

Letters

Silicone Antifoam Performance: Correlation with Spreading and Surfactant Monolayer Packing

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The relationship between the spreading of antifoam oils and their performance is much discussed in the literature, but a demonstrated connection between antifoam spreading and performance has been lacking. This paper reports the performance of a poly(dimethylsiloxane) (PDMS)-based antifoam on foam produced by 12 surfactant solutions. These include single or mixed surfactant systems, including impure surfactant mixtures to model fabric washing detergents. The oil film spreading pressure, $\pi_{o/w}$, is presented as a simple and relevant measurement of the thermodynamics of antifoam oil spreading. Antifoaming efficacy was measured as the relative reduction in the initial foam height, ΔH_{rel} , using cylinder shake tests at a fixed antifoam dosage. ΔH_{rel} is shown to increase with $\pi_{o/w}$, demonstrating a strong statistical correlation between antifoam oil spreading and its performance. Antifoam effectiveness varies with surfactant concentration, surfactant type, and surfactant hydrophobe size and also with increased density of surfactant packing. Surface shear viscosity, μ^s , was used to quantify surfactant packing. Antifoam effectiveness decreases with increasing surface shear viscosity. This finding provides a potentially useful link between antifoam efficacy and surfactant selection based on well-established surfactant molecular packing parameters. The role of spreading of antifoam oil at the air/surfactant solution interface is investigated. Oil film spreading pressure is shown to decrease by a power law function with increasing surface shear viscosity of the surfactant film. A new fluorescence technique was used to measure the extent of PDMS spreading. Initial results suggest a correlation between the spreading distance and antifoaming performance. An antifoam mechanism is proposed that features antifoam spreading as a direct contributor to bubble film rupture and incorporates surfactant type and concentration, surfactant packing density, and antifoam oil film spreading pressure as factors contributing to antifoam efficacy.

Introduction

The control or elimination of the foam that arises in many industrial processes can be the crucial factor promoting smooth plant operation. Foam can waste capacity of processing vessels and can interfere with the efficiency of separation units. For these reasons, antifoams

have become valuable process aids in a wide variety of industries.¹⁻³

Aqueous foams stabilized by synthetic surfactants commonly occur in detergents such as those used in industrial textile processing and laundry operations. Design of the surfactant system for these applications is typically motivated by the need for enhanced cleaning performance and cost effectiveness, while providing an

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acceptable environmental profile. Oftentimes today's highly foamy surfactant systems require the addition of antifoams to control foam formation.

Modern antifoams are complex formulated specialty chemicals but generally consist of an insoluble oil phase containing hydrophobic solids dispersed within it.⁴ One commonly used oil for antifoams is poly(dimethylsiloxane) (PDMS), which can be selected on the basis of viscosity and/or viscoelastic properties that are best suited to the application.⁵ The antifoam is typically provided in a delivery system such as an emulsion or dispersion, which liberates droplets of a controlled particle size and size distribution to the surfactant solution.

Several theories have been reported in the literature on the mechanism of antifoaming by PDMS-based antifoams.^{6–10} One often-discussed aspect of antifoam mechanism is the role of antifoam oil spreading across the surfactant solution surface. Robinson and Woods¹¹ reported a correlation observed between spreading and antifoam action. Pattle¹² demonstrated a strong correlation between results of spreading tests and foam breaking tests. Ewers and Sutherland¹³ speculated that spreading was the mechanism that distributed the antifoam across the foam.

Earlier literature^{14,15} attempts to quantify the thermodynamics of spreading of antifoams using the spreading coefficients, S , expressed as

$$S = \gamma_w - \gamma_{o/w} - \gamma_o \quad (1)$$

where γ_w is the surface tension of the foaming solution, $\gamma_{o/w}$ is the interfacial tension of the antifoam oil with the foaming solution, and γ_o is the surface tension of the spreading antifoam oil against air. A positive spreading coefficient indicates that spreading of a duplex film over the foaming solution is energetically favorable.

Garrett^{4,8,16} concluded that antifoam oil spreading to form a duplex film, as measured by the classical spreading coefficient, poorly predicts antifoam performance. Similar conclusions were reached by other studies.^{17–20} Further, a definitive correlation between bulk oil spreading and foam stability was not found as it applies to foam stability in porous media.²¹

It is well known that the performance of foam-control agents varies considerably with changes in the selection of foaming surfactants. This becomes a significant prob-

Table 1. Model Liquid Detergent Compositions

component	Liquid Detergent 1, wt %	Liquid Detergent 2, wt %
sodium citrate	8.3	8.3
propylene glycol	7.0	7.0
ethanolamine	2.0	2.0
coconut fatty acid ^a	1.0	1.0
alcohol ethoxysulfate ^b	20.0	19.6
alkylpolyglucoside ^c	5.0	7.8
alcohol ethoxylate ^d	5.0	2.6
deionized water	51.7	51.7

^a Emery 621 from Henkel Corporation/emery Group. ^b Witcolate LES-60 from Witco Corporation. ^c Glucocon 600 UP from Henkel Corporation. ^d Neodol 23-6.5 from Shell Chemical Company.

lem, for example, when manufacturers of detergents vary their surfactant blends. A better understanding of the relationship between antifoaming and surfactant type is needed to more efficiently design antifoaming agents.

This paper provides strong evidence of the link between antifoaming efficacy and antifoam spreading of PDMS-based antifoams. This correlation was demonstrated as the surfactant system is varied, to include single and mixed surfactant systems, including blends of impure detergent grade surfactants. Furthermore, a correlation is established between antifoam performance and surface viscosity and in turn to molecular packing of surfactant at the interface.

Experimental Section

Materials. PDMS-based antifoam (DC2-4248S) supplied by Dow Corning was used in this study. PDMS oil (100 cSt) was also obtained from Dow Corning. We employed a wide variety of different surfactants: anionic, sodium dodecyl sulfate (SDS), purchased from Sigma; cationic, alkyltrimethylammonium bromide (C_n TAB, $n = 8, 10, 12, 14, 16$) obtained from Kodak; nonionic, penta(oxyethylene) dodecyl ether ($C_{12}E_5$) received from Nikko, Japan. Dodecanol ($C_{12}OH$), Triton X-100, and fluorescent dye Rhodamine 6G were received from Sigma Chemicals.

Every solution was prepared with buffer solution of pH 8.5 and an ionic strength 0.012 M arising from NaCl or sodium citrate. Surfactants were compared at an equal dosage of 1.55 g/L, providing surfactant systems that varied from well below their expected critical micelle concentration (cmc) to well above that molar concentration, depending on the surfactant system used.

Model liquid detergent formulas designated as Liquid Detergent 1 and Liquid Detergent 2 were also included in the testing. These were designed²² to realistically mimic modern laundry detergent compositions and were composed of blends of commercial anionic and nonionic technical grade surfactants as shown in Table 1.

Antifoaming Efficacy Measurements. A conventional cylinder shake test was used to evaluate the foaming performance of surfactant/antifoam mixtures. Foaming experiments were carried out in 100 mL volumetric cylinders using 15 mL of the foaming solution. The stoppered cylinder was shaken by hand 10 times, and the foam height was measured immediately (within 10 s) after cessation of shaking. The foaming height was measured in both the absence and presence of antifoam. When antifoam was present, it was allowed to mix with the detergent solution and was fully dispersed prior to testing. All experiments were performed at least five times at ambient temperature, 23 ± 1 °C. Quoted results in this study are the average of five measurements. At the concentration of antifoam used, 6 mg/L of silicone antifoam, all of the surfactants studied contained enough foam to establish a measurable foam head.

Surface Tension Measurements. Surface tension measurements at the air/surfactant solution interface were made by the Wilhelmy plate method using a platinum rectangular thin blade (18 mm \times 7 mm \times 0.1 mm). The blade was hooked to a sensitive force transducer. The measured surface tensions of pure water and acetone with the Wilhelmy plate using a platinum blade

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Table 2. Antifoam Efficacy Data and Oil Film Spreading Data^a

surfactant	H_0 , mL	H_a , mL	ΔH_{rel}	γ^i , mN/m	γ^f , mN/m	$\pi_{o/w}$, mN/m
SDS	93.7	31.3	0.67	37.1	31.4	5.7
Triton X-100	60.3	17.3	0.71	31.2	24.7	6.5
C ₁₂ E ₅	36.0	10.7	0.70	30.0	23.9	6.1
C ₈ TAB	3.5	0.3	0.91	46.4	21.8	24.7
C ₁₀ TAB	11.5	1.5	0.87	35.6	22.4	13.2
C ₁₂ TAB	60.4	11.5	0.81	30.9	21.8	8.3
C ₁₄ TAB	75.0	21.3	0.72	29.5	22.5	7.0
C ₁₆ TAB	57.0	24.5	0.57	29.3	23.9	5.3
SDS + C ₁₂ OH ^b	90.7	46.2	0.49	29.4	26.9	2.5
SDS + C ₁₂ TAB ^b	84.0	47.3	0.44	29.5	28.4	1.2
Liquid Detergent 1	51.6	21.5	0.58	33.1	28.9	4.2
Liquid Detergent 2	50.8	20.0	0.61	31.9	27.4	4.6

^a Surfactant concentration of 1.55 g/L, ionic content 0.012 M as added NaCl or as sodium citrate present in the detergent models, $T = 23 \pm 1$ °C, pH 8.5 set with NaOH. H_a is measured with 6 mg/L of PDMS-based antifoam present. ^b 5 mol % in the surfactant system.

were in good agreement with literature reference values. This technique was also used to study the spreading of antifoam on the liquid surface. A 10 cm diameter circular Petridish was partially filled with 50 mL surfactant solution. The Wilhelmy plate was immersed in the foaming solution at one end of the Petri dish. About 30 mg of PDMS-based antifoam dry powder was gently placed on the surface of the surfactant solution about 2.5 cm from the Wilhelmy plate. Spreading of the PDMS-based antifoam across the surface of the surfactant solutions resulted in a measured reduction of surface tension. The decrease in surface tension was allowed to come to a constant value, which typically occurred within 10 min, and that value was reported as an equilibrium value.

Surface Shear Viscosity Measurements. The deep-channel surface traction viscometer¹⁷ was used to measure the surface shear viscosity of surfactant solutions. Briefly, in the deep-channel surface viscometer the channel walls are stationary concentric cylinders and the floor of the viscometer moves with a constant angular velocity. After the center-line velocity of the air/liquid interface is measured, the surface viscosity can be calculated with the following equation¹⁷

$$\mu^s = \frac{\eta y_0}{\pi} \left[\frac{8 V_b}{\pi V e^{\pi D}} - 1 \right] \quad (2)$$

where μ^s is the surface shear viscosity, η is the bulk viscosity of subphase, y_0 is the channel width, V_b is the plate rotation speed, V is the center-line velocity of the interface, and D is the ratio of depth to width of the liquid channel. To measure the center-line velocity, a small Teflon particle was placed at the interface and the time for that particle to make one complete rotation under a certain angular velocity was recorded from visual observations.

Black Spot Measurements at the Air–Surfactant Solution Interface. Aqueous surfactant solutions containing fluorescent dye Rhodamine 6G were used to observe the formation of a black spot on the surface of foaming solutions. The experiment consisted of an UV light source emitting only the long excitation wavelength ($\lambda = 346$ nm). The surfactant solution containing fluorescent dye was exposed to the UV light. A drop of PDMS oil (100 cSt) was gently dropped by using microsyringe at the center of a glass surface (4 in. \times 4 in.) covered by a thin layer (~ 1 mm) of surfactant solutions containing the Rhodamine 6G dye. By this method, we essentially measured the diameter or size of black spot and the spreading time (i.e., the time PDMS oil takes to create a maximum size of black spot before it gets ruptured).

Results

Antifoam Efficacy. The impact of silicone antifoam at a fixed concentration on the foaminess of a range of single and mixed surfactants was assessed using a simple shake test. The initial foam height was measured within seconds after cessation of shaking, allowing only enough time for determination of the foam height. These data are included in Table 2. The antifoaming efficacy, ΔH_{rel} , is calculated by the change in foam height upon addition of

antifoam and is expressed as a fraction relative to the height without antifoam as follows

$$\Delta H = H_0 - H_a \quad (3)$$

$$\Delta H_{\text{rel}} = \Delta H / H_0 \quad (4)$$

where H_0 and H_a are the foam heights in the absence and presence of antifoams. As expected, the initial foam height was reduced in the presence of silicone antifoam, giving positive ΔH values. As clearly seen in Table 2, the foam height reduction and relative antifoam efficacy, ΔH_{rel} , vary significantly with the surfactant system used to make foam.

Antifoam Oil Spreading Pressure. The equilibrium surface tensions of the various surfactant solutions are presented in Table 2 as the initial surface tension, γ^i . A small amount of the antifoam powder was deposited on the solution surface 2.5 cm from the point of measurement and allowed to equilibrate. Surface tension of the solution was observed to decrease and then reach an unchanging level after approximately 10 min. This value of the surface tension after equilibration is the final surface tension, recorded in Table 2 as γ^f . The reduction in surface tension is a measure of the oil film spreading pressure over the solution, $\pi_{o/w} = \Delta\gamma = \gamma^i - \gamma^f$. As shown in Table 2, $\pi_{o/w}$ is positive for all the surfactant solutions tested indicating that it is thermodynamically favorable for PDMS oil to spread on the surface of the surfactant solution.

Antifoam Efficacy Correlation with Spreading Distance of Antifoam Oil. The correlation observed between relative antifoam efficacy and oil film spreading pressure is shown in Figure 1. The open circles indicate surfactants whose molar concentration is below the cmc and show that these data fit well with the systems, which are above the cmc. This indicates that the presence of micelles in the bulk solution has no effect on the antifoaming efficiency. The relative antifoam efficacy, measured as ΔH_{rel} , increases with $\pi_{o/w}$, and there appear to be two distinct regions within this correlation. In the first region, designated by the solid line, antifoam efficacy increases monotonically with $\pi_{o/w}$. This region of the correlation encompasses 10 of the 12 surfactants studied and is statistically well represented by the fitted line ($R^2 = 0.94$, where R is the correlation coefficient).

The region at high $\pi_{o/w}$ is not well explored and is designated with a dashed line. This region is characterized by a reduced slope, indicating a lesser increase in ΔH_{rel} with increasing antifoam oil film spreading pressure. The surfactants that lie in this area are below their cmc and tend to be weaker foamers having lower H_0 values, such as C₈- and C₁₀TAB. Inclusion of these points in the data

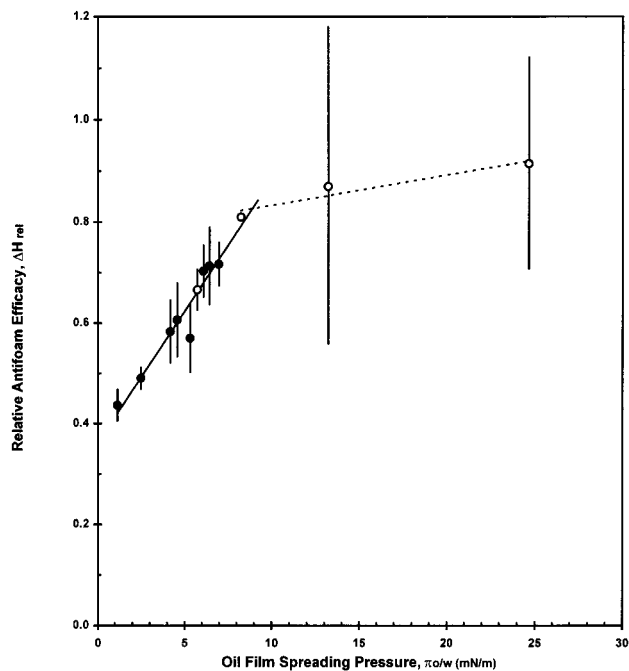


Figure 1. Dependence of relative antifoam efficacy, ΔH_{rel} , on PDMS-based antifoam oil film spreading pressure, $\pi_{o/w}$. Open points designate surfactant systems expected to be below their critical micelle concentration. Vertical lines are error bars 1 standard deviation long.

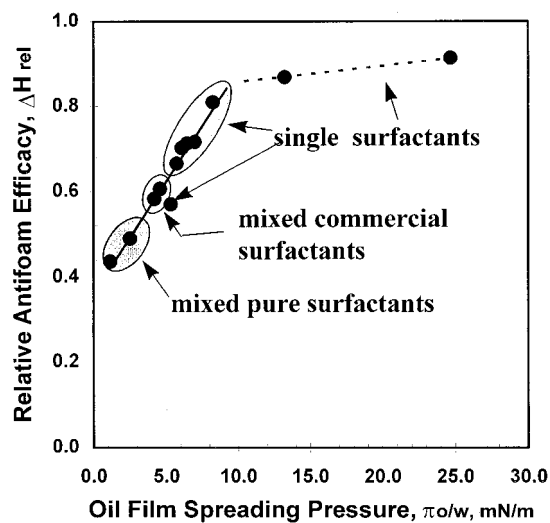


Figure 2. Relative antifoam efficacy and oil film spreading pressure dependence on type of surfactant system.

set is well justified by the other correlations to performance described below. Extrapolation of the fitted line to intercept with the ordinate predicts an antifoam efficacy of 0.36 at zero oil film spreading pressure, suggesting that even without spreading there should be a moderate antifoam efficacy due to various factors contributing to the foam collapse.

ΔH_{rel} and Surfactant Type and Surface Shear Viscosity. The observed correlation between ΔH_{rel} and $\pi_{o/w}$ (Figure 1) holds for a rather broad range of single and mixed surfactant systems. Figure 2 illustrates that the pure mixed surfactants (anionic + cationic and anionic + nonionic) lie at the lowest antifoaming efficacy. Impure mixtures in the model detergents lie at moderate antifoaming efficacies, while pure single surfactants, especially those below their cmc tend to reside at the highest ΔH_{rel} values. It is also possible to examine the impact of

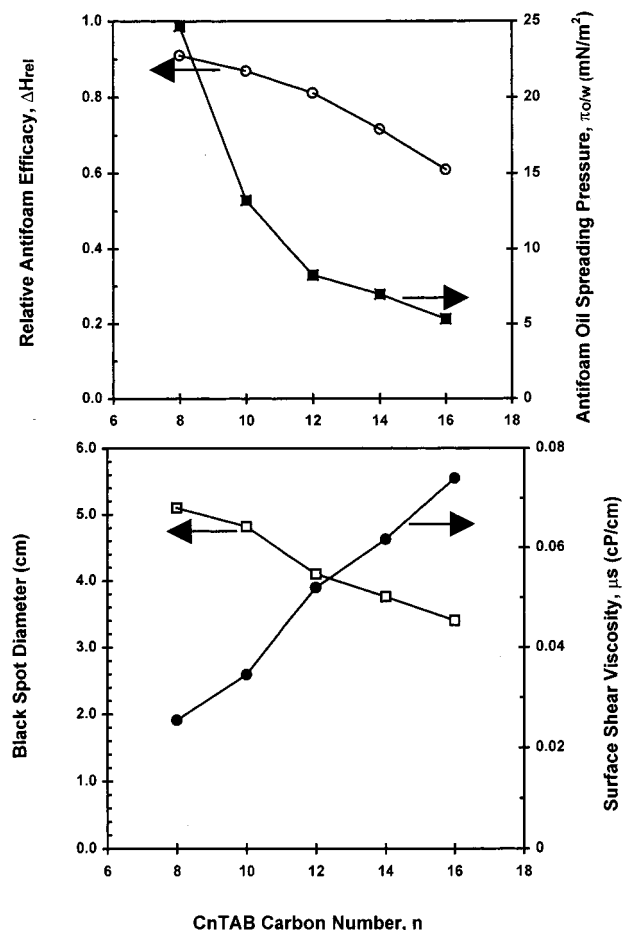


Figure 3. Dependence of ΔH_{rel} , $\pi_{o/w}$, black spot diameter and surface shear viscosity (μ^s) on alkyltrimethylammonium bromide alkyl chain length, n .

surfactant hydrophobe size on antifoam efficacy. As shown in Figure 3, the relative antifoaming efficacy for the homologous series of C_n TAB cationic surfactants is clearly related to carbon number in the chain. Figure 3 shows the relationship between antifoaming efficacy and size of black spot. The size of the circular black spot serves as an easily measured indicator of the extent of silicone spreading on a thin film of surfactant solution. The relationship shown in Figure 3 can be summarized in terms of molecular packing of surfactant. The surfactants with carbon number $n = 8, 10, 12$, are below their cmc and will provide lower density of packing, decreasing with lower n . Thus, increased density of molecular packing occurs with increased concentration of surfactant up to the cmc. Also, reduced repulsions between surfactant headgroups thought to occur in mixed anionic + nonionic or even Coulombic attractions that occur in anionic + cationic systems are generally expected to give greater surface concentration of surfactant molecules.

Table 3 contains the surface shear viscosity (μ^s) measured for each of the surfactant solutions (prior to addition of silicone-based antifoam). Juxtaposition of ΔH_{rel} with surface shear viscosity is shown in Figure 4. These results demonstrate that ΔH_{rel} correlates with μ^s across the range of surfactant solutions tested, with increasing surface viscosity giving a proportionate decrease in antifoaming efficacy (ΔH_{rel}). A linear model provides a good statistical fit to these data ($R^2 = 0.91$, where R is the correlation coefficient). Interestingly, a projected intercept with the ordinate at ΔH_{rel} of 0.98 suggests that essentially complete rupture of foam is expected at vanishingly low surface shear viscosity.

Table 3. Silicone Antifoam Efficacy and Surface Shear Viscosity of Surfactant Solution

surfactant	ΔH_{rel}	μ^s , cP/cm	black spot diameter, cm
C ₈ TAB	0.9143	0.026	5.1
C ₁₀ TAB	0.8696	0.035	4.82
C ₁₂ TAB	0.8096	0.052	4.1
C ₁₄ TAB	0.7167	0.062	3.76
Triton X-100	0.7131	0.066	
C ₁₂ E ₅	0.7028	0.074	
C ₁₆ TAB	0.5702	0.074	3.4
SDS	0.6660	0.077	
Liquid Detergent 2	0.6063	0.086	
Liquid Detergent 1	0.5833	0.106	
SDS + C ₁₂ OH ^a	0.4906	0.127	
SDS + C ₁₂ TAB ^a	0.4369	0.147	

^a 5 mol % in the surfactant system.

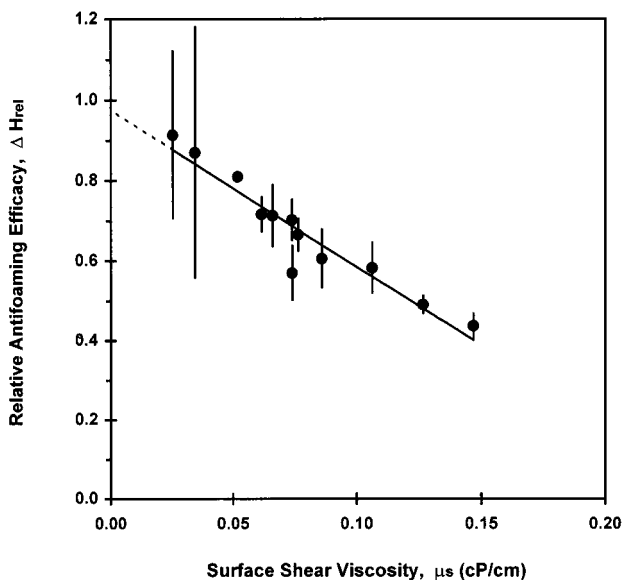


Figure 4. Relative antifoam efficacy of PDMS-based antifoam ΔH_{rel} and surface shear viscosity (μ^s). Vertical lines delineate error bars 1 standard deviation long. Dashed line illustrates extrapolation of the fitted line to the ordinate.

Extent of Spreading and Surface Shear Viscosity.

The extent or range of silicone fluid spreading on the surfactant solutions was briefly explored to see if there was a relationship with antifoam performance. For practical purposes the silicone antifoam was replaced with a small drop of PDMS delivered from a needle. The surfactant solution was spread as a weighed thin film on a square glass slide. Bulk flow of the solution was visualized through the addition of a fluorescent dye into the surfactant solution. A small drop of PDMS was placed on the wet surface of glass and PDMS spreading was observed to drive the solution away from the point of drop contact and resulted in removal of the solution to form a "black spot", a circular area that appeared dark under UV illumination because of the lack of dye in aqueous solution. Return flow of the liquid to the circle did not occur, because the silicone adhered to the underlying glass and prevented rewetting of the glass by the aqueous surfactant solution. As introduced before, the size of the circular black spot serves as an easily measured indicator of the extent of silicone spreading on the thin film of surfactant solutions. The data gathered for the series of C_nTAB cationic surfactants show the decrease of the black spot as alkyl chain length increases (Figure 5). Figure 5B shows an excellent correlation between spreading pressure and

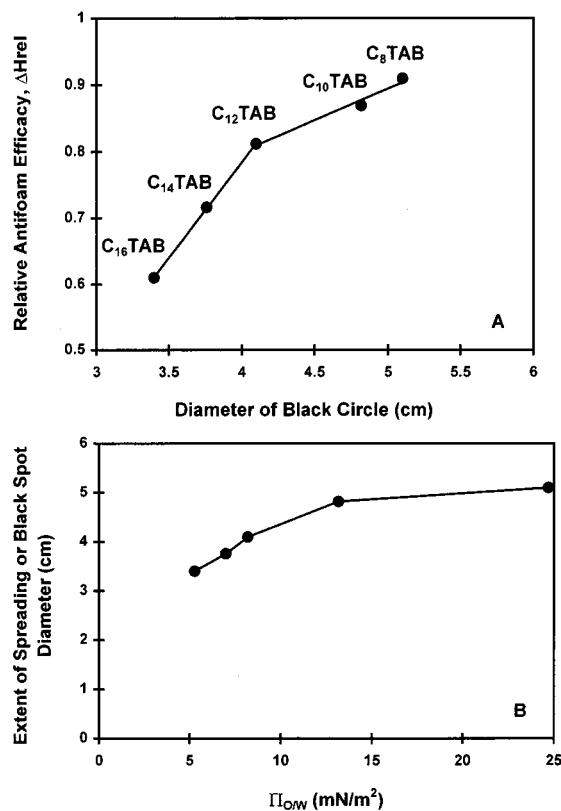


Figure 5. (A) Relative antifoam efficacy of PDMS-based antifoam, ΔH_{rel} , and diameter of spreading of 100 cSt PDMS oil. (B) Relation between extent of spreading (black spot diameter) and silicone oil film spreading pressure, $\pi_{o/w}$.

extent of spreading of silicone oil on the thin film of surfactant solution (i.e., black spot diameter).

Discussion

Antifoam Spreading As Measured by $\pi_{o/w}$. Oil film spreading pressure over a surfactant solution can be easily measured. This quantity was previously utilized as a measure of antifoam oil spreading.^{23,24} No explicit relationship to performance was established in these reports, however.

Mann²⁵ investigated surface tension reduction measured as PDMS is spread over surfactant solutions. Surface tension reduction increases nonlinearly with PDMS loading, with a sharp rise as PDMS concentration surpasses monolayer coverage, and then reaches a plateau. The exact surface tension reduction and nature of the curve are dependent on surfactant structure.²⁶ Bergeron²⁷ observed surface tension change upon PDMS spreading as being related to alkyl chain length and headgroup size of the surfactant. PDMS oil spreading over surfactant solutions was systematically investigated by Binks²⁸ who showed that surface tension reduction upon spreading is typically higher in surfactant systems with less dense packing and greater area per molecule.

In the experimental results reported here, there is sufficient antifoam oil present during the surface tension

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measurements to form a duplex film approximately 30 μm thick. The observed variation in antifoam oil film spreading pressure shows that spreading behavior varies depending on the surfactant system used. Low oil film spreading pressure (1.2 mN/m) was observed with SDS/ C_{12}TAB combination suggesting that the silicone-based antifoam is only weakly spreading over that mixed oppositely charged surfactant monolayer. A number of surfactant systems gave $\pi_{\text{o/w}}$ values in the 5–10 mN/m range, quite similar to spreading coefficient values typically calculated for spreading of PDMS over similar aqueous surfactant solutions.²⁷ Our results are consistent with the formation of a macroscopically thick film. Because the final surface tension measurements (γ^f) are the sum of the oil surface tension plus the oil/water interfacial tension, the oil film spreading pressure measured for duplex oil films will be equal to the spreading coefficient, S

$$\gamma^f = \gamma_{\text{o/w}} + \gamma_{\text{o}} \quad (5)$$

$$\pi_{\text{o/w}} = \gamma^i - \gamma^f = \gamma_{\text{w}} - (\gamma_{\text{o/w}} + \gamma_{\text{o}}) \equiv S \quad (6)$$

Oil film spreading pressure can be generalized to include film conditions between monolayer coverage and duplex film thickness. This is accomplished by including the energetic contribution of disjoining pressure, Π , to the energy of film spreading.²⁹ Disjoining pressure acts perpendicularly to the film and provides an oscillatory potential against thickness change in thin films.³⁰ Hirasaki³¹ describes a generalized spreading coefficient, S^{S} , which incorporates a disjoining pressure integral to modify the classical spreading coefficient. The oil film spreading pressure equation can be modified to incorporate the effect of disjoining pressure by making it a function of spreading film thickness, h . This is accomplished by incorporating an excess oil film tension, $\gamma^{\text{F}}(h)$ to delineate the disjoining pressure effect on spreading, and therefore sets oil film spreading pressure as equal to the generalized spreading coefficient

$$S^{\text{S}} = \pi_{\text{o/w}}(h) = \gamma_{\text{w}} - \gamma_{\text{o/w}} - \gamma_{\text{o}} - \gamma^{\text{F}}(h) \quad (7)$$

where

$$\gamma^{\text{F}}(h) = \int_{\Pi=0(h=\infty)}^{\Pi(h)} h' d\Pi \quad (8)$$

In conclusion, the utility of oil film spreading pressure is that, unlike S , it makes no assumptions about spreading geometry and characterizes the spreading behavior covering the range of thicknesses from monolayer spreading to duplex film formation. Values measured for $\pi_{\text{o/w}}$ are expected to vary from values calculated for S in cases where monolayer or thin film spreading occurs and therefore should produce a more appropriate measure of film spreading. No independent measurements of interfacial tension ($\gamma_{\text{o/w}}$) and antifoam oil surface tension (γ_{o}) were measured in this work, and no direct comparison between S and $\pi_{\text{o/w}}$ is possible.

Meaning of ΔH_{rel} . ΔH_{rel} possesses a clear correlation both with spreading pressure ($\pi_{\text{o/w}}$) and with surface viscosity (μ^{S}) and, thus, offers a demonstrated advantage for studying antifoaming effects. In contrast, foam decay

data, measured with a decay time of 120 s after cessation of shaking (data not included) shows no obvious correlation with any measurable parameter for our system of surfactants and antifoam.

One possible explanation for this advantage is that ΔH_{rel} is based on the measurement of initial foam heights. These measurements are restricted to times of less than 10 s and, as such, focus on processes that occur in the formation and immediate collapse of foam. By design, ΔH_{rel} is biased toward measuring antifoam performance defined by events that occur on a relatively short time scale (\approx seconds).

Denkov³² recently described observations of rupture of large single bubble films made using high-speed videophotography. His observations showed that in the presence of antifoam particles, bubble film rupture could originate from within the thinning bubble lamella or could originate from the Gibbs plateau border (GPB) at the bubble perimeter. The ruptures within the lamella occurred within 1 s or less after formation of the film. Ruptures thought to originate from the GPB occurred on a longer time scale, typically requiring minutes before rupture was observed.

Given the possibility that there is more than one class of antifoam rupture mechanism operating with distinctly different kinetics, then ΔH_{rel} may be understood to be a selective measurement, which emphasizes antifoam processes occurring at a fast time scale. It then follows that foam decay measurements might include contributions from different foam rupture processes operating on short and on longer time scales. If these processes are controlled by different physical attributes of the foam or antifoam, then the outcome of foam decay measurements is expected to be complex and will therefore lack simple correlations to measurable foam properties.

ΔH_{rel} Correlation with Surface Shear Viscosity.

ΔH_{rel} possesses a strong correlation to the surface shear viscosity of the surfactant solution (Figure 4). For this to be so, surface flow of the surfactant solution must be a significant contributor to the mechanism of antifoam action, as it applies to the short time scale antifoaming process. From the data currently available it is not clear in what way surface flow contributes to antifoaming efficacy. Two possibilities are considered:

(1) One possibility is that the surface shear viscosity of the bubble affects processes important to ΔH_{rel} but independent of any antifoam spreading. It is well established that increased surface shear viscosity reduces the rate of bubble film drainage³³ and correlates with an increase in foam stability.^{34–36} Hydrocarbon chain length and surfactant packing strongly influence the foam film stability of $Cn\text{TAB}$ surfactants.³² On this basis, it is possible that higher surface shear viscosity would lead to slower bubble lamella thinning rates and reduce ΔH_{rel} by reducing the probability of effective antifoam–bubble interactions leading to rupture in the short time scale antifoaming process.

(2) A second hypothesis is that the surface shear viscosity will directly affect the antifoam–bubble interactions. One possible direct impact is that surface shear viscosity of the surfactant solution would affect the rate or extent of

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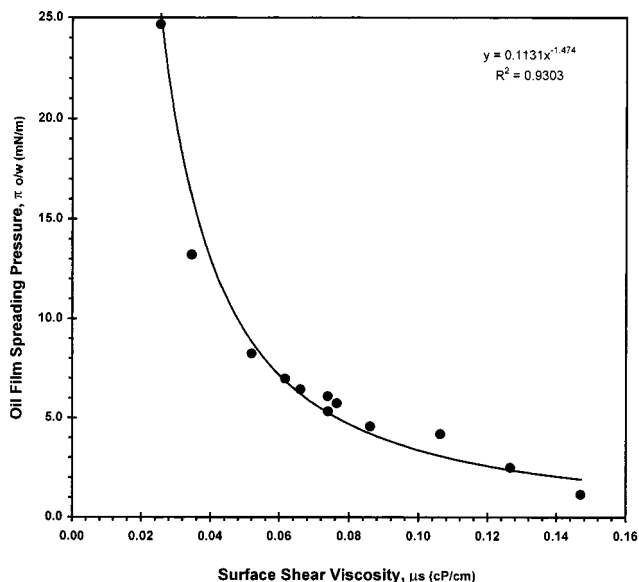


Figure 6. PDMS-based antifoam oil film spreading pressure ($\pi_{o/w}$) and surfactant solution surface shear viscosity (μ^s) showing line fitted using a power law equation.

silicone spreading in a way that directly impacts the process of bubble rupture.

Figure 6 shows that the oil film spreading pressure of the silicone antifoam follows a power law relationship with surface shear viscosity. There is a strong increase in film spreading pressure ($\pi_{o/w}$) with the surfactant systems that have low μ^s , with the greatest increase in systems that are below their cmc and have a low density of monolayer packing. This finding is consistent with Binks²⁸ and shows that the relationship arises because those systems with the lowest density of molecular packing provide for the greatest change in surface and interfacial energy upon spreading.

Black spot measurements reported here pursued a possible link between the extent of spreading and antifoam efficacy. The data for the cationic surfactants defined in Figure 3, show that increased surface shear viscosity correlates with a decrease in the extent of spreading. Illustrated in Figure 5, the surfactant systems, tested for PDMS spreading, which had a larger black spot diameter, also possessed a higher antifoam efficacy. It is interesting to note that the shape of the curve, with a second region containing the two lower molecular weight cationic surfactants is reminiscent of Figure 1. Figure 1 shows decreasing gain in ΔH_{rel} as the extent of spreading increases. Obviously, the link between antifoam efficacy and the extent of spreading requires a great deal more exploration before the relationship will be understood sufficiently.

ΔH_{rel} Correlation with Surfactant System and Surface Shear Viscosity. In practical terms, the correlation between antifoam efficacy and the type of surfactant system (Figure 2) and surfactant shear viscosity (Figure 4) offers an opportunity to connect antifoam understanding to a well-established base of knowledge on surfactant interactions and surface packing and a means to quantify the packing by measuring surface shear viscosity. It can be seen in Table 3 that variation in structure of single surfactants or various mixtures can have significantly different surface shear viscosities. Surface viscosity is established by the interactions between surface-adsorbed surfactant molecules. Systems below their cmc will be sensitive to surfactant concentration especially as they approach surface saturation and

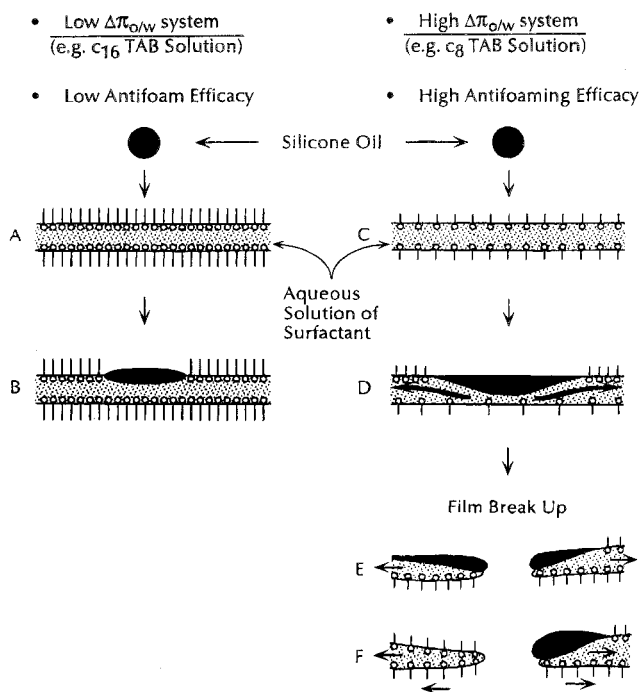


Figure 7. Schematic illustration of proposed mechanism for antifoam action of Silicone oils.

subsequently their cmc, with increased packing at higher concentrations. In systems above their cmc, lower repulsion between surfactant headgroups results in denser monolayer packing. Mixed surfactant systems such as anionic + nonionic surfactant blends will typically show greater density of monolayer packing. Modification of the sodium dodecyl sulfate systems with 5 mol % of dodecanol or C₁₂TAB behaved as expected, giving significantly increased surface shear viscosity. These systems are well known to exhibit better molecular packing compared to SDS alone.^{35–40} The packing at the air–water interface in mixed surfactant systems is also influenced by the hydrocarbon chain configuration, including length of alkyl hydrophobe,^{22–25} branching, etc.

The relationship between ΔH_{rel} and surfactant packing provides a means to rationalize the differences in antifoam efficacy measured between different surfactant systems. Second, surface shear viscosity provides a means to quantitatively measure subtle changes in surfactant packing that are directly related to antifoam efficacy. Further elucidation of these relationships should be possible through more systematic investigation.

Spreading and Antifoam Mechanism. It is clear from Figure 1 that there is greater antifoam efficacy with higher antifoam oil film spreading pressure. This suggests that the greater the rate or extent of silicone-based antifoam spreading, the greater the efficacy. Although not a conclusive link to the antifoam mechanism, the demonstration of greater extent of spreading offered in Figure 5 is supportive of the link between extent of spreading and higher $\pi_{o/w}$.

Figure 7 schematically illustrates our proposed mechanism for antifoam action of silicone oils. The left-hand side of the figures (A and B) shows the effect of silicone

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oil on surfactant systems that are resistant to antifoam due to high surface viscosity, which is due to close molecular packing at the surface. These systems also exhibit poor spreading of silicone oil and low $\pi_{o/w}$. Because of poor spreading, significant thinning of lamella does not occur. On the other hand, the right-hand side of Figure 7 (parts C and D) illustrates how certain systems that exhibit high antifoam efficacy work. Here, the silicone oil spreads significantly due to loose molecular packing of surfactant molecules. Such adsorbed films will exhibit higher compressibility. Such surfactants exhibit lower surface viscosity and higher $\pi_{o/w}$. The thinning of film occurs as the boundary layer of water is dragged by spreading of silicone oil. When aqueous film thickness reaches to a critical value, the thin liquid films break. If the silicone oil has low viscosity, the oil drops break into two (Figure 7E). This mechanism ultimately will produce smaller and smaller droplets and hence reduce the antifoam effectiveness. On the other hand, if the silicone oil is viscous, the drop is pulled on one side of the rupturing lamella (Figure 7F) and will not cause reduction in the size of the oil droplets. This will increase the duration or effective life of antifoam oil. This implication is in agreement with the results on foam half-life reported by Wasan and co-workers⁴¹ for silicone oils of different viscosities. Thus, we propose that thinning of the water layer by the spreading of a silicone oil drop on the lamella surface is the major mechanism for the antifoam action and that the spreading is influenced by the molecular packing of the surfactant at the air/water interface. With closure of the molecular packing, there is less spreading of silicone oil drop and less thinning, resulting in the poor

antifoam action. The effect of film rupture on the droplet size of the oil presumably controls the duration of action of antifoams. The lower viscosity of the oils leads to the decrease in size of droplets and hence less effective antifoam action by these silicone oils.

Conclusions

The work reported here explores the performance of PDMS-based antifoam in a variety of surfactant foaming solutions. Greater antifoam spreading tendency, measured as oil film spreading pressure, $\pi_{o/w}$, correlates with greater relative silicone antifoam efficacy, ΔH_{rel} , in reducing initial foam heights, by shake test. Further exploration of the region as $\pi_{o/w}$ approaches zero should provide evidence about the role of antifoam spreading as one of the key parameters for antifoam performance. A statistically strong correlation between surfactant solution surface shear viscosity and relative antifoam efficacy was demonstrated (Figure 4). This finding fits with the observed dependence of relative antifoam efficacy on surfactant molar concentration, hydrophobe size, and surfactant type especially in mixed surfactant systems. This finding can be used to rationalize differences in relative antifoam efficacy using well-known monolayer packing behavior and provides a potentially useful link between antifoam efficacy and surfactant selection.

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