I, Zheng Yuan, hereby submit this original work as part of the requirements for the degree of Master of Science in Materials Science.

It is entitled:
Impact of Colloidal Silica on Silicone Oil-Silica Mixed Antifoams

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Committee member: Gregory Beaucage, Ph.D.
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Impact of Colloidal Silica on Silicone Oil-Silica Mixed Antifoams

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Abstract

Antifoams are utilized as an industrial additive to control undesired foam during processing. This study focuses on the impact of silica on the antifoam stability. Antifoam stability refers to the ability to maintain efficiency in foam destruction after prolonged shelf storage. Common antifoams are a mixture of hydrophobic silica particles and silicone oil.

Based on the general mechanisms of antifoam action discussed in Chapter 1, silica particles play a significant role in foam destruction. Silica particles contribute to foam control by facilitating the entry and the penetration depth of oil-silica globules into surfactant-water films (foam bubble walls). The size, morphology and hydrophobicity of silica can be manipulated to generate optimal antifoam globules. For example, the two silicas with good shelf life performance (8375 and 9512) had the largest silica particles and both showed a tendency to aggregate in toluene solution.

We conclude that improved shelf life is related to the propensity of PDMS oil to adsorb on silica, which leads to aggregation and particle size increase. We measured the time-evolution of dynamic light scattering (DLS) from 3-vol% antifoam dissolved in toluene (Chapter 2). For the sample with the largest hydrodynamic radius (9512) the scattered intensity decreased significantly after applying ultrasonic dispersion. Decreasing intensity also occurred for 8375 albeit at later times. The decrease of intensity is attributed to the growth and precipitation of oil-silica globules. The concentration dependence of light scattering confirmed the growth-precipitation hypothesis. FT-IR (Chapter 3) was consistent with precipitation due to oil adsorption, but the data were not definitive.
Chapter 4 examines the time-evolution of silica structures by static light scattering and X-ray scattering. The combined data are consistent with a hierarchical structure for silica. Agglomeration occurred fastest for 9512, which is consistent with DLS observations above.

The last chapter concludes that PDMS-silica adhesion controls antifoam stability. The decline in performance with shelf-life aging is attributed to loss of hydrophobicity of silica, which could be due to adsorption of surfactants or some chemical alteration of the hydrophobic silica surface.
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Chapter 1 Introduction

1.1 Overview of Antifoam

Foaming is common and generally harmless in the daily life. Undesired foaming, however, can be a critical issue in many industries, such as food, paint and coating, pulp and paper, chemicals, pesticide and herbicide. Excessive foam may decrease the process capacity, and consequently, cause efficiency and quality problems.\(^1\) Therefore foam-control technology needs to be understood.

The foam control agents can be classified as antifoaming or defoaming.\(^2\) The two terms are often used interchangeably but in fact they refer to different approaches to foam reduction. Antifoams are predispersed in aqueous solution to prevent the formation of foam, whereas defoamers are added to eliminate foam by inducing rapid foam collapse. Antifoams and defoamers can have multiple components, including solid particles, carrier fluid (e.g. oil, water or polymers), and surfactants. Antifoam efficiency and stability are often used to characterize the antifoam performance. Efficiency refers to either the ability to prevent foam generation or the ability to destroying foam that has already been generated.\(^3\) In this study, the antifoam stability is the ability to maintain its efficiency in foam destruction after prolonged shelf storage, a.k.a. the shelf life. Stability is determined by the components of antifoams and the mechanism of antifoaming.

Previous research\(^4\) demonstrated that oil-solid antifoam compounds are more efficient than single-component antifoams consisting of either solid (typically silica particles) or oil. However, oil-solid antifoams are not compatible with water. In practice, emulsions of mixed oil-solid antifoams are formulated. Aqueous emulsified antifoams are nonflammable and more convenient than dry, bulk formulations. Antifoam-emulsions can be prepared by emulsifying silicone-silica compound antifoams or by adding silica fillers to emulsified silicone oil antifoams. The proportion of silicone oil is usually from 10% to 70%. Other ingredients include water, silica particles,
emulsifying agents, etc.⁵

When oil-solid antifoams are added to a foaming solution, solid-enriched oil globules form in the solution. In addition, some oil spreads on the solution surface to form oil lenses (Fig. 1.1). Both entities contribute to foam destruction. The solid particles trapped in oil globules play a key role in both efficiency and stability of foam-control agents.

![Microscope images](image)

**Figure 1.1 (A)** Microscope image of transmitted light from antifoam globules of micrometer size, with silica particles (dark objects) adsorbed on the surface. **(B)** Microscope image in reflected light of the surface of a foaming solution. 1: antifoam globules below the solution surface. 2: oil lenses containing silica (dark objects) in the center. 3: The spread layer of silicone oil. (Scale bar 100 µm).⁴

### 1.2 General Mechanism of Antifoams

Addition of surfactants is a common method to produce foam by decreasing the surface tension. Low surface tension allows liquid to form thin films with air trapped in bubbles. Fig. 1.2 presents the typical structure of foam, which consists of surfactant-stabilized films, air cells (bubbles), Plateau borders and nodes (junctions of Plateau borders). Foam films are the regions filled with
liquid between adjacent air bubbles. The two surfaces of a foam film are formed by surfactant molecules as shown in Fig 1.2 B. Plateau borders are the long, liquid-filled channels.

![Figure 1.2 (A) Photograph of foam structures obtained by cryo-scanning electron microscopy; (B) Schematic representation of foam structure. h is the film thickness. (C) The elements of foams. Plateau borders are thin channels with a length of L and nodes are where three Plateau borders meet.](image)

Aqueous foams are thermodynamically unstable. Spontaneous drainage occurs, resulting in film thinning and rupture. Drainage refers to the motion of liquid within both channels (Plateau borders) and films, driven by capillarity and gravity. The drainage rate is determined by several factors, e.g., surfactant concentration, surface viscosity, and interfacial chemistry. Surfactant molecules retard film thinning, but ultimately surface tension drives thinning. For foams with ionic surfactants, the electrical repulsive force between two charged surfaces can retard or prevent film thinning when the surfaces become sufficiently close. The dynamics are complicated and foam stability is eventually dominated by these opposing forces.

Antifoam entities enhance film rupture and hence foam destruction. Antifoam entities vary with antifoam type. For instance, these entities are silica particles for solid-silica antifoams, whereas they are silica-enriched oil globules for oil-silica antifoams.
1.3 Fast vs. Slow Antifoams

The action modes of antifoams are complicated. Various scenarios may occur after antifoam entities enter the foaming solution. Antifoams can be split into two types, fast and slow,4 which are distinguished by the location where the colloidal antifoam entities cause foam destruction and by the time-scale of foam collapse.

For fast antifoam, “bridging-stretching,” “bridging-dewetting” and “spreading fluid entrainment” mechanisms have been postulated in the literature.4, 11 Generally speaking, the antifoam entities of fast antifoams enter and rupture the film by forming a bridge or inducing local thinning inside the films. Most oil-solid mixed antifoams are in this category. Three stages of an oil-bridge evolution were observed by Denkov et.al.1 (Fig. 1.3). The antifoaming system they observed was a mixture of PDMS and hydrophobized silica particles (4.2 wt%) in 10-mM sodium dioctylsulfosuccinate aqueous solution. Bridging occurs during film thinning leading to film rupture, typically within one minute. A detailed discussion of bridging-stretching mechanism and bridging-dewetting mechanisms is presented in subsequent section.

For slow antifoams the location of antifoam action different from that of fast antifoams (Fig. 1.4). Whereas fast-antifoam entities enter the films directly and perforate them by bridging, droplets in slow antifoams first migrate to the Plateau borders. This mode takes several minutes or longer to cause a foam reduction.
Koczo et al.\textsuperscript{12} examined the slow mode when investigating antifoam consisting of hydrophobic particles and oil. These authors observed that oil drops containing solid particles flowed out of the film and entered the Plateau borders. Oil bridges then formed in the borders during drainage,
leading to rupture. This bridging process is similar to the mode of fast foam, but the location of antifoam action is different. Location is the crucial factor that distinguishes the two mechanisms. Single component antifoam (solid particles alone or oil alone) are often slow-acting antifoams.

The term “entry barrier” is the critical capillary pressure required for antifoam globules to pierce into the air-water interfaces.\(^4\) Typically fast antifoams have low entry barrier. A lower entry barrier means facile penetration of film surfaces.

The actions of antifoams depend on various factors, including the nature of antifoam entities (solid particles, oil droplets or solid enriched globules), the hydrophobicity of solid particles, kinetics of surfactant adsorption, and the presence of additives. In a word, the mechanisms of foam destruction are quite complex and poorly characterized.

### 1.4 Mechanism of Foam Destruction

Foam destruction depends on the structure and evolution of antifoam entities. For silicone-oil antifoams with dispersed hydrophobic silica, the oil globules and the oil lenses (aka. antifoam entities) are responsible for foam destruction. Globules are dispersed in the solution, whereas oil lenses typically float on the solution surface as a thin layer of oil (Fig. 1.1 B). The lenses can be viewed as an intermediate state between globules and oil bridges.\(^4\) Depending of silica loading, some faction of lenses and globules may not contain silica particles.

Bridging-stretching and bridging-dewetting mechanisms have been reported in oil-based antifoams.\(^1\)\(^,\)\(^13\)\(^-\)\(^14\) As the oil globule enters in the foam film, an oil lens forms on one of the film surfaces (Fig. 1.5 B) and then bridges the two surfaces during thinning. If the oil-water-air contact angle \(\alpha_w\) is smaller than 90°, mechanical equilibrium ensues by satisfying capillary pressure and the surface tension balance in the three-phase system. Both modes of film rapture require that \(\alpha_w\) is larger than 90°. Otherwise, the oil bridge remains stable. For the unstable oil bridge, either
stretching \((A \rightarrow B \rightarrow C \rightarrow D\) in Fig 1.5) or dewetting \((A \rightarrow B \rightarrow E \rightarrow F\) in Fig. 1.5) can induce film rupture.

**Figure 1.5** Schematic of the bridging-stretching and bridging-dewetting mechanisms. *(A-B)* Oily drop enters the film. The oil bridge formed at one of film surfaces is unstable if the entry contact angle oil-water-air \(\alpha_w > 90^\circ\). Either stretching or dewetting is possible. *(C-D)* The oil globule deforms under the capillary forces (red arrows). The unstable oil bridge is stretched until rupture. *(E-F)* The dewetting process occurs when the oil bridge doesn’t deform fast. Under the capillary forces (red arrows), the oil lens is dewetted by the liquid of the film. The film moves as black arrow shows and eventually is perforated at the sides of the oil bridge.

The stretching mechanism postulates deformation of oily globules. The globule become trapped in the water films during water drainage, eventually forming an oil bridge that spans the thickness of the film. Then the unbalanced capillary pressures make the oil bridge stretch in the radial direction, leading to a deformation and rupture in the bridge center (Fig 1.5 C→D). The direction of capillary forces are shown as red arrows in Fig 1.6. If the deformation of oil globule is slow, dewetting may occur before stretching. The capillary pressure makes the film dewet from the oil globule, causing film rupture as Fig. 1.5 E→F shows.\(^{12,15}\)
The size of oil globules strongly affects the antifoam properties. The size scale of silica-enriched globules should be close to the characteristic size of the structural elements: film thickness (typically about 1 µm within several seconds after film formation) for fast antifoam and thickness of Plateau borders (typically tens to hundreds of micrometers) for slow antifoam. The former is much smaller than the latter.\textsuperscript{16} Assuming that the concentration of antifoam in the solution is fixed, the number of globules would be very low if the average size of globules is large, resulting in low efficiency. On the other hand, if the average size of globules is too small, they can’t form oil bridges until the thickness of film thins to a thickness comparable to the globule diameter. The optimal globule size depends on the system in question, but is typically several micrometers in diameter.

Silica particles have a significant influence on the bridging-stretching process. First, particles increase the penetration depth of oil lenses, shown in Fig. 1.6 A-B. In this way silica particles facilitate the deformation of globules.\textsuperscript{4} Furthermore, silica particles encounter a lower entry barrier than globules deprived of silica particles. So when globules approach the surface of the film, the particles efficiently pierce the oil-water and the water-air interfaces.\textsuperscript{4} In other words, the hydrophobic particles assist the globule to reach the surface of thin films, shown as Fig. 1.6 C. This piercing is so-called “pin effect.”

Silica particles are also implicated in foam aging (decline of antifoam activity with time in use). Some research\textsuperscript{16} implies that the expulsion of silica particles from oil globules is responsible for antifoam exhaustion. Hydrophobic particles become hydrophilic during foam destruction due to surfactants being gradually absorbed on the particle surfaces in solution. However, there is still debate regarding the role of silica particles in antifoam exhaustion. One viewpoint\textsuperscript{12} suggests that silica particles do not play a critical role in antifoam exhaustion. Rather exhaustion primarily
results from the reduction of globule size. Denkov et al.\textsuperscript{14} attribute antifoam exhaustion to two combined processes, segregation of silica from oil drops and disappearance of spread-oil layers (oil lenses).

\begin{figure}[h]
\centering
\includegraphics[width=\textwidth]{figure1.6.png}
\caption{Schematic representation of the effects of solid particles on the foam films. (A) Oil lens formed by oil alone; (B) Oil lens formed by oil with dispersed solid particles, leading to a larger penetration depth $d_{CL}$; (C) A silica particle helps to pierce the air-water surface of foam films due to its lower entry barrier.}
\end{figure}

1.5 Summary

Antifoams have been developed as additives to control the volume of foams throughout various industries since the 1950s. In recent years, oil-silica mixed antifoams (e.g., hydrophobic silica particles dispersed silicone oil) have emerged as an efficient antifoam technology that is preferred for economic reasons. Antifoam stability is a significant issue in the antifoam industry. The terms used in this thesis are explained in Table 1.1.

In this work, six silicone oil-silica mixed antifoams are studied. The goal is to correlate antifoam stability as measured by P&G with the evolution of silica particle morphology with time after
dispersion in solution. Because antifoams alone are insolvable in water, in this research we choose toluene as the solvent. In toluene solutions light is primarily scattered by the silica particles. The relation between the silica properties and the antifoam stability is discussed. The results demonstrate a correlation between stability and oil adsorption on silica, which lays the groundwork for strategies to improve antifoam stability.

Table 1.1 Summary of the terms of antifoams used in this thesis.

<table>
<thead>
<tr>
<th>Category</th>
<th>Terms</th>
<th>Definition</th>
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<tbody>
<tr>
<td>Foam</td>
<td>Foam film</td>
<td>The regions separating adjoining air bubbles.</td>
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<tr>
<td></td>
<td>Film surface</td>
<td>The surfactant layer of films at the air-water interface.</td>
</tr>
<tr>
<td></td>
<td>Plateau border</td>
<td>Thin channels filled with liquid at where three films meet.</td>
</tr>
<tr>
<td></td>
<td>Node</td>
<td>The points where Plateau borders meet and are connected.</td>
</tr>
<tr>
<td>Antifoam</td>
<td>Activity</td>
<td>Ability to prevent foam generation and/or ability to destroying existing foam</td>
</tr>
<tr>
<td></td>
<td>Stability</td>
<td>Persistence of antifoam activity after shelf-storage.</td>
</tr>
<tr>
<td></td>
<td>Efficiency</td>
<td>A measure of antifoam activity in a qualitative sense.</td>
</tr>
<tr>
<td></td>
<td>Exhaustion</td>
<td>Loss of activity with time after deployment.</td>
</tr>
<tr>
<td></td>
<td>Antifoam entity</td>
<td>Objects causing rupture (oil lens, oil drops, silica-oil globule, solid particle).</td>
</tr>
<tr>
<td></td>
<td>Aging</td>
<td>Time evolution without agitation (in this study: 25 min and 40 min).</td>
</tr>
</tbody>
</table>
Chapter 2  Time-evolution by Dynamic Light Scattering

2.1 Overview

Variations among ostensibly similar colloidal silicas lead to unexpected changes in the efficiency and stability of the antifoam samples. As discussed in Chapter 1, the size of silica particles has a significant effect on anti-foam performance. Therefore, this chapter aims to characterize the hydrodynamic size of colloidal silica in solution, and to investigate the aging of colloidal silica solutions.

Colloidal silica has multiple levels of structure consisting of primary particle, aggregates and agglomerates, which may be “soft” or “hard.” Sonication reduces the size of soft agglomerates while the strongly bonded hard agglomerates remain intact. Therefore the effect of sonication on hydrodynamic size is measured and discussed.

2.2 Dynamic Light Scattering (DLS)

Dynamic light scattering (DLS) is based on the Brownian motion of particles in solution. DLS measures the intensity of scattered laser light intensity at short time intervals. The fluctuations of the intensity, I, can be converted electronically to a second-order intensity autocorrelation function by a correlator. The autocorrelation function contains the information on diffusional behavior and hydrodynamic size of samples.

According to the manual, the correlator obtains signals and performs a normalization automatically. A second-order intensity autocorrelation function $g^{(2)}(\tau)$ is given by:

\[
g^{(2)}(\tau) = \frac{\langle I(t) > \langle I(t+\tau) > \rangle}{\langle I(t) >^2}\) \tag{2.1}
\]

\[
g^{(2)}(\tau) = 1 + f \cdot e^{-2/\tau} \] \tag{2.2}
where \( I(t) \) is the intensity at time \( t \), and \( \tau \) is the lag time interval. Here prefactor, \( f \), depends on the degree of spatial coherence of scattered beam at the detector. \( \Gamma \) is the decay rate.\(^{18,19}\)

The cumulant method was used to interpret the data. Cumulant analysis fits a polynomial to the logarithm of the \( g^{(2)}(\tau) \). The first cumulant is the average decay rate, and the second and third terms in the polynomial describe the polydispersity. Because of limited accuracy of higher terms in the polynomial expansion, cumulant analysis reliably gives only the z-average size and an average polydispersity of the particle size. Methods are available to extract full distributions, but these methods are misleading when higher order cumulants are poorly known. Details of cumulant fitting are discussed in Appendix B.

The average decay rate is related to the Z-average (i.e. weighted by the square of the mass) translational diffusion coefficient \( D \) by:

\[
\Gamma = q^2 D
\]

\[
q = \frac{4\pi n}{\lambda} \sin(\theta/2)
\]

where \( q \) is the scattering vector, \( D \) is the diffusion coefficient, \( n \) is the reflective index for the sample, \( \theta \) is the scattering angle and \( \lambda \) is the wavelength of laser.\(^{18,19}\)

The hydrodynamic radius is calculated from the translational diffusion coefficient using Einstein-Stokes equation:\(^{19}\)

\[
D = \frac{k_B T}{6\pi \eta R_h}
\]

where \( k_B \) is the Boltzmann’s constant (1.38×10\(^{-23}\) m\(^2\) kg s\(^{-2}\) K\(^{-1}\)), \( T \) is the temperature, \( R_h \) is the hydrodynamic radius and \( \eta \) is the kinematic viscosity of the solvent. According to Eq. (2.3), the slope of a plot of decay rate \( \Gamma \) versus \( q^2 \) is the average translational diffusion coefficient \( D \). Fig. 2.1 displays a typical normalized second-order intensity autocorrelation function \( g^{(2)}(\tau) – 1 \).
Smaller particles have faster diffusion so the correlation would have a higher decay rate, and vice versa.

Figure 2.1 Second-order autocorrelation function of polystyrene microspheres (0.25 µm diameter) in water measured by dynamic light scattering at a scattering angle of 90° at 20±1 °C.

Count rates (photons/s) are also plotted as a function of time (i.e. measurement duration). Fig. 2.2 displays a typical intensity fluctuation of polystyrene standard spheres measured at 90° for 300 seconds. The behavior of particles in the solution can be monitored qualitatively by observing fluctuations and trends in the count rate. Basically, solutions containing uniformly dispersed particles show a normal fluctuation as Fig. 2.2. If sharp spikes in intensity are observed, it indicates the existence of dust. If counts are steadily increasing, the particles in this sample are probably aggregating, whereas the sample is undergoing sedimentation or dispersion if the count rates are decreasing.
Figure 2.2 A typical plot of intensity (counts) versus time of polystyrene microspheres (0.25 µm diameter) in water measured by dynamic light scattering at a scattering angle of 90° at 20±1 °C.

2.3 Experimental

The instrument used for DLS measurements is a Malvern CGS-3 multi-angle light scattering spectrometer in conjunction with an ALV correlator. According to the user’s manual, the laser has a wavelength of 632.8 nm. The instrument is capable of measuring particle sizes from 1 nm to 3 µm. Each DLS measurement was taken at 4 scattering angles (30°, 60°, 90° and 120°). All the samples were measured at room temperature. The data was interpreted using analysis Igor code written by Prof. Dale W. Schaefer (in Appendix B).

Antifoam samples were provided by Proctor & Gamble Corporation (P&G). Antifoam samples listed in Table 2.1 are named using the last four digits of their lot numbers. Other chemicals are listed in Table 2.2. The shelf-life tests were conducted by P&G. In the shelf-life tests, the antifoam-water emulsion was dispersed in the foaming solution during agitation. Meanwhile the volume of foam was recorded. The performance of antifoams is evaluated by determining whether the volume of residual foam meets proprietary specifications. The tests are repeated every three months to check if the antifoam emulsions have degraded over time (shelf life). Some antifoam emulsions
passed the test initially but failed after a few months of storage, indicating loss of activity. The antifoams that passed tests were considered good performers. Silica D-10 is the silica used in one or more antifoam samples in Table 2.1. As an antifoam component, D-10 has high hydrophobicity and high effectiveness.

**Table 2.1 Sample information and stability performance of the antifoams.**

<table>
<thead>
<tr>
<th>Sample No.</th>
<th>Main Ingredients</th>
<th>Shelf-Life Performance</th>
</tr>
</thead>
<tbody>
<tr>
<td>9512</td>
<td>Silicone oil, Silica, Silicone resins, Surfactants, Perfume, etc.</td>
<td>Good</td>
</tr>
<tr>
<td>8375</td>
<td>Good</td>
<td></td>
</tr>
<tr>
<td>8340</td>
<td>Bad</td>
<td></td>
</tr>
<tr>
<td>6165</td>
<td>Bad</td>
<td></td>
</tr>
<tr>
<td>4684</td>
<td>Bad</td>
<td></td>
</tr>
<tr>
<td>0963</td>
<td>Bad</td>
<td></td>
</tr>
</tbody>
</table>

**Table 2.2 Sample information of silica, PDMS, toluene (solvent) used in this study at room temperature.**

<table>
<thead>
<tr>
<th>Sample name</th>
<th>Mw</th>
<th>Density (g/cm³)</th>
<th>Viscosity</th>
</tr>
</thead>
<tbody>
<tr>
<td>Silica-D10</td>
<td>Unknown</td>
<td>0.15 (powder)</td>
<td></td>
</tr>
<tr>
<td>Polydimethylsiloxane (PDMS)</td>
<td>~25,000</td>
<td>0.97</td>
<td>820~1110 cp</td>
</tr>
<tr>
<td>Toluene</td>
<td>92.14</td>
<td>0.87</td>
<td>0.58~0.60 cp</td>
</tr>
</tbody>
</table>

Due to high viscosity of the fluids, tiny bubbles in antifoams are difficult to remove, making it impossible to measure bulk antifoam characteristics directly by DLS. To circumvent this problem toluene was used as a solvent. Toluene dissolves the silicone fluid and silica in antifoam, enabling DLS to study the colloidal silica component of the antifoams. Antifoams were diluted to 1, 3, 5 and 10 vol% in toluene. Each antifoam-toluene solution was sonicated for 2 minutes by an external sonication probe.
2.4 Results and Discussion

2.4.1 Hydrodynamic Radius

Each antifoam solution was measured for 300 seconds at each of four scattering angles, 30°, 60°, 90° and 120°. The viscosity of antifoam solutions is approximately equal to that of toluene due to dilution. Therefore, a viscosity of 0.59 centipoise (viscosity of toluene at 20°C) is used for calculations. The second-order autocorrelation functions are displayed in Fig. 2.3, all of which display a single significant decay rate, indicating a quasi-monodisperse size population. When $g_2-1$ is less than 0.005, the data are unreliable due to background subtraction error.

According to Eq. (2.3), the decay rate is related to the diffusion coefficient and the square scattering vector. In Fig. 2.4, the decay rates obtained from a cumulant fit are plotted against the square of scattering vector. By linear fitting, the diffusion coefficients are obtained from the slopes. Hydrodynamic radii are calculated through Einstein-Stokes equation. According to the USAXS results in the following section, the measured sizes are larger than primary particles; therefore DLS detects clusters of primary particles.

Calculations of hydrodynamic radius show that the sizes of silica clusters in 3-vol% antifoam/toluene solutions range from 0.5 µm to 1.3 µm. In Fig. 2.4, the linear fitting of Antifoam 6165, 4684 and 0963 overlap each other owing to their similar hydrodynamic radius, which is approximately 0.60 µm. Antifoam 9512 at 1.3 µm is almost twice large. The larger $R_h$ results imply that the shelf-life performance of antifoam may be related to the size of silica clusters used in antifoams.
Figure 2.3 Second-order autocorrelation functions of the 3-vol% antifoam-toluene solutions without sonication. DLS measurements were taken at 4 scattering angles (30°, 60°, 90° and 120°) at 20 ± 1°C. The duration of each single run is 300 seconds.
Table 2.3 Hydrodynamic Radius of silica particles in 3-vol% antifoam solutions characterized by DLS without sonication.

<table>
<thead>
<tr>
<th>Sample No.</th>
<th>$R_h$ (µm) at 3 vol% antifoam-toluene solutions</th>
</tr>
</thead>
<tbody>
<tr>
<td>9512</td>
<td>1.28 ± 0.15</td>
</tr>
<tr>
<td>8375</td>
<td>1.00 ± 0.14</td>
</tr>
<tr>
<td>8340</td>
<td>0.96 ± 0.04</td>
</tr>
<tr>
<td>6165</td>
<td>0.60 ± 0.06</td>
</tr>
<tr>
<td>4684</td>
<td>0.60 ± 0.07</td>
</tr>
<tr>
<td>0963</td>
<td>0.59 ± 0.06</td>
</tr>
</tbody>
</table>

2.4.2 Time-evolution of Correlation Functions

To investigate size evolution of silica in 3-vol% antifoam-toluene solutions, DLS measurements over a longer time of period (25 minutes) were done. Measurements were taken at a single scattering angle of 90° at 20 ± 1 °C. Fig. 2.5 compares the two measurement durations for each sample. A slowly decaying component appears in Antifoam 9512 and 8340 over 1500 s while other three samples are unchanged. The slow mode indicates that a population of larger aggregates appears in antifoam solutions. That is the colloidal silica of Antifoam 9512 and 8340 aggregates with time.

Figure 2.4 Decay rates ($\gamma$) plotted as a function of square of the scattering vector, fitted by a line through the origin. DLS measurements were taken at 4 scattering angles at 20±1 °C.
For each DLS measurement, the corresponding count rate is displayed in Fig. 2.5. Only Antifoam 9512 among the six samples shows a significant decrease of count rate over 1500 seconds, indicating a decreasing number of particles due to settling. The amplitude of the intensity fluctuations, however, gets larger from when the average intensity decreases, implying a size growth owing to silica aggregation. According to autocorrelation function of 9512 in Fig. 2.5, it can be concluded that large structures form and precipitate in the antifoam solution. For Antifoam 8340, the amplitude of intensity fluctuation becomes larger as well from about 900 seconds, implying silica aggregation. These observations show that colloidal silica in certain antifoam/toluene solutions is aggregating to form larger structures that precipitate over time. However, since 9512 is a good performer and 8340 is a bad performer shelf-life performance is not solely related to the precipitation behavior.

After 2 hours, precipitates in the bottom of vials can be visually observed in all the solutions. This observation reveals that precipitation is occurring in all the solutions while their aggregation and precipitation rates are different. These phenomena need to be further investigated.
Figure 2.5 Second-order autocorrelation functions and count rate at 90° at 20 ± 1 °C for 3-vol% antifoam/toluene solutions without sonication. The slow mode in 9512 and 8340 indicates propensity to aggregate. The amplitude of count-rate-fluctuations for 9512 and 8340 becomes larger with time owing to the growth of silica size in solution, but significant settling is observed only for 9512.
2.4.3 Effect of Sonication

To study the stability of silica clusters the samples were dispersed for 2 minutes utilizing a sonicator probe connected to a Microson ultrasonic cell disruptor. The sonication was performed in 25 ml vials with antifoam/toluene solutions. The output power was 7 watts. The sonicated samples were measured by DLS under the same conditions and DLS data were analyzed using approaches described in the previous section. Fig. 2.6 shows the comparison of hydrodynamic radii before and after sonication. Particle sizes in Antifoam 9512, 8340, 6165, 4684 and 0963 decrease by 0.1 µm or less, while particles in Antifoam 8375 show a more significant size reduction due to sonication. The $R_h$ in Antifoam 8375 is reduced by about 0.4 µm, which is approximately 40% of original size. It is assumed that the sonication breaks up soft agglomerates to leave smaller hard agglomerates.

![Figure 2.6](image)

**Figure 2.6** Hydrodynamic radius for 3-vol% antifoam/toluene solutions before and after a 2-minute continuous sonication by a sonication probe. Samples were measured by DLS right after the 2-minute sonication.
2.4.4 Effect of Silica Concentration

In Fig. 2.5, the appearance of slow-mode decays in the DLS autocorrelation functions of 9512 and 8340 indicates that larger structures form about 800 s after dispersion. The count rate data indicate that precipitation occurs after 800 s for 9512, but not for 8340.

To further investigate this behavior, silica D-10 and polydimethylsiloxane (PDMS, a typical silicone fluid) in toluene were prepared and measured by DLS to study the silicone oil and silica individually. Typically, silica-silicone oil compound antifoams contain approximately 1 wt% silica. Therefore silica D-10 (without PDMS) was dissolved in toluene at 0.03 wt%, 0.05 wt % and 0.1 wt%, in which the amount of silica is equivalent to that of 3, 5 and 10 vol% antifoam-toluene solutions respectively. 3-vol% PDMS (without silica) in toluene was also prepared.

All the solutions were sonicated for 120 seconds under same conditions as Section 2.4.2 and measured by DLS immediately after sonication (time delay < 5 min). Each DLS experiment was conducted at a scattering angle of 90° at room temperature (20 ± 1°C). The correlation function continuously measured for 2400 s to observe time-evolution. Autocorrelation function was averaged over the entire 2400 s.

The count-rate data in Fig. 2.7 show that silica in toluene is stable at 0.03 wt%, and has $R_h = 0.5$ µm. As the concentration of silica is increased, however, silica aggregates form. At 0.1 wt%, silica aggregates reach a $R_h$ of 1.4 µm and began to settle. These data show that silica D-10 in toluene will aggregate and precipitate at 0.1 wt%. Therefore, the precipitation behavior of antifoams needs to be analyzed considering both silica size and concentration.

In absence of silica, PDMS shows a $R_h$ of only 7 nm at 3 vol% in toluene and does not settle over 2400 s.
Figure 2.7 Behavior of colloidal silica and PDMS in toluene. Plot of count rates versus time for the D-10 silica/toluene solutions and PDMS/toluene solutions after a 2-min sonication. For 0.1 wt% silica/toluene solution, decreasing intensity and large amplitude fluctuations are observed after $t \approx 1100$ s due to aggregation and precipitation of silica.

These results indicate that silica concentration may play a significant role in antifoam aggregation. Therefore, we investigated the concentration dependence of the 90° DLS correlation functions for antifoam in toluene at 1 vol%, 3 vol%, 5 vol% and 10 vol%. Each run was correlated over the entire period of 2400 s. Solutions were sonicated for 120 seconds before measurements. The hydrodynamic radius was calculated using cumulant analysis. $R_h$ at each concentration is presented in Table 2.4.

Table 2.4 Hydrodynamic radius of silica in 1 vol-%, 3 vol-%, 5 vol-% and 10 vol-% antifoam solutions characterized by DLS.

<table>
<thead>
<tr>
<th>Sample No.</th>
<th>$R_h$ (µm)</th>
</tr>
</thead>
<tbody>
<tr>
<td>1 vol%</td>
<td>3 vol%</td>
</tr>
<tr>
<td>9512</td>
<td>0.7</td>
</tr>
<tr>
<td>8340</td>
<td>0.7</td>
</tr>
<tr>
<td>8375</td>
<td>0.5</td>
</tr>
<tr>
<td>6165</td>
<td>0.4</td>
</tr>
<tr>
<td>4684</td>
<td>0.4</td>
</tr>
<tr>
<td>0963</td>
<td>0.4</td>
</tr>
</tbody>
</table>
All the antifoams have the smallest $R_h$ at 1 vol%. The stable count rates (in Fig.2.8) indicate that settling does not occur at 1 vol%. Therefore, it can be assumed that $R_h$ at 1-vol% is the original hydrodynamic size of colloidal silica. According to Table 2.4, samples 8375, 6165, 4684 and 0963 have a $R_h$ of around 0.5 µm, while Samples 9512 and 8340 contained larger silica (0.7 µm). Thus the size-growth with antifoam concentration is discussed by size group.

**Figure 2.8** Second-order autocorrelation functions and count rate evolution measured by DLS for 1-vol% antifoam in toluene after a 2-minute sonication. DLS measurements were taken at a scattering angle of 90° at 20°C. Each run was correlated over the entire period. **Left:** large-silica antifoams (9512 and 8340), $R_h > 0.5$ µm. **Right:** small-silica antifoams (8375, 6165, 4684 and 0963), $R_h \leq 0.5$ µm. Slow mode decay is small but visible for most samples.
Fig. 2.9 (A) presents the time dependence of the hydrodynamic radius. The samples were all measured at 3 vol%. 9512 and 8340 have an apparent size growth over a longer time duration. However, the samples in small-silica group didn’t show a difference.

Fig. 2.9 (B) presents the concentration dependence of the hydrodynamic radius. According to the previous discussion, six antifoams are divided into two groups based on the size of silica particle size. For each sample, $R_h$ increases with the concentration of antifoam. Antifoams containing large silica show more significant size growth than antifoams in the small-silica group. In addition, the two good performers (9512 in large-silica group and 8375 in small-silica group) show the largest increase of $R_h$ within their respective group.

Figure 2.9  (A) $R_h$ is plotted as a function of the aging time for 3-vol% antifoams. (B) $R_h$ is plotted as a function of the antifoam concentration. DLS measurements were taken at a scattering angle of 90° at 20 ± 1 °C after 2-minute sonication.
2.4.5 Adsorption of Silicone oil

The oil-adsorption hypothesis proposed by Dr. Naiping Hu explains the time-dependent and concentration-dependent behavior in Fig. 2.9. The growth of $R_h$ is attributed to the absorption of silicone fluid on the silica surface, along with a possible silica aggregation in toluene. Fig. 2.10 illustrates how antifoams dissolved in toluene evolve with time. Initially, the silica and silicone oil in antifoams are separated and dispersed after ultrasonic dispersion. The silicone oil is gradually absorbed on the surface of silica particles. The adsorbed polymer enhances the aggregation by bridging the neighboring silica or depletion attraction induced by polymer chains surrounding the particle. The various interactions induced by the polymers facilitate the particle growth. The large droplets grow and precipitate over time. The time-dependence of $R_h$ is dominated by three factors: the attractive interaction between silicone oil and silica, the size of original silica particles and the concentration of the antifoam. Fig. 2.9 implies that the interaction of the silicone oil with silica varies with antifoam lot.

Figure 2.10 Schematic of the hypothesis that silicone oil adsorbs on the silica surface in antifoam/toluene solutions. (A) After the sonication, silica and silicone oil are fully dispersed. (B) Silicone oil gradually absorbs on the surface of silica. (C) Silicone oil-silica droplets precipitate after adsorption and aggregation.

This oil-adsorption hypothesis explains the concentration dependence of antifoam settling. For each sample the count rates are plotted as a function of time and concentration in Fig. 2.11. The
data on 1 vol% solutions are the same as that in Fig. 2.9. The large-silica antifoams (9512 and 8340) show a decreasing count rate at a concentration of 3 vol%, while none of the small-silica antifoams show such behavior. The declining count rates imply that the scattering entities are precipitating. More silicone is adsorbed silica in 9512 and 8340 due to larger size of the silica particles, resulting in faster settling. According to Fig. 2.9 (B), the increase of $R_h$ with concentration is faster for large-silica antifoams, indicating adsorption of silicone oil. This observation is consistent with the larger available surface.

The oil-adsorption hypothesis also relates the stability of antifoams to the attractive interaction of silicone oil and silica for antifoams within the same group. As Fig. 2.11 (A) shows, 9512 begins to precipitate at $t \approx 1000\,\text{s}$ whereas 8340 with the same initial $R_h$ precipitates later at $t \approx 1500\,\text{s}$. This observation is consistent with Fig. 2.9 (B), which shows that 9512 forms larger structures as concentration increases. Based on P&G shelf-life performance, among the large-size group, 9512 antifoam outperforms 8340. Thus the adsorption behavior seems to correlate particle size and with shelf life. That is, performance behavior is revealed by the silica size and settling behavior.

In Fig. 2.11 (B), the count rate data at 10 vol% differentiates the four small-size silica samples. Sample 8375 shows a small decrease in count rate and an increase in fluctuation amplitude at 10 vol% starting at $t \approx 1500\,\text{s}$, revealing size growth and precipitation. However, no such effect is observed in other three samples. Apparently 8375 has a stronger adsorption of silicone oil than 0963, 4684 and 6165. It is noteworthy that 8375 also shows the best shelf-life performance among the small-size group. The observation confirms that DLS and count-rate data correlate with shelf-life performance.
Figure 2.11 Count rates versus time at different concentrations after 2-minute sonication. Measurements were taken at 90° at 20 ± 1 °C and were correlated over the entire period. The solutions at each concentration were prepared individually (A): large-silica group (9512 and 8340). Settling is first observed at 3 vol% in both antifoam solutions. (B): small-silica group (8375, 6165, 4684 and 0963). Settling is observed for 10 vol% 8375/toluene solution whereas the other three remain stable at 10 vol%.
2.5 Conclusion

Table 2.5 summarizes the results from the DLS measurements. Characteristics that are considered to favor the oil-adsorption model are highlighted in green. Examination of Table 2.5 shows that antifoam performance improves with silica size and propensity to aggregate. The exception is 8340, which is very similar to 9512, but fails the P&G performance test.

Table 2.5 Summary of characteristics of antifoams based on DLS and count-rate measurements. The green highlight indicates characteristics that are consistent with the oil-adsorption hypothesis.

<table>
<thead>
<tr>
<th>Characteristic</th>
<th>9512</th>
<th>8375</th>
<th>8340</th>
<th>6165</th>
<th>4684</th>
<th>0963</th>
<th>Source</th>
<th>Test</th>
</tr>
</thead>
<tbody>
<tr>
<td>$R_h$ (µm) at 3 vol%</td>
<td>1.28</td>
<td>1.00</td>
<td>0.96</td>
<td>0.60</td>
<td>0.60</td>
<td>0.59</td>
<td>Table 2.3</td>
<td>$R_h$ from DLS</td>
</tr>
<tr>
<td>Performance</td>
<td>pass</td>
<td>pass</td>
<td>fail</td>
<td>fail</td>
<td>fail</td>
<td>fail</td>
<td>Table 2.1</td>
<td>P&amp;G tests</td>
</tr>
<tr>
<td>Robustness</td>
<td>hard</td>
<td>soft</td>
<td>hard</td>
<td>hard</td>
<td>hard</td>
<td>hard</td>
<td>Fig. 2.6</td>
<td>Decrease of $R_h$ after sonication</td>
</tr>
<tr>
<td>Slow mode</td>
<td>present</td>
<td>absent</td>
<td>present</td>
<td>absent</td>
<td>absent</td>
<td>absent</td>
<td>Fig. 2.5</td>
<td>Slow mode before sonication</td>
</tr>
<tr>
<td>Conc. dependence</td>
<td>strong</td>
<td>weak</td>
<td>strong</td>
<td>weak</td>
<td>weak</td>
<td>weak</td>
<td>Fig. 2.9</td>
<td>D decreases with concentration</td>
</tr>
<tr>
<td>Precipitation</td>
<td>Yes</td>
<td>No</td>
<td>Yes</td>
<td>No</td>
<td>No</td>
<td>No</td>
<td>Fig. 2.11</td>
<td>Count-rate decrease</td>
</tr>
<tr>
<td>Aggregation</td>
<td>Yes</td>
<td>Yes</td>
<td>Yes</td>
<td>No</td>
<td>No</td>
<td>No</td>
<td>Fig. 2.11</td>
<td>Count-rate fluctuations</td>
</tr>
</tbody>
</table>

The results are broadly consistent with the oil-adsorption model, which attributes antifoam shelf-life stability to the propensity of silica to adsorb silicone oil. In toluene solution the signature of oil adsorption is aggregation and precipitation, which are conveniently measured by DLS. Aggregation and precipitation are measured by the time-evolution of the diffusion constant and the count rate, both of which depend on the $R_h$ of original silica, the concentration of antifoam solution and the silicone oil-silica interaction. In other words, for antifoams with same silica size and at same concentration, the attractive interaction between silicone oil and silica improves shelf-life stability.
3.1 Overview

In order to further test the oil-adsorption hypothesis, Fourier transform infrared spectroscopy (FT-IR) was utilized to analyze the components in antifoam solutions. As discussed in previous chapter, precipitation occurs within 40 minutes for antifoams above a certain antifoam concentration (i.e., 3 vol% for large-silica antifoams and 10 vol% for small-silica antifoams). By comparing the amount of silicone oil in the top and in the bottom of solution, the role of silicone oil during precipitation can be elucidated. In this chapter FT-IR was used to estimate the degree to which PDMS co-precipitates with silica, thus testing the adsorption oil-hypothesis presented in Chapter 2.

FT-IR is widely used for composition analysis. The positions of peaks in FT-IR spectra depend on the characteristic frequencies of chemical bonds. FT-IR is capable of not only identifying unknown substances, but is also of quantitative analysis.

3.2 Experimental

FT-IR analysis utilized a Nicolet 6700 FT-IR instrument. The data were processed by OMNIC 7.4 code. The spectra were plotted and analyzed using Igor.

The 10-vol% Antifoam 9512 in toluene was sonicated for 2 minutes and settled for 40 minutes, consistent with the conditions of DLS measurements. The precipitate was visually observed at the vial bottom as shown in Fig. 3.1. The top and bottom solutions were collected and examined by FT-IR using air as the background. The curve fitting was done using Igor multiple-peak fitting tool, and the calculation includes the deviation from baseline correction and peak fitting.
Silicone fluid and silica, as components of antifoams, share characteristic peak positions due to common functional groups. Therefore solutions of 10-v% PDMS and 0.1-wt% silica D-10 in toluene were prepared to ascertain characteristic lines suitable to distinguish these compounds. These solutions were analyzed by FT-IR using toluene as background.

![Figure 3.1](image)

**Figure 3.1**: Photo of 10-vol% 9512 antifoam in toluene. (A) 10-vol% 9512/toluene solution after a 2-min sonication. (B) After 40 minutes, precipitate is observed at the bottom of the vial. The top solution was visually more transparent than the solution at $t = 0$ (left figure). Top and bottom solutions were separated and used for FT-IR analysis.

### 3.3 Results and Discussion

To investigate if adsorbed silicone oil settled together with silica, the amounts of silicone oil in top and at bottom were analyzed quantitatively by comparing FT-IR peak heights. During the precipitation, silica particles accumulate at the bottom of the vial (Fig. 3.1 B). However, silica accumulating at the bottom displaces PDMS, so the volume fractions of silicone oil and toluene are correspondingly reduced. Therefore, the spectra can’t be normalized using the characteristic peaks of toluene, which means that peak heights for silicone oil cannot be directly compared.
However the ratio of silicone oil to toluene is constant if silica particles don’tadsorb extra silicone oil at the bottom. Therefore the partitioning of PDMS can be approximated using the PDMS peak heights at the top and bottom divided by the toluene peak height.

Fig. 3.2 displays the fingerprint region of FTIR spectra for the PDMS/toluene solution and the silica D-10/toluene solution. The pure toluene spectrum was subtracted. The spectrum of silica shows a characteristic doublet corresponding to Si-O stretching at 1100 cm⁻¹. Due to similarity of functional groups, many peaks on PDMS spectrum overlap those of silica. Peaks at 1260 cm⁻¹ and 800 cm⁻¹, however, corresponding to in-plane bending or scissoring and out-of-plane oscillation of Si-CH₃ are least compromised by silica. Therefore, the peak at 1260 cm⁻¹ and the one at 800 cm⁻¹ represent the silicone oil.

![FT-IR spectra of PDMS (red) and Silica D-10 (blue) in toluene. Toluene background has been subtracted. The absorptions at 1260 cm⁻¹ and 800 cm⁻¹ are contributed mainly by PDMS.](image)

**Figure 3.2** FT-IR spectra of PDMS (red) and Silica D-10 (blue) in toluene. Toluene background has been subtracted. The absorptions at 1260 cm⁻¹ and 800 cm⁻¹ are contributed mainly by PDMS.

Fig. 3.3 presents the spectra for top and the bottom solution of 10-vol% antifoam in toluene, as well as pure toluene. These spectra are air-background subtracted. PDMS peaks at 1260 cm⁻¹ and 800 cm⁻¹ are observed in both the top and bottom fractions. The sharp absorption at 1500 cm⁻¹
results from the C-C stretching in aromatic ring, which is characteristic for the toluene. For analysis of peak heights, we assume that the sum of the peak height at 1260 cm\(^{-1}\) and at 800 cm\(^{-1}\) is proportional to the amount of silicone oil, and the peak height at 1500 cm\(^{-1}\) is proportional to the amount of toluene.

![Figure 3.3 FT-IR spectra of pure toluene (black), the top (red) and the bottom (blue) of 10-vol\% 9512 in toluene. An air background has been subtracted. The peaks 1260 cm\(^{-1}\) and 800 cm\(^{-1}\) are attributed to Si-CH\(_3\) bonding in PDMS. These peaks are the least compromised by toluene and silica. The sharp peak at 1500 cm\(^{-1}\) corresponds to C-C stretching in aromatic ring of toluene. The 1100 cm\(^{-1}\) peak is attributed to silica Si-O.]

As discussed previously, the ratio of silicone oil (height of peaks at 1260 cm\(^{-1}\) and at 800 cm\(^{-1}\)) to toluene (height of the peak at 1500 cm\(^{-1}\)) in supernatants and in precipitates is a measure of the amount of PDMS. If the precipitate were solely silica, the ratio of silicone oil to toluene would not change even though the fraction of silicone oil and the fraction of toluene are reduced due to the accumulation of silica at the bottom. According to the calculations in Table 3.1, the ratio of silicone oil peaks to the toluene peak in precipitates (0.65 ± 0.10) is larger than that in supernatant solution (0.58 ± 0.03), consistent with silicone oil accumulating at bottom as precipitation proceeds.
Unfortunately, due to the error bar on the bottom value, this result does not definitively prove the oil-adsorption hypothesis.

Table 3.1 The heights of peaks for silicone oil and toluene respectively. The data were collected on FTIR spectra of pure toluene, the top and the bottom part of 10-vol% 9512 in toluene, respectively.

<table>
<thead>
<tr>
<th>Sample</th>
<th>Height of Peak 1 for silicone oil (at 1260 cm⁻¹)</th>
<th>Height of Peak 2 for silicone oil (at 800 cm⁻¹)</th>
<th>Height of Peak 3 for toluene (at 1500 cm⁻¹)</th>
<th>Ratio of silicone oil to toluene [(Peak 1+ Peak 2) / Peak 3]</th>
</tr>
</thead>
<tbody>
<tr>
<td>Top</td>
<td>0.046 ± 0.001</td>
<td>0.062 ± 0.002</td>
<td>0.187 ± 0.006</td>
<td>0.578 ± 0.03</td>
</tr>
<tr>
<td>Bottom</td>
<td>0.049 ± 0.001</td>
<td>0.072 ± 0.003</td>
<td>0.187 ± 0.003</td>
<td>0.647 ± 0.10</td>
</tr>
</tbody>
</table>

3.4 Conclusion

The partitioning of PDMS to the silica-rich precipitate was tested by comparing the ratio of the peak heights of silicone oil to toluene. By comparing FT-IR spectra for silicone oil and silica, we determined that the peaks at approximately 1260 cm⁻¹ and 800 cm⁻¹ corresponding to the Si-CH₃ bonding are mainly attributed to silicone oil. The sum of the two peak heights was used to indicate the amount of silicone oil. Similarly, the height of the peak at 1500 cm⁻¹ indicates the amount of the toluene. However, even though the ratio of silicone oil to toluene for bottom is higher than that for the supernatant solution, the difference is too small to definitively establish the oil-adsorption mechanism.

Given the antifoam formula, 99% of bulk antifoam is the silicone oil while silica particles account for 1 wt%. Therefore, after silica has precipitated, both the top solution and the bottom solution are still largely silicone oil. Even if we assume that some silicone oil has been dragged into the bottom by silica, the difference between top and bottom is small. Thus the difference on the measured ratio is not large. Nevertheless, Table 3.1 shows that the PDMS silica ratio is higher at the bottom than the top, consistent with, but not proving the oil-adsorption hypothesis.
Chapter 4 Ultra Small-Angle X-ray Scattering and Light Scattering

4.1 Overview

Ultra-small angle X-ray scattering (USAXS) is widely used to determine structure in the range of 10 Å ~ 1 µm. USAXS measures the overall size of scattering entities and gives information on the morphology as a function of length scale. With different size-scale ranges, the combination of static light scattering (LS) and USAXS is a powerful method for studying the hierarchical structure of colloids. This chapter focuses on the multi-level structure (structure at different lengths scales) of colloidal silica in antifoams and the structural changes with solution aging.

4.2 Ultra Small Angle X-ray Scattering (USAXS)

USAXS instrument is capable of measuring objects from 1 nm to over 1 µm. USAXS data can be combined with small-angle X-ray scattering (SAXS), wide-angle X-ray scattering (WAXS) and/or LS to cover a broad size-scale range. A simplified schematic of the USAXS instrument is displayed in Fig. 4.1. An incident X-ray beam passes through slits and is aligned and wavelength selected by a crystal-pair collimator. By rotating the analyzer crystal pair, USAXS scans a range of scattering vector, \( q \), and detects the x-ray photons scattered by electrons of the sample.

![Figure 4.1](image)

*Figure 4.1 A schematic representation of USAXS instrument on beam line 9-ID at the Advanced Photon Source, Argonne National Laboratory.*
The Guinier-Porod model is usually applied to deduce size and internal morphology of colloidal objects. The intensity, plotted as a function of scattering vector, \( q \), contains one or more “decays,” indicating different levels of structure. Guinier’s region at low \( q \) range\(^1\) gives the overall size of particles. In high-\( q \) region, fitting by a power law\(^1\)\(^7\), \(^1\)\(^8\) yields a slope \( P \). The Porod power-law exponent. \( P = -4 \) indicates a smooth surface of the colloidal objects. If \( P \) is between 3 and -4, the profile corresponds to a surface fractal (rough surface). If \(-1 < P < -3\), the internal structure of the colloidal particle is a mass fractal (typically an aggregate of smaller primary particles) with a fractal dimension of \(|P|\). A Porod exponent of -2 is typical for aggregated particle clusters\(^1\)\(^0\), \(^1\)\(^9\).

4.3 Experimental

The USAXS/SAXS/WAXS experiments were conducted using 9-ID beamline at Advanced Photon Source (APS) at Argonne National Laboratory, Lemont IL. SAXS data were merged with USAXS data. The data were processed and analyzed using Irena package developed by Ilavsky\(^1\)\(^9\), which employs Dr. Beaucage’s unified fitting tool\(^2\)\(^0\). LS experiments were done utilizing a Saturn DigiSizer 5200 at the University of Cincinnati. This instrument has a laser wavelength of 658 nm and covers a measurable range from 0.1-\(\mu\)m to 1000-\(\mu\)m equivalent spherical diameter.

Limited by beam time, sample 0963 in small-silica group wasn’t measured by USAXS. All the other antifoams were dissolved to 3 vol% in toluene. Antifoam/toluene solutions were sonicated for 2 minutes for full dispersion, consistent with DLS procedure. The solutions were loaded in capillaries with an internal diameter of 1.40 mm ± 0.02 mm. Then all the samples were put in sample holder and measured by USAXS. The delay between sonication and measurement may be as long as 10 minutes due to the sample loading and sample holder installation before scanning. Several empty capillaries were also measured by USAXS, from which the sample background was determined and subtracted from the sample data. For LS, the antifoam samples were diluted to 3
vol% in toluene and sonicated in the vials using an external probe. The antifoam samples were loaded in a glass cuvette with a path length of 4.6 mm and measured immediately by LS (time delay within 5 minutes).

4.4 Results and Discussion

4.4.1 Morphology of Silica

Samples were measured every ten minutes after an initial 2-min sonication to monitor the morphological changes during process of aging. Fig. 4.2 presents the desmeared USAXS data of large-silica antifoam solutions (9512 and 8340) over 40-min. Fig. 4.3 shows the data for small-silica group antifoams (8340, 6165 and 4684). All the curves in both Fig. 4.2 and Fig. 4.3 show two levels of structure. The large size-scale, level-2 structure, however, is not completely visible because the instrument does not measure to low enough q.

First-level structure at \( q \geq 0.02 \text{ Å}^{-1} \) is the primary particle, containing both a Guinier region and a Porod region. At \( t = 0 \) min, the Guinier region implies that the radii of gyration of primary particle for the six samples are in the range of 100 ~ 200 Å. The sizes of primary particles didn’t change measurably with aging.

The power-law slopes obtained from level-1 Porod regions reveal the morphology of primary particle. In Fig. 4.2 and Fig 4.3, the Porod slope, \( P \), at \( t = 0 \) is -4, indicating a smooth surface. With time, however, the apparent \( P \) of all antifoams reduce to \( P = -2.6 \sim -3 \) at \( t = 40 \) min. Porod exponents in this range are typically attributed to rough-surfaced primary particles. In this study, however, the change of Porod exponent cannot be unequivocally attributed to the morphological change of primary particles. The background \( (0.2 \text{ Å}^{-1} < q < 1 \text{ Å}^{-1}) \) in USAXS data increases with time, which compromises the determination of \( P \) at longer aging times.
Level 2 at lower $q$ probes the larger scale silica aggregates. Only a Porod region is observed without a Guinier region, which implies that the size of the aggregates is larger than 5 µm. Regardless of group, all antifoams show similarity at level 2, which is characteristic of aggregates of primary particles. At $t = 0$. All the six aging samples have a Porod exponents between -2.7 ~ -2.9, corresponding to a mass fractal. At $t = 40$ min the Porod exponents for all antifoams are in a narrow range, from -2.6 to -2.7. This behavior is typical of aggregated silica showing minimal evolution of aggregate morphology with time, due to strong chemical bonding between primary particles. The intensities decrease with time due to settling. 9512 also shows a different shape consistent with more compact level-3 agglomerates.

![Graphs showing USAXS profiles of antifoams 9512 and 8340 after sonication and aging.](image)

**Figure 4.2** Desmeared USAXS profiles of the large-silica antifoam solutions (9512 and 8340) after sonication over 40-min aging in toluene. Porod exponents at $t=0$ are -4 indicating a smooth-surface structure.
Figure 4.3 Desmeared USAXS profile of small-silica antifoam solutions after sonication and 40-min aging. For 8375 and 6165, their right panels show vertically shifted curves to reveal differences in Porod's region. For all samples the intensity decreases over time. Initially the Porod exponents are -4 indicating a smooth-surface structure. As time proceeds, the high-q background precludes accurate determination of the Porod exponents.
4.4.2 Time-evolution of Silica from Light Scattering

This section focuses on the size-scale in the initial and terminal states of silica over 40-minute aging using static light scattering (LS). LS covers a lower $q$ range than USAXS and therefore makes it possible to measure larger structures. Each sample was sonicated for 2 minutes before measurement. The measurement takes about 3 minutes. After sonication, each sample was tested by LS to give the $t = 0$ data. After the initial measurement, the sample settled in cell without agitation for 40 minutes. Then the sample was tested again at $t = 40$ min.

Table 4.1 presents the scattering-related parameters of the components in antifoams. The scattering contrast between PDMS and the toluene is not very strong so most of the scattering is from silica. However, the lab-grade PDMS used in this study (shown in Table 4.1) may not be identical to the complex silicone oil used in antifoam samples. There is the possibility that both silica and silicone oil contribute to the scattered intensity.

Table 4.1 The scattering parameters of major components in the antifoam/toluene solution. SLD refers to scattering length density. SLD for PDMS is calculated using its monomer molecule. The scattered intensity is proportional to the square of the difference of refractive index (light) or SLD (x-ray).

<table>
<thead>
<tr>
<th>Component</th>
<th>Density (g·cm$^{-3}$)</th>
<th>Refractive index</th>
<th>SLD ($10^{-6}$ Å$^{-2}$)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Silica</td>
<td>2.1</td>
<td>1.46</td>
<td>17.7</td>
</tr>
<tr>
<td>PDMS</td>
<td>0.97</td>
<td>1.41</td>
<td>8.8</td>
</tr>
<tr>
<td>Toluene</td>
<td>0.87</td>
<td>1.50</td>
<td>7.9</td>
</tr>
</tbody>
</table>

Fig. 4.4 presents the light scattering data for the 3-vol% antifoams in toluene at $t = 0$ and at $t = 40$ minutes, showing large-scale structures in antifoam samples. The intensity decreases for most antifoams over time. However, if the curves at $t = 40$ min (blue dashed curve) are shifted up to the curves at $t = 0$ (red curve), the overlap Porod’s region at high-$q$ indicates that the morphology of silica aggregates do not change significantly for 9512.
Figure 4.4 Light scattering profiles of 3-vol% antifoam/toluene solutions after sonication. Each sample was tested at $t = 0$ and 40-min. 9512 shows a 2-level structure. At $t = 40$ min, a 3rd level shows up for 8375 consistent with formation of soft agglomerates. For the small-silica antifoams, 8375, 6165 and 4684. The 3rd level is not very visible, but is required for fitting to the unified model. At the end of aging, 9512, 8340 and 8375 all have 2-level structures.
Antifoam 9512 is unique among the samples for its 2-level structure, whereas the others show 1-level structures. At the end of aging, however, 8340 and 8375 evolve to a 2-level structure similar to 9512, consistent with formation of soft agglomerates during 40 min aging. In the case of 8375 the third level is barely visible, but is required to fit the data using the unified model.

Fig 4.5 presents the light scattering data from Fig. 4.4 combined with the desmeared USAXS data for each antifoam. These profiles, covering a wide range of $q$, show the hierarchical structures of colloidal silica. Due to lack of USAXS on Antifoam 0963, the LS-USAXS combined data don’t include 0963. USAXS (high-$q$ region) was analyzed in last section, thus the low-$q$ and mid-$q$ region will be specifically discussed here.

For all samples, observation in the mid-$q$ region ($\sim 5 \times 10^{-4}$ Å$^{-1}$) indicates that the morphology of silica barely changes with time. Most samples exhibit a Porod exponent of 3.0 – 3.3 corresponding to uniformly dense structures with rough surfaces. After 40 min, 8340 evolves to larger, more open structures as shown in low-$q$ region of $10^{-5} – 10^{-4}$ Å$^{-1}$, consistent with soft agglomerate formation. For 9512, the two-level structure is present even before aging, but the structure is “hard.” The Porod exponent -2 indicates a mass fractal with a dimension of 2.

The low-$q$ Guinier region reveals the mean size of largest structures present. The fitting gives the radius of gyration, $R_g$, which is plotted in Fig. 4.6. Sample 9512, has an $R_g$ of 15.6 µm, which is largest among the samples. After 40 minutes, $R_g$ of 9512 slightly decreases, which is due to preferential settling of larger agglomerates.
Figure 4.5 Combination of LS and desmeared USAXS data for antifoam-toluene solutions after a 2-min sonication.
8340 and 8375 both increase in size, which is attributed to soft agglomeration. In mid-\( q \) region, 9512 shows smaller structures with an \( R_g \) of 1.3 \( \mu \)m, which implies quite compact, uniformly dense aggregates that don’t change in size or morphology over time. By contrast to 9512, the other large-group silica, 8340, shows agglomeration with \( R_g \) increasing from 3.5 \( \mu \)m to 11.8 \( \mu \)m.

Among small-silica group, only 8375 shows agglomeration with \( R_g \) increasing from 4.0 to 6.6 \( \mu \)m over time. Due to the appearance of a 3\textsuperscript{rd} level structure for this sample, the size increase is attributed to soft agglomeration. The aggregates in the other three antifoams (6165, 4684 and 0963) are stable around 3 \( \mu \)m over 40 minutes.

\[\begin{align*}
\text{Figure 4.6} & \text{ Radius-of-gyration for the 3-vol\% antifoam/toluene solutions measured by light scattering at } t = 0 \text{ and } t = 40 \text{ min. For each sample, } R_g \text{ at } t = 0 \text{ marked as red and } R_g \text{ at } t = 40 \text{ min marked as blue. 9512 has largest } R_g \text{ and shows a slight size decrease with time. 8340 and 8375 show a considerable size growth over time, while 6165, 4684 and 0963 barely change over time with an } R_g \text{ of 2.0–3.5 } \mu \text{m.} \\
\text{The } R_g \text{ results confirm the two categories of the silica identified by DLS. Large silica agglomerates are observed in 9512 and 8340. Among small-silica group, 6165, 4684 and 0963 didn’t show agglomeration possibly due to the weak interaction between silica aggregates. These samples require either higher antifoam concentration or longer settling duration to form larger...}
\end{align*}\]
agglomerates. Antiform 8375 shows intermediate behavior with agglomeration barely visible at 40 min, but a substantial size increase over 40 min.

Typically the morphology of precipitated silica is determined by post-synthesis processing of silica, such as drying. It may be that lack of control of drying leads to $t = 0$ differences in the large-scale properties of 9512. Such structures are typically not recognized in manufacturer’s specifications. In the case of 8340 and 8375, however, agglomerates are not observed initially but appear after 40 minutes. In this case, there may be differences in surface chemistry that control the propensity to agglomerate.

The ratio of $R_g/R_h$ is a shape factor, $\rho$, which depends on the aspect ratio and compactness of the particles. The value of $\rho$ reflects the conformation of particles or chains. Generally, $\rho$ for a hard sphere is $\sim 0.775$ and $\rho = \sim 1.5$ is calculated for a polymer in a good solvent. The ratio $\rho$ for colloidal silica in 3-vol% antifoam/toluene solution after aging are presented in Table 4.2.

**Table 4.2 The ratio of $R_g/R_h$ for 3-vol% antifoam solutions.**

<table>
<thead>
<tr>
<th>Sample</th>
<th>$R_h$ (µm)</th>
<th>$R_g$ (µm) (at $t$=40 min)</th>
<th>$\rho$ ($R_g/R_h$)</th>
</tr>
</thead>
<tbody>
<tr>
<td>9512</td>
<td>1.5</td>
<td>1.3</td>
<td>0.87</td>
</tr>
<tr>
<td>8340</td>
<td>1.4</td>
<td>1.3</td>
<td>0.93</td>
</tr>
<tr>
<td>8375</td>
<td>0.6</td>
<td>1.6</td>
<td>2.67</td>
</tr>
<tr>
<td>6165</td>
<td>0.5</td>
<td>2.5</td>
<td>5.00</td>
</tr>
<tr>
<td>4684</td>
<td>0.5</td>
<td>2.9</td>
<td>5.80</td>
</tr>
<tr>
<td>0963</td>
<td>0.5</td>
<td>1.9</td>
<td>3.80</td>
</tr>
</tbody>
</table>

For 9512 and 8340, after 40-min aging, their $R_g/R_h$ values are close to the ratio of a solid sphere ($0.775$) $^{10}$. This value indicates more compact, symmetric structures. However, for 8375, 6165, 4684 and 0963, the ratio is unexpectedly large. The high values of $\rho$ possibly result from the
aggregation to form open, non compact structures. It should also be stated that DLS detects the intensity over the entire period of the 40-min aging to give an averaged size scale whereas LS measures the $R_g$ at the ending of the aging. According to Fig 2.11 by DLS, the adsorption and aggregation occur slowly for these small-silica samples during aging. Thus DLS measurements may underestimate $R_g$ for 8375, 6165, 4684 and 0963, which explains the high values of $R_g/R_h$ ratios in Table 4.2.

4.5 Conclusion

USAXS combined with LS data reveals the hierarchical structure of colloidal silica of antifoam in toluene (Fig. 4.7).

![Hierarchical structure of silica](image)

**Figure 4.7** A typical schematic of the hierarchical structure of silica. Primary particles are the smallest units to form aggregates, clusters and agglomerates. Hard agglomerates are more compact than soft agglomerates.

After ultrasonic dispersion, 9512 shows 3-level structures. In addition to primary particles and aggregates, 9512 contains large agglomerates with an $R_g$ of 15.6 µm and a fractal dimension of 2,
signifying an open large-scale structure. All antifoams in toluene except for 9512 show 2-level structures, consisting of primary particles of 10 ~ 20 nm and aggregates of 3-4 µm. Silica aggregation and settling are observed by USAXS and LS after 40-min quiescent aging. Scattering data for 8340 and 8375 indicate they have 3-level structures, with larger agglomerates formed during aging. The third level (largest structure) for 8340 is attributed to agglomerates around 11.8 µm with an open structure. For 8375, the third-level structure is also attributed to agglomerate structures but half the size of 8340 (6 µm). The other antifoams (6165, 4684 and 0963) didn’t change significantly with time.

The time-evolution of these samples show conformity with the oil-adsorption hypothesis. According to the hypothesis, the good performers, 9512 and 8375, should have stronger interaction between silicone oil and silica in toluene than the others. Therefore the silica of 9512 and 8375 absorbs more silicone oil during aging and the attached polymer chains may facilitate the silica agglomeration because of depletion effect\(^2\), leading to large structures. 8340 also shows agglomeration during aging, revealing that it may not be as bad as the other bad performers.

In high-\(q\) region, the six samples have primary particles, which don’t change significantly over 40 min. Due to background scattering it was not possible to observe the evolution of the surface morphology with time, but it is safe to assume the surface remains smooth.

In one word, the agglomerates formed in 9512, 8340 and 8375 imply that these three antifoams show greater tendency to cluster antifoams, which is generally consistent with both DLS observations and the oil-adsorption hypothesis.
Chapter 5  Conclusions

This research provides considerable evidence for the correlation of antifoam aging performance with silica particle size and propensity to aggregate (Table 5.1). Aggregation is attributed to adsorption of oil on the silica particles. Oil adsorption, however, requires maintenance of the hydrophobicity of the silica surface. If hydrophobicity is lost during shelf-life storage, then antifoam performance declines.

Table 5.1 Summary of measurements reported in this thesis. Green shading indicates measured parameters that are consistent with the oil-adsorption hypothesis for antifoam performance.

<table>
<thead>
<tr>
<th>Characteristic</th>
<th>9512</th>
<th>8375</th>
<th>8340</th>
<th>6165</th>
<th>4684</th>
<th>0963</th>
<th>Source</th>
<th>Test</th>
</tr>
</thead>
<tbody>
<tr>
<td>$R_h$ (µm) at 3 vol%</td>
<td>1.28</td>
<td>1.00</td>
<td>0.96</td>
<td>0.60</td>
<td>0.60</td>
<td>0.59</td>
<td>Table 2.3</td>
<td>$R_h$ from DLS</td>
</tr>
<tr>
<td>Performance</td>
<td>pass</td>
<td>pass</td>
<td>fail</td>
<td>fail</td>
<td>fail</td>
<td>fail</td>
<td>Table 2.1</td>
<td>P&amp;G tests</td>
</tr>
<tr>
<td>Robustness</td>
<td>hard</td>
<td>soft</td>
<td>hard</td>
<td>hard</td>
<td>hard</td>
<td>hard</td>
<td>Fig. 2.6</td>
<td>Decrease of $R_h$ after sonication</td>
</tr>
<tr>
<td>Slow mode</td>
<td>present</td>
<td>absent</td>
<td>present</td>
<td>absent</td>
<td>absent</td>
<td>absent</td>
<td>Fig. 2.5</td>
<td>Slow mode after sonication</td>
</tr>
<tr>
<td>Conc. dependence</td>
<td>strong</td>
<td>weak</td>
<td>strong</td>
<td>weak</td>
<td>weak</td>
<td>weak</td>
<td>Fig. 2.9</td>
<td>Decrease of D with conc.</td>
</tr>
<tr>
<td>Precipitation</td>
<td>Yes</td>
<td>No</td>
<td>Yes</td>
<td>No</td>
<td>No</td>
<td>No</td>
<td>Fig. 2.11</td>
<td>Count-rate decrease</td>
</tr>
<tr>
<td>Aggregation</td>
<td>Yes</td>
<td>Yes</td>
<td>Yes</td>
<td>No</td>
<td>No</td>
<td>No</td>
<td>Fig. 2.11</td>
<td>Count-rate fluctuations</td>
</tr>
<tr>
<td>FT-IR</td>
<td>uncertain</td>
<td>uncertain</td>
<td>uncertain</td>
<td>uncertain</td>
<td>uncertain</td>
<td>uncertain</td>
<td>Table 3.1</td>
<td>Evidence of adsorption</td>
</tr>
<tr>
<td>2-level aggs</td>
<td>Yes</td>
<td>uncertain</td>
<td>Yes</td>
<td>No</td>
<td>No</td>
<td>No</td>
<td>Fig. 4.5</td>
<td>Intensity vs $q$ profile</td>
</tr>
<tr>
<td>$R_g$ growth</td>
<td>Yes</td>
<td>Yes</td>
<td>Yes</td>
<td>No</td>
<td>No</td>
<td>No</td>
<td>Fig. 4.6</td>
<td>$R_g$ increase after sonication</td>
</tr>
</tbody>
</table>

Silica particles contribute to foam control by facilitating the entry and increasing the penetration depth of oil-silica globules into surfactant-water films (foam bubble walls). Based on
the foam destruction mechanism discussed in Section 1.4, hydrophobic particles assist the oil globule to breach the surface of thin bubble films. This so-called “pin effect” requires hydrophobic silica aggregates whose size is comparable to the bubble film thickness (about 1 µm), consistent with the hydrodynamic radii ($R_h$) reported for good-performing antifoams (9512 and 8375) in Table 5.1.

Dynamic light scattering (DLS) is a rapid method to assess the antifoaming potential of silica. DLS measures the size (hydrodynamic radius, $R_h$) and size evolution of silica in solution. Good performers have large initial $R_h$ and are characterized by a tendency to aggregate ($R_h$ increases) after sonication. In 3-vol% toluene solutions we observed that all silicas with a $R_h$ of less than 0.7 µm were poor performers. Poor performing silicas (6165, 4684 and 0963) also show no tendency to aggregate. Good performing silicas (9215 and 8375), on the other hand, are larger at 3-vol% and tend to aggregate. Antifoam 8340 is an outlier in that it is a poor performer, yet has an initial $R_h = 1.0$ µm and tends to aggregate.

Silica particles are implicated in foam aging (decline of antifoam activity with time) due to decline of hydrophobicity. Based on the oil-adsorption hypothesis, silicone oil adsorbs to the silica surface and induces aggregation. As hydrophobic particles become hydrophilic however oil adsorption ceases and silica particles no longer aggregate sufficiently to control foaming.

Loss of hydrophobicity may be due to hydrolysis of surface Si-O-C$_3$H$_{2x+1}$ groups. The resulting Si-OH groups are hydrophilic. Maintenance of hydrophobicity therefore requires suppression of hydrolysis or actively regenerating alkyl silane surface groups. Based on the patent literature, it appears that the latter strategy may be active in Dow Corning antifoam agents.
Dow Corning Patents EP1167502B1, *Silicone based foam control compositions stable in detergents* and US 8536109 B2, *Foam control composition*, contain sufficient information to postulate a working hypothesis for foam stability. EP1167502B1 describes antifoam constituents with the exception of M (R₃SiO−) & Q (SiO₄−) resins, which are the focus on US8536109B2. In addition, EP1167502B1 contains considerable information on the influence of composition on foam activity and the roles of some constituents on performance. Based on these patents our hypothesis is that, in the presence of M and Q resins (plus at least one polyoxyalkylene oligomer) hydrophobicity is maintained due to base-catalyzed polymerization of the siloxane resins to form siloxane oligomers, trimethyl siloxane surface groups and polyoxyalkylene surface groups on silica. If the reactive constituents are exhausted during storage (due to side reactions that yield free polymers) then the ability to regenerate silica hydrophobicity after deployment is compromised.

The reactive regeneration hypothesis can be tested by a combination of techniques to relate the reactive constituents to the evolution of silica surface properties and the morphological evolution of silica aggregates. The role of the reactive resin package can be established using NMR and FT-IR to observe chemical reactions (if any) occurring as the foam ages with and without MQ resin. The surface energy of silica can be monitored and correlated with the progress of the regenerative chemical reactions. Finally, the impact of various resin package constituents on evolution of silica-PDMS formulations can be determined by scattering methods.
References


Appendix A  Emulsion Preparation and Efficiency Tests

We attempted to prepare water based antifoam emulsions in order to compare the antifoam efficiency and to characterize the silicone-silica globules. Efficiency tests were conducted using the antifoam-water emulsions prepared by following procedure.

Both PEG-40 Stearate and Span 60 (Table A.1) were used as emulsifiers, and their water solutions were prepared respectively. The emulsifying solution contains 1.0 wt% PEG 40 stearate solution and 0.7 wt% Span 60 solution in the volume ratio 1:1. Then six antifoam samples were added in mixed emulsifying solution in the volume ratio of 1:10 respectively. The emulsion for each antifoam was sonicated for 5 seconds and heated up to 50°C for a couple of hours. However, some oil droplets and thick oil layers were still observed by the naked eye in the emulsions. Antifoams were not completely emulsified in water even after quiescently aging for 1 week.

Table A.1 Parameters of emulsifiers and surfactant used in efficiency tests.

<table>
<thead>
<tr>
<th>Name</th>
<th>Formula</th>
<th>Concentration (wt%)</th>
</tr>
</thead>
<tbody>
<tr>
<td>PEG-40 Stearate</td>
<td>((C_2H_4O)<em>nC</em>{18}H_{36}O)</td>
<td>1.0</td>
</tr>
<tr>
<td>Span 60</td>
<td>(C_{24}H_{46}O_6)</td>
<td>0.7</td>
</tr>
<tr>
<td>Sodium dodecyl sulfate</td>
<td>(NaC_{12}H_{25}SO_4)</td>
<td>1.0</td>
</tr>
</tbody>
</table>

1 wt% sodium dodecyl sulfate (SDS) in water was used as a foaming solution in order to test the ability of antifoams to control foaminess. As Fig. A.1 shows, 1 ml antifoam/water emulsion and 20 ml SDS solution were added in the graduated cylinder and let stand for 2 minutes. After filtered air flowed in for 10 seconds, the connection to the air was immediately cut. Foams
collapsed rapidly as the air flow stopped, which made it difficult to observe the defoaming process. Therefore, the volume change of foams for each sample was recorded after a 1-minute delay.

![Diagram of efficiency test](image)

**Figure A.1** Schematic representation of the efficiency test.

**Table A.2** The volume change of foams for each antifoam samples and the control group (SDS solution without any antifoam, Emulsifying solution without any antifoam).

<table>
<thead>
<tr>
<th>Sample</th>
<th>Initial $V(t=1\text{ min})$</th>
<th>Final $V(t=15\text{ min})$</th>
<th>$\Delta V$</th>
</tr>
</thead>
<tbody>
<tr>
<td>SDS solution</td>
<td>$\geq100$</td>
<td>23.0</td>
<td>$\geq77.0$</td>
</tr>
<tr>
<td>Emulsifying solution</td>
<td>85.0</td>
<td>23.5</td>
<td>61.5</td>
</tr>
<tr>
<td>0963</td>
<td>24.0</td>
<td>23.1</td>
<td>0.9</td>
</tr>
<tr>
<td>4684</td>
<td>24.2</td>
<td>23.3</td>
<td>0.9</td>
</tr>
<tr>
<td>6165</td>
<td>24.0</td>
<td>23.5</td>
<td>0.5</td>
</tr>
<tr>
<td>8340</td>
<td>26.5</td>
<td>25.0</td>
<td>1.5</td>
</tr>
<tr>
<td>8375</td>
<td>25.3</td>
<td>23.3</td>
<td>2.0</td>
</tr>
<tr>
<td>9512</td>
<td>25.5</td>
<td>23.5</td>
<td>2.0</td>
</tr>
</tbody>
</table>

By comparing initial volume of foams (Table A.2), one observes that all antifoams reduce foaming tendency in surfactant solutions. Initially 0963 and 6165 are the most effective in that these generate the lowest foam volume at 1 min. After 15 minutes, however, the reduction in foam volume, $\Delta V$, implies that 8375 and 9512 are more effective in destroying an existing foam.
Producing antifoam-water emulsion in small scale is challenging. The non-uniformity of antifoam-water emulsions increases uncertainty in the measurements. Specifically, the air bubbles generated are thin and unstable because of the small volume of the graduated cylinder and the low concentration SDS. If the experimental equipment were improved, an efficiency test would be very helpful to further this research. By repeating the efficiency tests over a period of time we can observe the degradation of antifoam emulsions and compare the stability between antifoam formulations.
Appendix B  Instructions for the DLS Processing Panel in Igor

The data fitting in this study was performed by a powerful analysis panel for DLS in Igor (Fig. B.1). This panel is capable of importing data and parameters, fitting DLS curves and calculating results. The analysis code written by Prof. Schaefer is available as supplementary files. An Igor macro package, Load UC macros.ipf, should be loaded first by clicking the main menu Macros/Load UC macros. To open the DLS panel, click ALV DLS Panel under Plot&Fit tab of main menu. Fig. B.1 shows the panel when processing the DLS data for polystyrene spheres measured at 90°. The plot, clip, restore, cum, and load buttons in the middle perform data importing, plotting and fitting. The parameters (temperature, refractive index, viscosity, etc.) can be input manually. The data loading procedure depends on the file type (excel, text, asc, etc). Consult the Igor help utility if the button does not work for your data. The supplementary files include Example.asc, which contains data for polystyrene spheres exported from the Malvern CGS-3 correlator using the File/SaveAs button in the ALV-CGS-3 operating software.

To fit a DLS curve, first, plot the data in the window and move the cursors to the ends of decay. There is more than one way to select the decay region as shown in Fig. B.1. Then choose appropriate order of cumulant (ord button) and click cum button (abbreviation for cumulant). High-order polynomial fits (up to 5) may be needed when the sample has a broader size distribution. After data are fitted, the diffusion coefficient (D), hydrodynamic radius (Rh) and the decay rate (Gam) will calculated and displayed in the panel automatically.
Figure B.1 Two ways to fit autocorrelation functions using the Igor panel. The sample shown in the panel is 2 wt% polystyrene microspheres in water measured by DLS at 90 degree at room temperature.
Appendix C  Supplementary Files

Description:
The accompanying files are Igor procedure files written by Dr. Dale W. Schaefer.

The Igor application must be purchased from Wavemetrics (wavemetrics.com), Inc. after the trial period. After installation of Igor 7 (try Igor 6.37 if there are compatibility issue), visit Dr. Jan Ilavsky’s homepage and follow the instruction to download and install the Indra package and the Irena package (http://usaxs.xray.aps.anl.gov/staff/ilavsky/irena.html). Navigate to the Igor program (typically the path is WaveMetrics/Igor Pro Folder). Put the file Boot UC.ipf in the Igor Procedures subfolder and put the DWS_ALV_LightScattering.ipf and all the other procedure (.ipf) files below in the User Procedures subfolder. Launch Igor after the procedures are placed in the appropriate folders. Follow the instructions presented in Appendix B to load the panel. Please contact the author (yuanzg@mail.uc.edu) or Prof. Dale W. Schaefer (dale.schaefer@uc.edu) for guidance if the DLS panel doesn’t work properly.

File Names:

Boot UC.ipf
DWS_ALV_LightScattering.ipf
Load UC macros.ipf
DWS_Utilsities SAS.ipf
DWS_SNS_LR.ipf
DWS_Reflectivity.ipf
DWS_Plot Fits.ipf
DWS_DataManipulation.ipf
DWS_Data Loader.ipf
Example.asc