barrier for PDMS is above 200 Pa, whereas it is equal to 5 ± 2 and 7 ± 1 Pa for CA and EA, respectively. Note that all values for the mixed antifoams in the presence of spread oil are well below 15 Pa (i.e., correspond to fast antifoams), which is in agreement with the results from the foam tests.

Let us compare now the data obtained with and without a prespread oil layer for mixed antifoams (CA and EA) in AOT and Triton solutions. In all four systems of this type, the removal of the spread oil layer results in significantly higher entry barriers. This increase is particularly important for Triton solutions, because the measured barriers $P_C^{\text{CR}} = 30 \pm 1$ Pa for CA and $P_C^{\text{CR}} = 22 \pm 1$ Pa for EA are higher than the boundary separating the fast from the slow antifoams (15 Pa). Therefore, one could expect that if the silicone oil did not spread on the surface of Triton solutions, both mixed antifoams (CA and EA) would not be able to rupture the foam films, that is, would behave as slow antifoams. Similar is the case with EA in AOT solutions; without spread oil, this antifoam has a barrier $P_C^{\text{CR}} \approx 20$ Pa, which would place it in the group of the slow antifoams. For CA in AOT solutions, the increase of the barrier is about 3 times, from 3 ± 2 to 8 ± 1 Pa, but in both cases it is sufficiently low to make this compound very active (fast antifoam).

An interesting conclusion from the above results is that in many systems the presence of solid particles is

insufficient to reduce the entry barrier below the boundary of 15 Pa, which separates the fast from the slow antifoams, unless an oil layer is prespread on the solution surface. In other words, many antifoams act as fast ones only because of the synergistic action of the solid particles present in the antifoam globules and the spread oil layer on the solution surface. Although this conclusion is drawn from results obtained with only four different surfactant–antifoam pairs, in view of the explanation presented in the following subsection, we expect that it is rather general and is valid for most mixed oil–silica antifoams.

The influence of the spread oil on the entry barrier of oil drops deprived of silica is different. In a previous study,²⁹ we measured the drop entry barriers for a series of linear alkanes: decane, dodecane, and hexadecane. The results convincingly showed that the presence of a spread oil reduced P_C^{CR} at least 2 times for decane and dodecane. However, for hexadecane we observed a 5-fold increase of P_C^{CR} after spreading a very thin oil layer on the solution surface. We can conclude from these results that there is no general rule about the effect of oil spreading on the entry barrier of pure oil drops.

For the oils used in the present study, we find (Table 1) that the entry barrier for pure PDMS is moderately reduced by spread oil for AOT solutions (by about 30%). For Triton solutions, the entry barrier was rather high, above 200 Pa, in both cases (with and without spread oil) and we were unable to induce drop entry by the used setup. Thus, we cannot say at the moment how the spread oil affects the entry barrier for PDMS in Triton solutions.

3.3. Explanation of the Reduced Entry Barriers in the Presence of a Spread Oil. The idea that the solid particles, if sufficiently hydrophobic, facilitate the entry of the antifoam globules was expressed in quantitative terms by Garrett¹⁶ and Aveyard and Clint.¹⁵ They considered the equilibrium configuration of a solid sphere, which bridges the surfaces of the asymmetric oil–water–air film, formed when an antifoam globule approaches the surface of a foam film (Figure 5A,B). If the three-phase contact angles solid–water–oil, θ_O , and solid–water–air, θ_A , satisfy the condition

$$\theta_O + \theta_A \geq 180^\circ \quad (2)$$

there is no equilibrium position of the particle in the film, and the two contact lines would slide along the particle surface until they coincide; thus the globule entry will be effected with the help of the solid particle.¹⁶ On the contrary, if the solid particle is not sufficiently hydrophobic, there is a well-defined thickness of the asymmetric film¹⁵

$$h_{\text{AS}} = R(\cos \theta_O + \cos \theta_A) \quad (3)$$

at which the solid particle would be in equilibrium and the distance between the two contact lines will be equal to h_{AS} (R is the particle radius). In the latter case, the particle would facilitate the thinning of the asymmetric film only until its thickness reaches h_{AS} . Thus, the solid particle is unable to induce the oil emergence on the surface of the foam film (at least, under quasi-equilibrium conditions) and could even stabilize the asymmetric film.¹⁵

Let us analyze how the above concept is modified if a spread layer of oil is present on the water–air interface. One obvious effect from the oil spreading is the reduced surface tension, σ_{AW} (by 2.65 and 6.5 mN/m for the studied AOT and Triton solutions, respectively; see Table 2). Since the contact angle θ_A obeys the Young equation

Table 2. Surface Tension of the Surfactant Solution, σ_{AW} , in the Presence and in the Absence of a Spread Oil Layer^a

	AOT		Triton X-100	
	without spread oil	with spread oil layer	without spread oil	with spread oil layer
σ_{AW} , mN/m	27.85 ± 0.1	25.2 ± 0.2	31.3 ± 0.1	24.8 ± 0.2
contact angle, deg	$\theta_A = 34 \pm 4$	$\theta_O = 135 \pm 5$	$\theta_A = 44 \pm 9$	$\theta_O = 108 \pm 4$

^a θ_A and θ_O are the three-phase contact angles air–water–solid and oil–water–solid, respectively (see Figure 5).

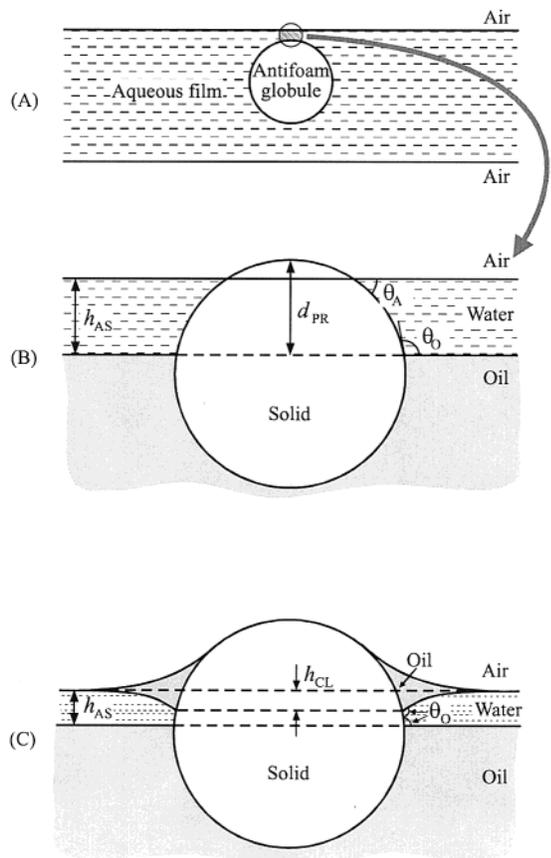


Figure 5. (A) When an antifoam globule approaches the foam film surface, an asymmetric oil–water–air film of thickness h_{AS} is formed. (B) If the protrusion depth, d_{PR} , of the solid particle is larger than h_{AS} and the condition for dewetting, inequality 2, is satisfied, the solid particle pierces the air–water interface and induces a film rupture. (C) If a layer of prespread oil is available on the solution surface, an oil collar can be formed around the hydrophobic solid particle. In this case, the entry of the oil from the antifoam globule on the solution surface depends on the contact angle, θ_O (see inequality 5), and on the volume of the oil collar.

$$\cos \theta_A = (\sigma_{SA} - \sigma_{SW})/\sigma_{AW} \quad (4)$$

the reduction of σ_{AW} would lead to a decrease of θ_A . On the other side, the oil present on the water–air interface is allowed to spread on the solid–air interface, as well. As a result, the value of σ_{SA} would decrease and, subsequently, θ_A would increase.³⁵ It is difficult to predict in advance which of these two effects would prevail for the typical antifoam systems. By analogy with the definitions of the spreading, entry and bridging coefficients (see, e.g., refs 16, 26, and 27), one can define initial and equilibrium contact angles, θ_A^{IN} and θ_A^{EQ} , which are calculated or measured in the absence and in the presence of a spread oil layer, respectively.

To check how important is the effect of oil spreading on the contact angle, θ_A , we performed experiments with

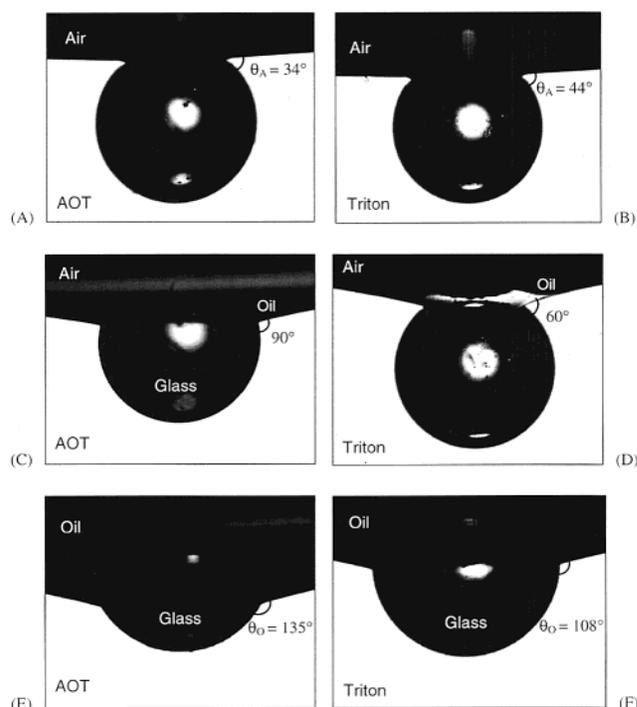


Figure 6. Hydrophobized glass particles at the interface of a 10 mM AOT solution or a 1 mM Triton solution with (A,B) air, (C,D) air in the presence of a small amount of PDMS, and (E,F) bulk PDMS. The prehydrophobized particles were washed with hexane in (A) to (D), whereas no washing was used in (E) and (F); see section 2.2.3 for details.

hydrophobized glass spheres. The measured values of the three-phase contact angle θ_A in the absence of spread oil were $34 \pm 4^\circ$ and $44 \pm 9^\circ$ for AOT and Triton solutions, respectively (see Table 2 and Figure 6A,B). The spreading of oil on the surface of these solutions resulted in a small increase (by several degrees) of θ_A for the AOT solution. It was impossible for us to quantify this effect, however, because we could not deposit very small amounts of oil on the solution surface without formation of lenses of bulk oil. No change of θ_A for the Triton solutions was detected when a thin layer of silicone oil was spread. The conclusion from these experiments was that the effect of a spread thin layer of oil on the contact angle θ_A is relatively small for the studied solutions.

On the other hand, the experiments with glass particles revealed another phenomenon, which is certainly important for the mechanism of antifoaming. When a larger amount of oil was deposited on the solution surface, so that lenses of bulk oil were formed, we observed an accumulation of oil around the solid particle; see Figures 5C and 6C–F. Thus, an oil collar replaced the upper three-phase contact line solid–water–air. The main driving force for this phenomenon is the particle hydrophobicity; as evidenced by the contact angle $\theta_O > 90^\circ$, the used particles are rather lyophilic and the displacement of the aqueous phase by oil on the particle surface is thermodynamically favored. Furthermore, since the oil collar acquires an equilibrium shape with contact angle θ_O , the lower end of the collar slides along the particle surface, penetrating at

(35) Aveyard, R.; Beake, B. D.; Clint, J. H. *Phys. Chem. Chem. Phys.* **1999**, *1*, 2513.

a depth h_{CL} below the level of the air–water interface (Figure 5C). The depth of penetration, h_{CL} , increases with both the contact angle θ_0 and the volume of the oil collar and can be calculated, in principle, from the Laplace equation of capillarity^{15,24,36,37} (the contact angle solid–oil–air also affects h_{CL}). Note that the surfaces of the oil collar are concave, which means that the pressure (and thereby the chemical potential) in the oil phase is reduced therein. Therefore, the collar can “suck in” oil from the spread layer and/or from distant oil lenses by a mechanism suggested in ref 24 to explain the effect of the spread oil on the stability of oil bridges in foam films.

A simple geometrical consideration shows that when h_{CL} becomes larger than h_{AS} (defined by eq 3), the two separated oil phases, in the antifoam globule and on the solution surface, will coalesce and a globule entry will be effected. The necessary conditions for this process to occur are as follows: (i) the volume of the oil collar should be sufficiently large, ca. comparable to the volume of the solid particle, and (ii) the contact angle θ_0 should satisfy the condition

$$\theta_0 \geq 90^\circ \quad (5)$$

Note that condition (ii) is virtually always satisfied for typical hydrophobic particles, whereas our measurements (Table 2 and other, unpublished results) showed that inequality 2 is often unsatisfied for typical antifoam systems. This consideration suggests that many mixed oil–solid antifoams behave as fast antifoams (i.e., they have low entry barriers) mainly because of the synergistic action of the solid particles and the spread oil.

If there is an excess of oil on the surface and condition (i) is satisfied, a rough estimate of the distance between the two contact lines, $h_{AS} - h_{CL}$, can be made by an analogy with eq 3

$$h_{AS} - h_{CL} = 2R \cos \theta_0 \quad (6)$$

Equation 6 predicts that for hydrophobic particles, $\theta_0 > 90^\circ$ ($\cos \theta_0 < 0$), the equilibrium distance between the two contact lines is negative, that is, they would coincide and the entry will spontaneously occur.

3.4. Relation to Results Described in Other Studies. The above quantitative relations are valid for solid spheres and cannot be directly transferred to the real antifoam compounds and emulsions, which contain non-spherical (usually fractal in shape) solid particles. Nevertheless, several experimental observations described in other studies complement the results from section 3.1 and confirm the important role of oil spreading for the entry barrier in the real antifoam systems. Model microscopic observations²³ of single foam films revealed that the entry of mixed antifoam globules of emulsion A (EA) and the subsequent film rupture occur only if there is a prespread oil layer on the film surfaces. If the foam film surfaces are deprived of spread oil (after loading the experimental cell by the TTP), the antifoam globules left the foam films during their thinning, without the occurrence of entry and film rupture.²³ Furthermore, as discussed in ref 25, the process of antifoam exhaustion (loss of antifoam activity in the course of foam destruction) is related to the gradual disappearance of the layer of spread oil on the solution surface, along with another effect, which will not

be discussed here (segregation of the antifoam globules into silica-free and silica-enriched ones).

It is quite probable that the presence of a spread oil affected the results in the experiments by Aveyard et al. (see ref 15), who tried to verify eq 2. They studied the coalescence of heptane drops, coated with monodisperse silica spheres (3 μm in diameter), with the surface of AOT solution, as a function of the contact angles of the silica particles. Since heptane is rather volatile and water soluble, a spread layer of this oil was probably formed on the surface of the surfactant solution (see Figure 18 in ref 15). Therefore, the experimental conditions in these measurements correspond to inequality 5, rather than to inequality 2. The authors found that the solid particles facilitate the drop coalescence at contact angles corresponding to unexpectedly hydrophilic particles, $\theta_A + \theta_O \approx 50^\circ$. Assuming that $\theta_A < \theta_O$ (which is usually the case), one may expect that the angle θ_0 was probably around 30–40° in these experiments, which is still well below the predicted limit of 90° (inequality 5). Therefore, some dynamic wetting effects were probably involved in these experiments, as suggested by Aveyard et al.¹⁵ Dynamic effects were certainly present in the more recent experiments reported by Jha et al.,²⁸ where a correlation between the ability of an oil to suppress the foam generation and its spreading pressure was established.

The explanations given above are valid only for mixed oil–solid antifoams and cannot be transferred to the case of oil droplets deprived of silica. One may expect that for pure oils the variation of P_C^{CR} (as a result of spreading) is mostly related to changes in the structure of the adsorption layer at the water–air interface.^{38–40}

4. Conclusions

Direct measurements of the entry barriers of mixed oil–solid antifoam globules were performed by the film trapping technique in AOT and Triton solutions. The results show that the presence of a prespread oil layer on the solution surface leads to significantly lower entry barriers. For most of the studied systems, only the combination of solid particles plus spread oil leads to entry barriers, which correspond to very active (fast) antifoams;^{29,34} see Table 1. Without spreading of the silicone oil, these antifoams would be much less active and would fall in the category of the slow antifoams. Therefore, a synergistic effect between the solid particles and the oil spreading has been established.

A simple mechanistic explanation of this synergistic effect is given; see Figure 5. The presence of a spread oil changes the condition for dewetting of the solid particles, which bridge the surfaces of the asymmetric oil–water–air film formed between the antifoam globule and the solution surface. If there is a spread oil, the condition for dewetting is expressed by inequality 5, which is always satisfied for the typical hydrophobic particles used in antifoams. In the absence of a spread oil, the condition for dewetting of the particles is expressed by inequality 2, which is not always satisfied for typical antifoams. This explanation is supported by optical observations and contact angle measurements of model glass beads attached to the solution surface in the presence and in the absence of a spread oil (Figure 6).

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The spread oil also affects the entry barrier of pure oil drops (deprived of silica). However, in some systems the spread oil reduces the barrier, whereas in other systems the effect is the opposite.²⁹

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