FOAMING OF ANIONIC SURFACTANT SOLUTIONS
IN THE PRESENCE OF CALCIUM IONS AND
TRIGLYCERIDE-BASED ANTIFOAMS

A thesis submitted to The University of Manchester for the degree of
PhD in the Faculty of Engineering and Physical Science

2011

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The University of Manchester

ABSTRACT OF THESIS submitted by Li Ran for the degree of Doctor of Philosophy and entitled Foaming of Anionic Surfactant Solutions in the Presence of Calcium Ions and Triglyceride-based Antifoams. Date of Submission: 14/04/2011

Sodium linear alkylbenzene sulphonate (NaLAS) is the usual surfactant present in high foam laundry detergents. The foam behaviour of NaLAS is significantly dependent upon the foam generation methodology, water hardness and the antifoam action of deterged sebum soils. Here a study of the foam behaviour of NaLAS (and C_{12} 4-phenyl SO_3 Na) solutions at different Ca^{2+} concentrations and pHs in the absence and presence of antifoam is presented. Two foam generation methodologies were used – tumbling tube rotation and cylinder shaking. It has been found that these two methodologies correlate well with a coefficient of ≥ 0.95 when comparing foamabilities. The correlation coefficient however declines to ~0.82 when comparing foam stabilities. The reason of this deterioration has been attributed to the differences of antifoam effect in foam films after foam generation due to differences in bubble size distribution formed by these two methodologies.

In the absence of antifoam, the foam behaviour is independent of pH and is dominated by the formation of Ca(LAS)_2 (or Ca(C_{12} 4-phenyl SO_3)_{22} lamellar phase liquid crystals. Dynamic surface tension measurements confirm that low foamability after the micellar-precipitate boundary of the Ca^{2+}-LAS^{-} (or Ca^{2+} - C_{12} 4-phenyl SO_3^{-}) precipitation phase diagram is due to low rates of transport of surfactant to the rapidly expanded air-water surfaces.

Mixtures of triolein/stearic acid and triolein/tristearin are used as models for sebum soil antifoam, as they show similar antifoam effects regardless of pH and calcium concentration. In these two systems, crystalline particles are always present provided, in the case of triolein/stearic acid, formation of soaps is suppressed at low pH. Both stearic acid and tristearin particles adopt an oil-water contact angle θ_{OW} > 90° measured through the aqueous phase. They invert the O/W emulsion behaviour shown by triolein alone to W/O by rupturing the oil-water-oil emulsion films. They will also rupture the air-water-oil pseudoemulsion films provided the conditions of θ_{AW} > 2.6° for stearic acid and θ_{AW} > 0° for tristearin are satisfied. This behaviour of particles will facilitate the emergence of triolein droplets into air-water surfaces. Foam film rupture however only occurs under dynamic conditions, where bridging coefficients for triolein are expected to be positive. However under the near-equilibrium conditions prevailing during foam stability, bridging coefficients for triolein are negative. Little or no antifoam activity is therefore observed under those conditions with these triolein-based mixtures.

Oil/particle mixed antifoams probably deactivate through a splitting and coalescence process. Triolein/stearic acid antifoam deactivates more rapidly than sebum soil and triolein/tristearin. This is mainly caused by formation of large inactive agglomerates which occurs both after antifoam dispersion and after continuous foam generation.
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Acknowledgements

I would like to thank many people for all the help and support I have received throughout my PhD. First and foremost, I would like to thank my supervisor, Prof. Peter Garrett for his support and patience during my PhD studies. I would also like to thank my co-supervisors Dr. Paul Grassia and Prof. Gordon Tiddy for their helpful discussions. I would like to thank the EPSRC and Procter & Gamble for providing the financial support of this project. I would like to thank Dr. Patrick Hill for obtaining the stearic acid and tristearin SEMs, Anthony Diggle for building the vertical film apparatus, and Gary Burns for building the Ross-Miles apparatus. I would also like to thank Paul Lapham for making the antifoam viscosity measurement, and Prof. Nikolai Denkov, Dr. Slavka Tcholakova and Radka Petkova (all of the University of Sofia, Bulgaria) for their discussions and for making the FTT measurements. I must also thank my families and friends for their love, patience and support over the years.
Chapter 1 Introduction

1.1 Objectives of This Project

The objective of this project is to study the physical chemistry of foam, especially the foaming behaviour of the multi-component systems present during hand washing of clothes. This is designed to facilitate Procter & Gamble (P&G) understanding of the fundamental foaming behaviour of potential new formulations in the laundry detergents under various conditions (including different water hardresses, pHs and in both the absence and presence of soil antifoams mainly derived from sebum), thus guiding their future formulation optimization.

Procter & Gamble (P&G) is one of the largest companies in fabric, household care industry around the world. There are two main categories of laundry detergent products in P&G, which are divided according to foaming performance: High Foam Products (for hand-washing users) and Low Foam Products (for automatic washing machine users). The foaming profile is particularly important for High Foam Products, due to the special needs of their target consumers. This aspect is our research emphasis. In the minds of these consumers, the ideal detergents should not only have a strong capability of cleaning but also high-quality foaming effects, which include the fast-generation of foam at the product dissolving stage and long-lasting foams during washing. In addition to the volume of foam, some other sensorial characteristics of foams will also influence consumers’ preference for laundry products, such as the sizes of bubbles, the feeling on the hand between foams and fabrics during scrubbing, although those will not be studied in this project. Therefore, a comprehensive study of foam behaviour in the whole laundry process will provide a clear technical instruction for P&G on product design and benefit their home care business.

Understanding of the process of foam generation in the context of the washing of clothes by hand is surprisingly limited in view of the ubiquitous nature of a habit employed by
hundreds of millions of consumers across the globe. It is characterised by three key interrelated factors – methodology, surfactant solution properties and the antifoam action of deterged soil, all of which are studied in this project:

1) The methodology of consumers in this context simply involves rapid air entrainment into a surfactant solution containing emulsified antifoam materials derived from soil. The resulting foam is necessarily polydisperse. Obviously the volume of entrained air, and therefore foam, formed at this stage represents the key point of satisfaction or otherwise of consumers. The stability over prolonged times of the resulting foam is of less significance. Foam tests intended to simulate this aeration process use shaking, tumbling or impinging jets rather than pneumatic methods. We intend to explore the correlation of two such tests – shaking and tumbling in the measurement of foamability and foam stability.

2) With anionic surfactants the main constraint on effectiveness, in the absence of antifoam, derives from the presence of calcium and other polyvalent ions in hard water which result in the formation of mesophase (liquid crystalline) or crystalline precipitates. In practice this problem is usually avoided by the addition of a suitable complexing agent. Such complexing agents are usually referred to as “builders”. Here we seek understanding of surfactant foam behaviour (especially the effect of Ca$^{2+}$-surfactant precipitation) in the absence of such agents, an interest which reflects the potential cost and environmental disadvantage which can be involved in use of builders.

3) In the absence of precipitation of anionic surfactant, foam behaviour is often totally dominated by the effect of sebum soil. This sebum soil is usually simulated in practical tests with a synthetic mixture of various saturated and unsaturated triglycerides (using for example olive oil and sunflower oil), saturated and unsaturated fatty acids and hydrocarbons. Such a mixture may be realistic but complexity implies a probable lack of clarity in establishing its mode of action. Here we therefore sought first to find a simpler combination of materials which had essentially the same antifoam behaviour as the oily soil. Then we sought to establish the mode of action of that material.
1.2 High Foam Powder Detergent Formulation

A typical high foam detergent powder formulation usually contains several components and each of them has different functions in the washing process, as shown in Table 1.1 [1]. Surfactants are the foaming agents in a laundry product. Sodium Linear Alkyl Benzene Sulphonate (NaLAS) is the key foaming surfactant, being used at a level around 13 to 18% by weight in high foam powder detergents sold in current markets. Other linear anionic surfactants, like Sodium Alkyl Ether Sulphate (NaAES), Sodium Primary Alkyl Sulphate (NaPAS) and ethoxylated fatty alcohol are also added in both high foam detergents and other personal care products to enhance the cleaning and foaming performance of surfactant systems [2-4].

<table>
<thead>
<tr>
<th>Components</th>
<th>Percentage by weight / %</th>
<th>Function</th>
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<tbody>
<tr>
<td>Surfactants</td>
<td>15 – 20</td>
<td>Cleaning, foaming</td>
</tr>
<tr>
<td>Builder</td>
<td>10 – 15</td>
<td>Cleaning, water softening</td>
</tr>
<tr>
<td>Buffer</td>
<td>10 – 15</td>
<td>Maintaining an alkali condition</td>
</tr>
<tr>
<td>Polymers</td>
<td>3 – 5</td>
<td>Cleaning, stabilizing foams</td>
</tr>
<tr>
<td>Bleaches</td>
<td>3 – 5</td>
<td>Cleaning</td>
</tr>
<tr>
<td>Enzymes</td>
<td>2 – 4</td>
<td>Cleaning</td>
</tr>
<tr>
<td>Other additives</td>
<td>2 – 4</td>
<td>Delivering sensorial profile</td>
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<td>(perfumes, dyes, etc.)</td>
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<tr>
<td>Filler (Na₂SO₄)</td>
<td>40 – 50</td>
<td>Balancing the formulation</td>
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</table>

Chelating agents (so-called builders) such as Sodium TriPolyPhosphate (Na₅P₃O₁₀, STPP) and Sodium Aluminosilicates (zeolite), which bind divalent Ca²⁺ and Mg²⁺ contained in washing solutions are usually present. Complexation between builder and Ca²⁺ can improve the foaming behaviour of anionic surfactants by minimizing the formation of Ca²⁺-surfactant precipitates. However, we will exclude builders from our study. As stated above, this derives from consideration of the high cost and environmental contamination.
sometimes associated with their use [5]. Other components like bleaches, enzymes and polymers are added simply as cleaning agents, so then do not have any impact on the foaming profile of final detergent products and are essentially irrelevant for our study. The rest of this section is laid out as follows - section 1.2.1 deals with Sodium Linear Alkyl Benzene Sulphonate and section 1.2.2 deals with cosurfactants.

1.2.1 Sodium Linear Alkyl Benzene Sulphonate (NaLAS)

Commercial NaLAS is a blend of different isomers and chain lengths which have a chain length distribution generally from C_{10} to C_{15} and include several different phenyl isomers for each chain length [6]. NaLAS paste, used in laundry products, is synthesized from Linear Alkyl Benzene (LAB). The molecular structure of NaLAS is exemplified by a typical component of such blends - C_{13} 6-phenyl SO_3Na - shown in Fig.1.1.

![Fig.1.1. A molecular structure of NaLAS (C_{13} 6-phenyl SO_3Na)](image)

The different hydrocarbon chain lengths and phenyl isomers derive from the nature of the catalyzed benzene alkylation procedure which uses kerosene as alkane feed-stock [7, 8]. The production process of NaLAS is briefly summarized in Fig.1.2.
Fig. 1.2. A scheme of production process of industrial NaLAS (a) from kerosene to LAB; (b) from LAB to NaLAS.

By way of illustration, Fig. 1.3 gives the chemical structure of all the dodecyl benzene isomers present in a typical commercial LAB after alkylation with a catalyst such as hydrogen fluoride (HF), aluminum chloride (AlCl₃) or aluminosilicic acid [9]. A similar range of isomers is present for each of the C₁₀ to C₁₄ chain lengths, which means that a typical commercial LAB sample contains upwards of twenty compounds (of different isomers and chain lengths). LAS acid is then produced by sulfonating LAB with either oleum (10 – 25% sulfur trioxide SO₃ in sulfuric acid) or an SO₃-air mixture. The last step of the production process shown in Fig 1.2 involves neutralization of the alkyl benzene sulfonic acid with sodium carbonate. This is not usually an exact process and often produces samples of NaLAS contaminated with excess Na₂CO₃ and Na₂SO₄ (the latter due to excess acid added at the sulfonation step). Commercial LAS samples therefore often dissolve to produce alkaline solutions irrespective of the presence of other formulation additives.
1.2.1.1 Ca$^{2+}$-LAS$^-$ Precipitation Phase Diagram

A key property of NaLAS solution concerns sensitivity to precipitation by divalent metal ions. Excess divalent metal ions can result in precipitation of LAS$^-$ as an apparent stoichiometric salt of for example formula Ca(LAS)$_2$. This precipitation can result in a significant decrease in effective surfactant concentration. However at low concentration of divalent metal ions where no precipitate is formed, they can increase surface activity, producing a reduction in surface tension of solutions of NaLAS [10]. Cohen et al. [11, 12] measured the foaming profile of solutions at various LAS$^-$ and Ca$^{2+}$ concentrations, and suggested the foaming capability is determined by the relative position of Ca$^{2+}$ and LAS$^-$ on the so-called Ca$^{2+}$-LAS$^-$ precipitation phase diagram. An example of such a diagram for three different commercial NaLAS samples (Table 1.2) by Matheson et al. [13] is shown in Fig.1.4.

**Fig.1.3.** Molecular structures of all the dodecyl benzene (LAB) isomers produced by alkylation of benzene with a typical catalyst, such as hydrogen fluoride, aluminum chloride and aluminosilicate acid.
Table 1.2. Analytical data for commercial NaLAS samples [13]

<table>
<thead>
<tr>
<th>NaLAS sample</th>
<th>A</th>
<th>B</th>
<th>C</th>
</tr>
</thead>
<tbody>
<tr>
<td>Average molecular weight LAS</td>
<td>339</td>
<td>343</td>
<td>363</td>
</tr>
<tr>
<td>Chain length distribution</td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>C\textsubscript{10}</td>
<td>20</td>
<td>13</td>
<td>-</td>
</tr>
<tr>
<td>C\textsubscript{11}</td>
<td>34</td>
<td>31</td>
<td>2</td>
</tr>
<tr>
<td>C\textsubscript{12}</td>
<td>36</td>
<td>29</td>
<td>22</td>
</tr>
<tr>
<td>C\textsubscript{13}</td>
<td>9</td>
<td>24</td>
<td>48</td>
</tr>
<tr>
<td>C\textsubscript{14}</td>
<td>1</td>
<td>3</td>
<td>28</td>
</tr>
<tr>
<td>Activity / %</td>
<td>96.3</td>
<td>96.4</td>
<td>97.1</td>
</tr>
</tbody>
</table>

Fig 1.4. Ca\textsuperscript{2+} - LAS\textsuperscript{-} precipitation boundary diagrams measured at room temperature; — Sample A, —— Sample B, ——— Sample C [13].

In our research, Ca\textsuperscript{2+} - commercial NaLAS and Ca\textsuperscript{2+} - C\textsubscript{12} 4-phenyl SO\textsubscript{3}Na phase diagrams are measured in the presence of NaCl where the concentration of the latter reproduces the ionic strength typical of that present during consumer use of high foam detergent products. This permits establishment of the relationship between precipitation, equilibrium and dynamic surface tensions and foaming behaviour.
Some environmental issues have been raised recently regarding the contamination of LAS in drinking water [14, 15]. It has been estimated that the global annual consumption of LAS is around one million tons [15]. Although wastewater treatment can remove around 90% LAS and the degradation of LAS is rapid, still, under some anaerobic conditions, LAS can persist in water as a contaminant [16]. Methods of removing LAS from drinking water by adding active ions for precipitation are used now, but further work on improving this technique still needs to be made in the future [14, 17].

1.2.2 Cosurfactants as Foam Boosters

High foam powder detergent formulations often contain two or three other surfactants besides NaLAS. These can include Sodium Primary Alkyl Sulphates (NaPAS), Sodium Alkyl Ether Sulphates (NaAES) and Ethoxylated Fatty Alcohol (nonionic, NI) [1]. These cosurfactants are added to formulations to improve either the cleaning ability or foaming behaviour of NaLAS, in the latter case, as so-called “foam boosters” [3].

The NaPAS used in detergent products usually contains linear alkyl chains of C₈ to C₁₈. As with NaLAS, NaPAS in detergent solutions can form precipitates with metal ions (Ca²⁺ and Mg²⁺). Few reports mention the effect of this type of surfactant as a foam booster, but some synergistic effect between NaLAS and Sodium Primary Alkyl Sulphates in enhancing foamability has been observed by P&G [18]. We therefore plan to study the effect of NaPAS on the foaming behaviour of NaLAS. The molecular structures of NaPAS can be written as:

\[
\text{H}_3\text{C} \quad \text{(CH}_2)_m \quad \text{O} = \text{O}^{-} \quad \text{Na}^+ 
\]

Fig.1.5. Molecular Structure of commercial Sodium Linear Alkyl Sulfate (NaPAS), where \(8 \leq m \leq 18\).

Sodium Alkyl Ether Sulphates (NaAES) are more difficult to precipitate with metal ions
than either NaLAS or NaPAS, with a higher solubility product for Ca(AES)$_2$ than that for Ca(LAS)$_2$ or Ca(PAS)$_2$, presumably due to the hydrophilic nature of the ethylene oxides (EO) groups in the NaAES [19, 20], as shown in Table 1.3. The NaAES used in laundry formulations has a linear hydrocarbon chain with an EO number from 1 to 3, as shown in Fig. 1.6.

![Molecular structure of commercial Alkyl Ether Sulphate (NaAES), where 12 ≤ m ≤ 15, 1 ≤ n ≤ 3](image1.png)

**Fig.1.6.** Molecular structure of commercial Alkyl Ether Sulphate (NaAES), where 12 ≤ m ≤ 15, 1 ≤ n ≤ 3

**Table.1.3.** Solubility products of C$_{12}$ anionic surfactants with Ca$^{2+}$ at a concentration below the Critical Micelle Concentration (CMC).

<table>
<thead>
<tr>
<th>Anionic Surfactant</th>
<th>Temperature / °C</th>
<th>Solubility Product (precipitating with Ca$^{2+}$) / M$^3$</th>
</tr>
</thead>
<tbody>
<tr>
<td>C$_{12}$ 4-phenyl SO$_3$Na</td>
<td>25</td>
<td>9±1 × 10$^{-12}$ * [21]</td>
</tr>
<tr>
<td>Sodium dodecyl sulfate (SDS)</td>
<td>30</td>
<td>5.02 × 10$^{-10}$ [22, 23]</td>
</tr>
<tr>
<td>Sodium dodecyl ether sulfate (EO$_3$)</td>
<td>22</td>
<td>3.2 × 10$^{-8}$ [24]</td>
</tr>
</tbody>
</table>

* not corrected for ionic activities

Ethoxylated fatty Alcohols represent another type of cosurfactant used in laundry industry. These nonionic surfactants have an alkyl chain length distribution of C$_8$ to C$_{18}$ and ethoxylated head group with an average EO number of 3 to 10. The typical molecular structure of this fatty alcohol surfactant can be written as:

![Molecular structure of commercial ethoxylated Fatty Alcohols, where 8 ≤ m ≤ 18, 3 ≤ n ≤ 10](image2.png)

**Fig.1.7.** Molecular structure of commercial ethoxylated Fatty Alcohols, where 8 ≤ m ≤ 18, 3 ≤ n ≤ 10
1.3 Antifoams

Antifoams are widely used in various industries to control the volume of foams. They are usually present as un-dissolved entities. For example, silica / silicone oil mixed antifoams are added to the detergent products for use in front loading automatic washing machines to avoid the over-flow of foams out of the equipment during the washing process [25].

The detergent products sold to hand washing consumers are designed to be high foaming and unlike the products used for automatic washing machines, usually therefore contain high levels of surfactant and no antifoam [5]. The in-use foam behaviour of hand wash detergent products is in fact dependent upon many factors, including mainly:

1). The surfactant system (NaLAS and other cosurfactants) - whether there is enough effective surfactant which can balance the need for both cleaning and foaming in the washing process [26, 27];

2). Water hardness - tap water usually contains ions, like Ca$^{2+}$, which can cause precipitation with anionic surfactants, and therefore decrease the effective surfactant concentration [19]. This hardness varies markedly across the globe being as low as $4 \times 10^{-4}$ M in Brazil and as high as $4 \times 10^{-3}$ M in parts of India.

3). Sebum soils - derived from clothes, are generally believed to behave as effective antifoams, destabilizing foams during washing [28].

Sebum soil is a mixture of different triglycerides, fatty acids, cholesterol and hydrocarbons [29]. It is also a mixture of particles and oils, where the fatty acid can react at high pH to form sodium and calcium soaps. In turn formation of soaps (especially calcium soaps) has been associated with enhanced antifoam effects which have been attributed to oil-particle antifoam synergy [30, 31]. However, these studies concerned triolein/oleic acid mixtures which only form synergistic oil/particle mixtures when the oleic acid reacts with Ca$^{2+}$ at high pH in solution to form calcium soap particles. Sebum on the other hand is intrinsically a mixture of particles and oil before it interacts with solutions containing calcium at high pH. In that respect, triolein/oleic acid mixtures are not representative of the actual soil usually present in clothes washing solutions. We therefore
need to study an actual model sebum in order to better understand the antifoam effect found with these materials.

Understanding the nature of sebum soil as an antifoam requires a detailed study of the hydrophobicity (by measuring the contact angles), geometry and roughness (by measuring the crystal behaviour) of any particles present; entry, spreading and bridging behaviour of oil phases; and the effect of these particles on rupturing the air-water-oil pseudoemulsion film [32].

If sebum functions as an oil-particle synergistic antifoam, it is possible that it exhibits deactivation during the continuous agitation accompanying foam generation. Such deactivation is well-known in the case of polydimethylsiloxane/silica antifoams [33, 34] but is less well known in the case of other oil/particle antifoams [32]. It is therefore of relevance to establish the extent or otherwise of deactivation of the antifoam effect of sebum soil during continuous washing or scrubbing processes.

1.4 Outline of the Thesis

Chapter 2 presents a review of the processes in liquid foams and the mode of action of antifoams. This chapter begins with a discourse on the foaming behaviour of surfactant solutions and the stability and thinning of liquid foam films, and is followed by a description of the antifoaming mechanisms of hydrophobic particles, oils and mixed oil/particle antifoams. The deactivation mechanisms of oil/particle antifoams are also described.

Chapter 3 includes two sections. The first describes the materials, their sources and their preparation. The second part describes the experimental techniques used throughout the whole project.
Chapter 4 presents the results of foamability and foam stability of NaLAS and C_{12} 4-phenyl SO_3Na solutions in the absence of antifoam. The relevant Ca^{2+}-LAS^- and Ca^{2+}-C_{12} 4-phenyl SO_3^- phase diagrams are presented. The foaming behaviour of NaLAS and C_{12} 4-phenyl SO_3Na solutions in the absence of antifoam is correlated with the Ca^{2+}-LAS^- (and Ca^{2+}-C_{12} 4-phenyl SO_3^-) precipitation, in particular the origin of the low foamability associated with Ca^{2+}-LAS^- (and Ca^{2+}-C_{12} 4-phenyl SO_3^-) precipitation is explored by considering the effect on surfactant transport to air-water surfaces and possible antifoam role of the Ca^{2+}-LAS^- (and Ca^{2+}-C_{12} 4-phenyl SO_3^-) precipitate.

Chapter 5 presents the results of foamability and foam stability of NaLAS and C_{12} 4-phenyl SO_3Na solutions in the presence of sebum soil antifoam and other antifoams. The role of pH and Ca^{2+} ion concentration in determining the antifoam behaviour is a particular concern of this work. The selection of suitable oil-particle combinations of pure ingredients which simulate the antifoam behaviour of sebum soil is also described.

Chapter 6 concerns the relationship between different foam generation methodologies: tumbling tube method and cylinder shaking method.

Chapter 7 discusses the defoaming mechanism of triolein/stearic acid and triolein/tristearin antifoams as models for sebum soil. It mainly concerns the entry, spreading, and bridging behaviours of antifoams at equilibrium and dynamic conditions; and the roles of fatty acid and triglyceride crystalline particles in rupturing the oil-water-oil and air-water-oil pseudoemulsion films.

Chapter 8 describes the study of the deactivation of sebum soil, triolein/stearic acid and triolein/tristearin antifoams in NaLAS solutions at two conditions: pH 3, nil Ca^{2+} and pH 10.5, Ca^{2+}: 5.25×10^{-4} M.

Chapter 9 describes the effect of SDS as co-surfactant on the precipitation and foam behaviour of C_{12} 4-phenyl SO_3Na is described in this chapter.
Chapter 10 and 11 are the discussion, summary and conclusions drawn together based on all the studies presented in the previous chapters.

1.5 References


Chapter 2 Processes in Foam and Mode Action of Antifoams

2.1 Introduction

Foams can be found ubiquitously wherever bubbles of gas are contained within a liquid or solid [1]. Liquid foams usually have a white colour and often short life-time, such as bubbles generated by shampoos, shaving creams, or dish washing products in water. Solid foams are formed starting from liquid foams. Examples are gas bubbles in bread, metal foams applied in aerospace and automobiles [2] or polyurethane and other plastic or rubber foams in some new environment-friendly constructing materials as reported recently [3].

In this review, we will focus on a discussion of liquid foams, as our experimental system will concern the foaming behaviour of laundry detergent formulations. This chapter therefore includes three sections, beginning with a discourse on the foaming behaviour of surfactant solutions and the stability and thinning of liquid foam films formed after generation. The second part follows with a description of the antifoaming mechanism of hydrophobic particles, oils and oil/particle mixtures as antifoams when they are present in aqueous foam films. The third part discusses the deactivation mechanism of oil/particle synergistic antifoams in a continuous foam generation process.

2.2 Surfactants and Foaming

2.2.1 Structures of Foams and Drainage

Foams cannot be generated from a pure liquid without the presence of some surface active materials (for example anionic surfactants in detergents) in the solution [4]. A scheme of the structure of foams formed by shaking a surfactant solution in a vertical glass cylinder is given in Fig.2.1 (a) and (b) [5].
Spherical bubbles (so-called \textit{Kugelschaum} in Fig. 2.1 (a)) dispersed in liquids are produced at the initial stage after shaking and they are separated by thick liquid films. If the cylinder is simply allowed to stand for several minutes, the liquid will gradually drain out of the foam films due to the gravitational force. The structure of bubbles at the higher part of cylinders then changes from spherical to polyhedral (so-called \textit{Polyederschaum}, Fig. 2.1 (b)) and the volume fraction of liquid in the foam decreases. Because of the effect of drainage, foam films will continuously thin until they either form metastable films or rupture.

The channels connecting the plane-parallel films in polyhedral foams are called Plateau borders, illustrated in Fig.2.1.(c) [7]. As described, at this stage, the pressure in the polyhedral bubbles ($P_{\text{air}}$) is higher than that in the Plateau borders ($P_2$) due to the convex curvature towards the liquid phase. According to the Laplace equation, this difference of
the pressure (i.e. the capillary pressure) is given by [8]:

\[
\Delta P_c = P_{air} - P_2 = \gamma_{AW} \left( \frac{1}{R_1} + \frac{1}{R_2} \right)
\]  

(2.1)

where \( \gamma_{AW} \) is the air-water surface tension, \( R_1 \) and \( R_2 \) are the principal radii of the curvature and where in the case of a Plateau border, \( R_1 \ll R_2 \), so that \( 1/R_2 \sim 0 \). As the pressure in the foam film \( P_1 \) (in the particular case where the curvature radius is infinite) is equal to \( P_{air} \), a capillary suction force would cause the liquid from the adjacent films to drain into the Plateau borders until a balance between the capillary pressure and disjoining pressure in the foam films is achieved. This condition requires that the disjoining pressure in the films is positive and is therefore dominated by electrostatic repulsions across both films as discussed later in section 2.2.2.4 [9].

Drainage is an important process causing changes in the structure of the foams, the process of which is dominated mostly by gravity according to the quasi-one-dimensional drainage model developed by Grassia and Neethling [10]. In this model, drainage is dependent on the cross-sectional area of the Plateau borders \( A \). If the property \( A \) varies only with the vertical coordinate \( y \) in a foam, \( \eta \) is the liquid viscosity, \( \rho \) is the liquid density, \( g \) is the gravitational acceleration, and \( \gamma_{AW} \) is the air-water surface tension, then the velocity of liquid averaged across the Plateau border cross-section \( u \) is written as:

\[
u = \frac{1}{3 f \eta} \left( -\rho g A - \frac{C \gamma_{AW} }{2 \sqrt{A} } \frac{\partial A}{\partial y} \right)
\]

(2.2)

where \( C \approx 0.201 \) and \( f \approx 49 \). The gravity driven and capillary suction driven drainages are two contributions to the velocity \( u \). A forced drainage rate can also be studied by pouring liquids into the top of standing foams [11]. It has been observed that liquid moves down a foam with a front moving at a constant velocity \( v_f \) after it has been poured onto the top of that foam. The relationship between the
entering liquid flow rate $Q$ and the front velocity $v_f$ follows a power law, which can be described as:

$$v_f \propto Q^\alpha$$

(2.3)

where the value of $\alpha$ is variable and determined by different structures and surface properties of nodes and channels in foams.

### 2.2.2 Diffusional Disproportionation in Foam

After foam generation has ceased, gas diffusion from small bubbles to large bubbles through intralamellar liquid due to an unbalanced capillary pressure usually occurs as shown in Fig. 2.2. This produces changes in the bubble size distribution [12-14].

![Fig.2.2. A scheme of bubble disproportionation due to diffusion](image)

The pressure difference between a spherical small bubble and a large bubble can then be written as:

$$\Delta P = 2\gamma_{aw} \left( \frac{1}{R_1} - \frac{1}{R_2} \right)$$

(2.4)

where $R_1$ is the radius of small bubble and $R_2$ is the radius of large bubble, and $\Delta P$ is the pressure difference between them.

For a treatment of this process in a polydisperse foam, Lemlich [14] defined a notional reference bubble where all larger bubbles expand and all smaller bubbles shrink. If the radius of the reference is $R_L$, then the difference in pressure with respect to any other
bubble of radius $r$ is:

$$\Delta P = 2\gamma_{AW} \left( \frac{1}{R_L} - \frac{1}{r} \right)$$  \hfill (2.5)$$

Gas in small bubbles must first diffuse into the liquid before reaching the air-water surface of the large bubbles. According to Lemlich [14], the molar rate of gas transfer from the bubble to the liquid ($N$) is given by:

$$N = -JA\Delta P$$  \hfill (2.6)$$

where $J$ is the effective permeability, and $A$ is the surface area through which the transfer takes place. This transport behaviour will determine the rates of bubble shrinkage and growth.

### 2.2.3 Foam Film Thinning and Rupture

#### 2.2.3.1 Thinning by Viscous Drainage

The reason why foams cannot be prepared from pure liquids is largely because of the liquid’s response to any external unbalanced force of gravity or capillary suction. As shown in Fig.2.3.(a), in a vertical film, if there are no surface active materials present in the liquid, and therefore no surface tension gradients, then plug flow will occur in the film because no external viscous forces could slow it down [4]. This unbalanced force will therefore lead to an accelerated catastrophic film rupture.

![Fig.2.3.](image)

**Fig.2.3.** Velocity performance of draining foam films (a) a plug flow; (b) flow in a film with immobile surface.
However, this behaviour can be significantly changed by adding surfactants to the pure liquid which can produce surface tension gradients, and therefore velocity gradients, in a direction perpendicular to the plane of the film surface, as shown in Fig. 2.3 (b). A viscous shear force acting against the external force of gravity or capillary suction will then be exerted in the film. As this viscous shear force is balanced by the surface tension gradient at the air-water surface, we can write [4]:

\[
\frac{d\gamma_{AW}}{dy} = \eta \frac{du_y}{dx}
\]

(2.7)

where \( \gamma_{AW} \) is the air-water surface tension, \( \eta \) is the intralamellar liquid viscosity and \( u_y \) is the liquid velocity, \( y \) is the direction of movement and \( x \) is horizontal distance.

This effect is to some extent determined by the transport of surfactants from the bulk to the air-liquid interface [15, 16]. If the surfactant concentration is low and therefore the rate of transport is slow, surface tension gradients in the films will be necessarily relatively low because the surface tension will everywhere tend to that of the solvent. Under these conditions, films will drain more rapidly, leading to possible rupture by a plug flow. Higher concentration of surfactants on the other hand, will mean higher surface tension gradients, leading to slower drainage and more stable films. However, if the concentration of surfactants is extremely high, surface tension gradients will tend to be eliminated as a result of rapid transport of surfactants to the air-liquid surface. This will again lead to plug flow and unstable films in the absence of any other stabilization force such as a positive disjoining force deriving from electrostatic effect [17].

Malysa et al. [18] have studied the foamability of fatty acids (n-pentanoic to n-decanoic acid) by a pneumatic method. As shown in Fig.2.4, the foamability is indicated by a retention time \( (rt) \), which is approximately the life-time of a bubble in the foam. In the foamability measurement, the same equilibrium surface tension was maintained for these homologous series of fatty acids solutions by using the same \( c_0/a_L \) value, where \( c_0 \) is the
surfactant concentration and $a_L$ is the concentration at which the surface concentration of the appropriate acid reaches half its maximum value $\Gamma_\infty$. The longer the fatty acid chain length, the lower the $a_L$ value is. The concentration of fatty acid in solutions ($c_0$) therefore decreases from $C_5$ to $C_{10}$. A Low foamability profile was found at both high and low surfactant concentration regions, indicating that foams are unstable in the condition where the surfactant transport is either too fast or too slow.

Fig.2.4. Foamability of fatty acid surfactants with different chain lengths ($C_n$, 5 ≤ n ≤ 10) in an increased concentration condition; $c_0/a_L$: (1) 0.2, (2) 0.4, (3) 0.8, (4) 1.6 and (5) 2.0; $a_L$ is the concentration of half surface coverage [18].

2.2.3.2 Thinning by a Stretching Mechanism

If foam films are stretched to thin under static conditions, the film surface area will expand while the volume and total amounts of surfactants will be constant. This increase in foam film area will cause a decrease of the concentration of surfactants in the film surfaces. To balance this decrease, surfactants in the intralamellar solution will adsorb at the air-liquid interfaces, which will then in turn result in a decrease of surfactant concentration in the liquid if the film is thin enough. This will cause the surface tension of the film surfaces to
be higher than that before stretching. This latter is the origin of Gibbs elasticity.

The initial decrease of the surfactant concentration will result in an additional increase in the surface tension of foam films, and therefore an elastic response to resist the film stretching [19]. Gibbs [20] first defined the relationship between the surface elasticity $E$, the surface tension and film thickness as:

$$E = \frac{2dY_{AW}}{d \ln A} = -\frac{2dY_{AW}}{d \ln h}$$ (2.8)

where $A$ is the film area, $h$ is the film thickness, $Y_{AW}$ is the air-water surface tension. The factor two means the effect concerns two sides of the film. $E$ defined in this way is usually referred as the Gibbs elasticity of a foam film.

The Gibbs elasticity $E$ is mainly dependent on two factors. One is the concentration of surfactants; the other is the thickness of films [19]. The results of calculations by Lucassen [4], for example, illustrate that there is little elastic response to film stretching when the surfactant concentration is extremely low where the surfactant adsorption is relatively low. When the surfactant concentration is increased, $E$ increases toward to a maximum value. At extremely high surfactant concentrations, however, the Gibbs elasticity will be eliminated, because any stretching in the film does not produce a significant depletion of the intralamellar liquid.

The Marangoni effect, a mass transfer in a liquid layer, results from the difference of surface tension between a newly stretched foam film and the adjacent borders. The presence of a gradient in surface tension will drive solution quickly from the Plateau borders where a lower surface tension region into the foam films prevails. This will tend to stabilise the stretched film [21].

\[ h_d \]
\[ d \]
\[ A_d \]
\[ E \]
\[ A \]
\[ h \]
\[ Y_{AW} \]
2.2.3.3 *Thinning by Marginal Regeneration*

Marginal regeneration appears as fluctuations in film thickness caused by a hydrodynamic instability [22]. In the Plateau borders, pressure in the liquid is less than that of adjacent atmosphere due to capillarity. This negative pressure against the film cross section will induce a net force proportional to the negative pressure and the thickness of the film. This leads to a suction effect in the Plateau borders causing liquid drainage from foam films, as shown in Fig.2.5 (a). The negative force on a thicker film element is larger than that on a thinner film element ($\Delta F$) if these two film elements are connected with the same border, a movement of intralamellar solution will then result and this movement will cause an expansion in thinner area of foam films at the expense of thicker films (seen in Fig.2.5 (b)).

**Fig.2.5.** A scheme of mechanism of marginal regeneration (a) a net force proportional to the negative pressure and the thickness of the film; (b) a movement of intralamellar solution causing thick film elements to be sucked into the Plateau border and thin elements to replace them.
In a vertical foam film, the marginal regeneration will cause the elements of the thinner films to expand and move upwards because of their lower density than that of surrounding films. These thinner elements will keep rising until they reach the film areas which have an equal thickness. An image of marginal regeneration in a thin vertical film of aqueous surfactant solution is shown in Fig.2.6 [23]. It should be emphasized that the rate of the drainage of a vertical thin film is mainly determined by the effect of marginal regeneration in such films when stabilized by soluble surfactants with surfaces of low dilatational elastic moduli [23-25].

**Fig.2.6.** A marginal regeneration observed in a vertical liquid film [24]

### 2.2.3.4 *Disjoining Forces and Equilibrium in Foam Films*

A vertical foam film continues thinning until it reaches a metastable condition where repulsion forces in the film equal the capillary suction from the Plateau border. Those forces depend upon film thickness. They are only sufficiently large to prevent thinning by Plateau border capillary suction when the films are so thin that destructive interference of reflective light from the front and rear surfaces of the film means that they appear to be black.
Contributions to the disjoining forces as described by the DLVO theory, are mainly from two aspects: an electrostatic double layer repulsion potential from the charged surfactant head groups in lamella ($V_{el}$); and a Van der Waals attractive interaction between molecules and ions ($V_{vdw}$). The total potential per unit film area is therefore [5, 8]:

$$V = V_{el} + V_{vdw}$$  \hspace{1cm} (2.9)

The negative derivative of the potential with respect to film thickness is the disjoining pressure ($\Pi$), so [26]:

$$\Pi = -\frac{dV}{dh}$$  \hspace{1cm} (2.10)

The disjoining pressure is positive if it acts to resist thinning of films. As for the potential there are two main contributions to the disjoining pressure, so that we can write:

$$\Pi = \Pi_{el} + \Pi_{vdw}$$  \hspace{1cm} (2.11)

Other contributions to the disjoining pressure $\Pi_s$ at short distances are due to steric forces, the so-called hydrophobic effect and Born repulsion etc. The total disjoining pressure can therefore be written:

$$\Pi = \Pi_{el} + \Pi_{vdw} + \Pi_s$$  \hspace{1cm} (2.12)

A typical plot of disjoining pressure against thickness for a foam film formed by an aqueous anionic surfactant solution is shown in Fig.2.7. Two minima are often found as a consequence of the combination of Van der Waals, electrical double layer and other forces to the overall disjoining pressure as predicted by DLVO theory [5]. Stable films are possible at any thickness if [27, 28]:

\[ \vdots \]
A metastable equilibrium can therefore exist in this region when a capillary pressure \( P_1 \) equals the disjoining pressure \( \Pi_1 \), and a common black film is formed as the film thins to a thickness below the first minimum as shown in Fig. 2.7. Such films are typically 20 – 40 nm. Further thinning of the film will see a maximum in disjoining pressure followed by another minimum due to the relative prevalence of Van der Waals forces. Decreasing a film thickness beyond this point results in a steep increase in the disjoining pressure due to short range forces. At a still higher capillary pressure \( P_2 \) (>\( P_1 \)), another metastable equilibrium is possible to form so-called Newton black films. These films are extremely thin ~ 5 nm – little more that molecular bilayer leaflets.

\[
\frac{d\Pi}{dh} < 0
\]  

(2.13)

**Fig.2.7.** Disjoining pressure \( \Pi \) of a foam film as a function of thickness \( h \)
The capillary pressure which determines this behaviour is in fact that due to the Plateau borders. The increase of capillary pressure causes the foam film also to drain until a condition of equilibrium is achieved where the capillary pressure in the Plateau border $\Delta P_c$ equals both the disjoining pressure in the film and the hydrostatic head $P_g$, so that we have:

$$\Pi = \Delta P_c = P_g = \rho g H$$

(2.14)

where $\rho$ is the mass density of the aqueous phase, $g$ is the acceleration of gravity and $H$ is vertical height measured from the bottom of the foam.

When this condition is realized, the foam ceases to drain. However, it should be emphasized that even if such a condition of apparent stability with respect to drainage can be achieved, diffusion will still occur producing coarsening of the foam and eventual collapse by diffusion of gas to the atmosphere.

It should be stressed that the condition of metastability represented by equation (2.14) can only be realized if the foam films exhibit stable regions in the disjoining pressure curve where $d\Pi/dh < 0$. Otherwise, decreasing thickness will always lead to foam film rupture at a certain critical thickness in a region of the disjoining pressure curve where $d\Pi/dh > 0$. As we describe below, this condition for example prevails everywhere for a film dominated by a Van der Waals force with a positive Hamaker constant [27, 28].

### 2.2.3.5 Disjoining Forces and Film Rupture

Thickness fluctuations analogous to capillary waves, are always present in the foam films [27, 29]. These fluctuations are caused by thermal and mechanical perturbations, forming thinner and thicker regions in a thin film, as shown in Fig.2.8.
In the case where only Van der Waals negative contributions to the disjoining pressure are present, then we have:

$$\frac{d\Pi}{dh} > 0$$  \hspace{1cm} (2.15)

and the film is intrinsically unstable. However, when a flow is squeezed by fluctuations from a thick part of the film to a thin part, a capillary pressure will be generated to oppose the Van der Waals attractive interaction. The foam films will therefore be stabilized by this force. The strength of this capillary pressure is determined by the fluctuation wavelength. To some extent, if the wavelength is extremely long, the foam film will be easily ruptured by Van der Waals interaction as the capillary pressure is tending to be zero. If the wavelength of the liquid movement is extremely short, the disjoining capillary pressure will be high enough to resist any attractive forces, maintaining the liquid film without rupture.

This combination of forces means that above a certain critical wavelength, the fluctuations will grow catastrophically to produce film rupture. If the film is sufficiently thin, these fluctuations will grow faster than the rate of thinning by normal drainage. The thickness at
which that occurs, in the theory of Vrij and Overbeek [28], is so-called critical thickness, and is given by that theory as:

$$h_{cr} = 0.267\left(\frac{a_f A_m^2}{6\pi \Delta p}\right)^{1/7}$$  \hspace{1cm} (2.16)

where $A_m$ is the Hamaker constant, $\Delta p$ is the excess pressure in the film, $\gamma$ is the surface tension and $a_f$ is the initial area of the foam film.

2.3 Defoaming by Antifoams

Antifoams are widely used in various industries to control the volume of foams. They are usually present as un-dissolved entities. For example, silica / silicone oil mixed antifoams are added to the detergent products for use in front loading automatic washing machines to avoid the over-flow of foam out of the equipment during the washing process [30]; in the petroleum industry, some types of polydimethylsiloxanes are added as antifoams to avoid the generation of foams in the production and refining of crude oil, which can result in a reduction of process efficiency [31].

The detergent products sold to hand washing consumers, unlike the products used for automatic washing machines, usually contain high levels of surfactant and do not have any antifoam [32]. In this context, the consumer preference is for copious amounts of foam. The body soils attached to the clothes, however cause a significant defoaming effect during washing. Components in these body soils, such as hydrocarbons, triglycerides, and fatty acids are effective antifoam materials [33].

Some authors [34, 35] mention fatty acid/triglyceride mixtures which model typical body soils. Understanding of the mode of antifoam action of these systems is far from complete, however, due in part to the complex composition of such soils [33]. Studying the antifoam
behave of these body soils will provide a useful guidance to future optimization of the formulation of high foam products particularly with respect to improving their resistance to antifoam effects. The importance in this context of antifoam effects therefore justifies that we give here a review of the antifoam mechanism of different hydrophobic particles, oils and oil/particle mixtures dispersed in an aqueous phase.

2.3.1 Hydrophobic Particles as Antifoams

2.3.1.1 Spherical Particles

It has been described in many publications that some solid particles behave as antifoams in various systems, such as those (silica particles) in improving the recovery of minerals by froth flotation [36] or those used in some personal and home care products [37]. Mokrushin [38] first suggested that metal sulfide particles with a characteristic of low wettability can cause defoaming effects in froths of gelatin solutions. Based on this, Livshitz and Dudenkov [39, 40] made further studies of the defoaming behaviour of solid particles. They found in their froth stability measurements, that the defoaming behaviour of particles can be observed only when they adopt a contact angle $\theta_{AW} > 90^0$ at the air-water interface measured through the aqueous phase and they suggested that foam rupture may occur if such particles bridge foam films.

Following experimental and theoretical studies [41-46] the behaviour of hydrophobic particles in foam film rupture is now generally accepted as a “bridging-dewetting” process. According to this explanation, the antifoam efficiency is mainly determined by the hydrophobic characteristics of particles, or in other words the air-water contact angle $\theta_{AW}$. The “bridging-dewetting” effect of a spherical or cylindrical particle in a foam film can occur when the contact angle $\theta_{AW} > 90^0$ [41, 42, 47, 48]. In this process, the hydrophobic particle first inserts into a foam film and a bridge spontaneously forms. The capillary force in the film will then tend to enhance the drainage of water out of the foam film. Finally, the air-water-air film ruptures when the particle is completely dewetted. This process of foam...
film rupture, in the case of a spherical particle is shown in Fig.2.9.

![Diagram of film rupture](image)

**Fig.2.9.** A scheme of “bridging-dewetting” by spherical particle antifoams with a contact angle $\theta_{AW} > 90^\circ$ measured through the aqueous phase.

An example of the correlation between the contact angle and antifoam behaviour of particles with smooth curved surfaces, such as cylindrical rods is given by Aveyard *et al.* [45] in a single vertical film stability experiment. They found the film ruptured rapidly only when penetrated by rod particles with an air-water contact angle $\theta_{AW} > 90^\circ$, as shown in Fig.2.10, where a plot of the percentage of films ruptured within the first 30 seconds of penetration against the contact angle in cetyl trimethylammonium bromide (CTAB) solutions is shown.
Fig.2.10. Percentage of thin films (drawn from 0.2 mM CTAB at 20 °C) ruptured during the first 30 seconds after introduction of octadecyltrichlorosilane-coated cylindrical rods with different contact angles.

If an air-water contact angle $\theta_{AW} < 90^\circ$ is adopted by a smooth spherical or cylindrical particle, no foam film rupture will occur. On the contrary, a bridging effect will stabilise a foam film, as illustrated in Fig.2.11. In addition to stabilization by inhibiting drainage, they may even further stabilise the foam films, because the particles if present as a close packed layer can create a steric barrier to coalescence [49, 50]. Solid particles as foam stabilizers are also used in many industries, such as foods and mining [51].
2.3.1.2 Smooth Particles with Edges

The defoaming effect is not only determined by the hydrophobicity of particles, but also by the geometry of particles. Theoretical and experimental studies about the effect of shape, roughness, size and contact angle of particulates on the antifoam behaviour have been made by Garrett [41] and Dippenaar [47, 48]. It has been found that the necessary condition that air-water contact angle $\theta_{AW} > 90^0$ for foam film rupture is violated for particles with edges, such as for example crystals, so that film rupture is then possible even if $\theta_{AW} < 90^0$.

Garrett modeled a disk-shaped polytetrafluoroethylene (PTFE) particle antifoam with different aspect ratios. This model suggested that the particle with a large aspect ratio can cause the rupture of films even if its contact angle is lower than $90^0$, seen in Fig.2.12 [41].

---

**Fig.2.11.** A scheme of stabilizing effect due to the capillary force by spherical particles with a contact angle $\theta_{AW} < 90^0$ measured through the aqueous phase.
This argument was simply based upon calculation of the Helmholtz free energy accompanying dewetting and therefore suffered from the flaw that viscous dissipation was neglected.

Fig. 2.12. Foam film ruptures by a disk-shaped particle; (a) partially inserted in foam film; (b) fully submerged in foam film.

Dippenaar [52] studied the effect of galena crystals of a cubic habit (with a smooth face bound by sharp rectangular edges) with an air-water contact angle \( \theta_{AW} \) of 80\(^\circ\)±8\(^\circ\) on rupturing a foam film. This cubic particle could adopt two different orientations with roughly equal probability when it was dropped into a horizontal air-water interface, as shown in Fig. 2.13 (a) and (b).

Fig. 2.13. An entry configuration of cubic particle at air-water interface in the condition of (a) \( 0^\circ < \theta_{AW} < 90^\circ \); (b) \( 45^\circ < \theta_{AW} < 135^\circ \).

Dippenaar [52] observed, by using a high-speed cinematography, that when this cubic particle entered the air-water interface adopting the configuration in Fig. 2.13 (a), the foam
films would tend to be stable, as shown in Fig. 2.14 (a). By contrast, if the particles adopted an orientation as shown in Fig. 2.13 (b), they would cause rapid foam film rupture after bridging (taking around 20 ms) by the process shown in Fig. 2.14 (b).

![Diagram of foam film behaviour](image)

**Fig. 2.14.** Behaviour of a cubic particle at air-water interface; (a) Foam film stabilised, $0^\circ < \theta_{AW} < 90^\circ$; (b) Foam film ruptured, $45^\circ < \theta_{AW} < 135^\circ$.

Garrett [17] summarized the defoaming mechanism of smooth particles with various edges based on the work by Dippenaar [47, 48]. A hypothetical crystalline particle which has a hexagonal cross-section and an edge angle $\theta_p$, was considered and is shown in Fig. 2.15, where the length $Z \gg X$.

![Hypothetical particle](image)

**Fig. 2.15.** Hypothetical particle with straight edges.
If this particle is energetically favored to sit at the air-water interface, there are six different entry possibilities with $\theta_{AW} > 0^\circ$. Three examples are shown in Fig.2.16. One is when $\theta_{AW} < \theta_p$, where the particle bridging the foam film produces a capillary pressure resisting drainage without breaking it, shown in Fig.2.16 (a), which is analogous to the condition shown in Fig.2.14 (a). Another is when $\theta_p < \theta_{AW} < 180^\circ - \theta_p$ (analogous to the condition described in Fig.2.14 (b)), this particle will rupture the film due to dewetting even when $\theta_{AW} < 90^\circ$, shown in Fig.2.16 (b). If $180^\circ - \theta_p < \theta_{AW} < 180^\circ$, the film rupture will only occur when the critical thickness for the spontaneous rupture of the liquid film on the solid is greater than that of liquid film alone, shown in Fig.2.16 (c).

**Fig.2.16.** Entry behaviour of particles with edges in a foam film. (a) $0 < \theta_{AW} < \theta_p$; (b) $\theta_p < \theta_{AW} < 180^\circ - \theta_p$; (c) $180^\circ - \theta_p < \theta_{AW} < 180^\circ$ [17]

The condition for particles with sharp edges for rupture of a foam film: $\theta_p < \theta_{AW} < 180^\circ - \theta_p$ means only relatively low air-water contact angles are required, which depend on $\theta_p$. 

---

**Diagram Description:**

- **Stabilising:**
  - $\theta_{AW} < \theta_p$
  - $\theta_{AW}$ is the air-water contact angle.
  - $\theta_p$ is the particle's contact angle with the solid.

- **Rupturing:**
  - $\theta_p < \theta_{AW} < 180^\circ - \theta_p$
  - $\theta_{AW}$ is the air-water contact angle.
  - $\theta_p$ is the particle's contact angle with the solid.
  - $180^\circ - \theta_p < \theta_{AW} < 180^\circ$
  - $\theta_p$ is the particle's contact angle with the solid.

---

**Notes:**

- $\theta_{AW}$ is the air-water contact angle.
- $\theta_p$ is the particle's contact angle with the solid.
- The condition for particles with sharp edges for rupture of a foam film is $\theta_p < \theta_{AW} < 180^\circ - \theta_p$. This means only relatively low air-water contact angles are required, which depend on $\theta_p$. 

---

**Figures:**

- **Fig.2.16:** Entry behaviour of particles with edges in a foam film. (a) $0 < \theta_{AW} < \theta_p$; (b) $\theta_p < \theta_{AW} < 180^\circ - \theta_p$; (c) $180^\circ - \theta_p < \theta_{AW} < 180^\circ$ [17]
rather than that required for smooth spherical particles ($\theta_{AW} > 90^\circ$). Particles with sharp edges are therefore expected to be more effective than spheres or cylinders as antifoams for the same surfactant solutions. Frye and Berg [42] showed for example that sharp-edged particles alone (ground glass) consistently caused more foam breakage when compared with that caused by spherical particles (glass spheres) in surfactant solutions with the same contact angles, as shown in Fig. 2.17.

\[\text{Foam removal (vol %)}\]

![Graph showing foam removal as a function of receding contact angle](image)

**Fig. 2.17.** Antifoam effect of hydrophobed glass particles as a function of receding contact angle; Ground glass, ■ sodium dodecyl benzene sulphonate, ● nonionic octylphenol decaethylene glycol ether (Triton X-100), ♦ hexadecyltrimethyl ammonium bromide; Spherical glass particles, □ sodium dodecyl benzene sulphonate, ○ Triton X -100, ◊ hexadecyltrimethyl ammonium bromide [42].

### 2.3.2 Hydrophobic Oils as Antifoams

Hydrophobic oil-based antifoams are usually present in the aqueous phase as undissolved droplets. The defoaming behaviour of such antifoams is believed to be mainly related to the formation of bridging configurations in foam films by oil lenses [53, 54]. To form such a bridging configuration, the oil antifoams are required to enter into the air-water interface.
first, meaning the initial entry coefficient \( E^i \) must be positive:

\[
E^i = \gamma_{AW}^i + \gamma_{OW}^i - \gamma_{AO}^i
\]  

(2.17)

where \( \gamma_{AW}^i \) is the initial air-water surface tension, \( \gamma_{OW}^i \) is the initial oil-water interfacial tension, and \( \gamma_{AO}^i \) is the initial air-oil interfacial tension. These initial entry coefficients and surface tensions refer to the non-equilibrated systems where oil and surfactant solution are not mutually saturated. We should note here however that, emergence into the air-water interface requires rupture of the pseudoemulsion oil-water-air film. The role of particles in oil-particle synergistic antifoams is rupture of such pseudoemulsion films, and is discussed below in section 2.3.3.

If equilibration between the oil and foaming solutions is achieved, a “semi-initial” entry coefficient \( E^{si} \) can be written as:

\[
E^{si} = \gamma_{AW}^i + \gamma_{OW}^e - \gamma_{AO}^e
\]  

(2.18)

where \( \gamma_{OW}^e \) is the equilibrium oil-water interfacial tension, and \( \gamma_{AO}^e \) is the equilibrium air-oil interfacial tension. When the air-water surface is also equilibrated with respect to the antifoam oil, a final equilibrium entry coefficient is written as:

\[
E^e = \gamma_{AW}^e + \gamma_{OW}^e - \gamma_{AO}^e
\]  

(2.19)

where \( \gamma_{AW}^e \) is the equilibrium air-water surface tension and where we must have \( 0 \leq E^e \leq 2\gamma_{OW}^e \) [55, 56].

Oil droplets will spread at the air-water surface after emergence to form duplex films, if the spreading coefficient \( S^i > 0 \), where:
here a semi-initial spreading coefficient $S^{si}$ and a final equilibrium spreading coefficient $S^e$ analogous to the entry coefficients can also be written. We note however, that at equilibrium, we must have $S^e \leq 0$ [56], where $S^e = 0$ means a continuous duplex oil film and $S^e < 0$ means an either oil lens in equilibrium with a thin oil-contaminated layer or an oil-free surface.

Ewers and Sutherland [57] have suggested that an antifoam oil droplet must enter the air-water surface of the foam film, so that $E^i > 0$, but also that $S^i > 0$. A Marangoni flow driven by the surface tension gradient between the centre and edge of the spreading droplet is then expected to be generated. This flow means that the underlying liquid is forced out of the foam film, resulting in catastrophic thinning until the film ruptures, as shown in Fig.2.18. The shear force is equal to the gradient in the initial spreading coefficient ($dS^i / dy$), and we can write:

$$\frac{dS^i}{dy} = \eta \frac{du_y}{dx}$$

(2.21)

where $y$ is the spreading distance. The greater this spreading coefficient, the higher the dragging force will be and the greater the supposed efficiency of the antifoam oil.
It has been shown by Garrett et al. [58] that mixed liquid paraffin/hydrophobed silica antifoams showed significant antifoam effectiveness in sodium alkyl benzene sulphonate solutions under both equilibrium and non-equilibrium conditions. This antifoam did not spread at the air-water surface (so \( S' \), \( S'' \) and \( S^c \) < 0). It was concluded that a positive spreading coefficient is not a necessary condition for an oil droplet to behave as an antifoam. Therefore, foam films may still be ruptured by an oil droplet when \( E^i > 0 \) and \( S^i < 0 \).

When oil droplets enter the air-water surface (\( E^i > 0 \)) without spreading (\( S^i \), \( S'' \), \( S^c < 0 \), or \( S^c < 0 \), \( S', \) \( S'' > 0 \)), a lens forms where Neumann’s triangle is satisfied, as shown in Fig.2.19 (a). If such a lens bridges a foam film, the bridge may form a configuration like
that shown in Fig. 2.19 (b). This configuration has been shown to be unstable if the angle \( \theta^* > 90^\circ \) [53, 59]. The angle \( \theta^* \) is determined by Neumann’s triangle. It can therefore be deduced that if \( \theta^* > 90^\circ \), the so-called bridging coefficient \( B \) is greater than zero. That coefficient is defined by Garrett [53] as:

\[
B = \gamma_{AW}^2 + \gamma_{OW}^2 - \gamma_{AO}^2
\]  

where \( 0 \leq B \leq 2\gamma_{OW} \gamma_{AO} \).

\[\text{(2.22)}\]

Fig. 2.19. (a) A scheme of an oil lens in the air-water surface; (b) case of bridging drop where stability cannot be achieved because the capillary pressure drop across the oil-air surface \( \Delta P_{OA} \) is not equal to that across the oil-water surface \( \Delta P_{OW} \) if \( \theta^* > 90^\circ \) [17, 60]

If \( B \geq 0 \), then the bridging oil droplet is unstable because the capillary pressure of droplet across oil-water surface \( \Delta P_{OW} \) cannot equal that across the air-oil surface \( \Delta P_{OA} \) in the case of a plane-parallel foam film. Denkov [59] has shown that this condition of instability
should be slightly modified if the latter condition is relaxed. Since $\gamma_{AW} \gg \gamma_{OW}$, then the condition $B \geq 0$ can usually be satisfied if $\gamma_{AW} \gg \gamma_{AO}$.

If the angle $\theta^* \to 180^0$, a “bridging-stretching” effect will occur as shown by Denkov et al. [54]. These workers studied the rupture of a foam film by a bridging drop using a high speed camera (the same method as used in Dippenaar’s experiment [47]), as described in Fig. 2.20 [54, 60].

![Fig. 2.20](image)

**Fig. 2.20.** A scheme of “bridging-stretching” behaviour of oil antifoams; (a) photographs taken in experiment; (b) a schematic illustration of the process [60].

The sample was a polydimethysiloxane oil in Sodium dioctylsulfosuccinate (AOT) solutions. An oil droplet rapidly forms a bridge by penetrating into the film lamellae once it emerges into the air-water interface. This oil bridge is spontaneously stretched until a thin
oil film is formed in the center of the bridge, which breaks when it is sufficiently thin due to attractive van der Waals interactions, directly causing film rupture, seen in Fig. 2.20 (b).

If however, $B = 2\gamma_{ow} \gamma_{oa}$, then a duplex film will exist, which again will mean an unbalanced forces should a bridge form between two such films on either side of the foam film. Again we would expect a similar mechanism of foam film collapse to that shown in Fig. 2.20.

**Fig. 2.21.** A scheme of oil antifoam behaviour after entering into the air-water surface; (a to d) mechanism of “bridging-dewetting”; (a to f) stable bridge with no film rupture [6].

Another possible behaviour of bridging oil droplets concerns a dewetting effect. This is analogous to the foam film rupture effect caused by particle antifoams [17, 60]. This process is different from the “bridging-stretching” as the oil bridge when formed dewetted...
by the liquid phase and not physically stretched, as shown in Fig. 2.21 from a to d [60]. On the other hand if $B < 0$, and therefore $\theta^* < 90^0$, foam films will be stabilized after the entry of oil droplets, as shown Fig. 2.21 (a to f). The oil bridge can therefore rupture the foam film only when $B > 0$, as explained above.

### 2.3.3 Mixtures of Hydrophobic Particles and Oils as Antifoams

Hydrophobic solid particles and oils exhibit synergistic antifoam behaviour [17]. These mixtures show more effective antifoam action than either particles or oil droplets, which are often only weakly effective when used alone. The main reason is because solid particles sit in the oil-water interface and promote emergence of oils into the air-water foam films by rupturing the air-water-oil pseudoemulsion films. The oils can then participate in a bridging effect as described section 2.2.2 [53, 59-61].

Garrett et al. [58] for example, showed that addition of hydrophobed silica particles to liquid paraffin enhanced the antifoam efficiency significantly in the case where foams were generated by cylinder shaking a solution of sodium alkyl benzenesulphonate (SABS). Results are shown in Fig. 2.22 (a), where $F = \frac{\text{Volume of air in foam in the presence of antifoam}}{\text{Volume of air in foam in the absence of antifoam}}$. The lower the $F$ value, the higher the antifoam efficiency. Hydrophobed silica particles adhere to the oil–surfactant solution interface (as shown in Fig. 2.22 (b)) [58].
Fig. 2.22. (a) $F$ profile of a dispersion of 1.2 g l$^{-1}$ liquid paraffin / hydrophobed silica particle mixed antifoam in 0.5 g l$^{-1}$ SABS solution as a function of antifoam composition; (b) Electron micrograph of liquid paraffin / hydrophobed silica particle droplets dispersed in 0.5 g l$^{-1}$ SABS solution by shaking. The scale bar represents 1.0 µm [58].

The role of hydrophobic particles in rupturing air-water-oil pseudoemulsion films was first established by Garrett et al. [17, 58, 62]. They measured the time of emergence of liquid paraffin droplets into the air-water surface in the absence and presence of hydrophobed silica particles, as shown in Fig. 2.23 using the same system as illustrated in Fig. 2.22. The presence of silica particles obviously reduced the time of oil droplet emergence, enhancing the antifoam efficiency.
Garrett [17] deduced the condition necessary for a spherical hydrophobic particle to rupture an air-water-oil pseudoemulsion film. In this case, the particle is preferably wetted by the oil so that it adopts a contact angle $\theta_{OW}$, satisfying the condition:

$$90^0 < \theta_{OW} < 180^0$$ \hspace{1cm} (2.23)

measured through the aqueous phase. Particles meeting this contact angle condition can also cause an inversion of oil-in-water emulsion to water-in-oil emulsion [17].

If the particles are to rupture pseudoemulsion films, they must also adhere to the air-water surface, so that

$$\theta_{AW} > 180^0 - \theta_{OW}$$ \hspace{1cm} (2.24)
Fig. 2.24. An antifoam mixture scheme of special particles in oils

where $\theta_{AW}$ is the air-water contact angle measured through aqueous phase. The angle $\theta_{AW}$ therefore does not need to be greater than $90^\circ$ to rupture the air-water-oil pseudoemulsion film. This means that these spherical particles alone will not act as antifoams because then $\theta_{AW}$ must be greater than $90^\circ$. The rupture of air-water-oil pseudoemulsion film by spherical particles is illustrated in Fig. 2.25. Other factors effecting the efficiency of the process of rupture of the pseudoemulsion films by particles [17, 63] include the effect of particle geometry [43, 45], and spread oil layers [64]. We return to the effect of particle geometry, particularly of crystalline particles in Chapter 7.

A film trapping technique (FTT) has been developed recently by Hadjiiski et al. [64-68] to study the magnitude of the entry barrier of antifoam oil droplets into air-water surfaces. This technique is described in section 3.3.8. It permits measurement of the applied capillary ($P_{cCR}$) necessary to rupture a pseudoemulsion film.
Fig. 2.25. Rupture of air-water-oil film by a spherical particle with $\theta_{AW} > 180^0 - \theta_{OW}$, where $\theta_{AW}$ and $\theta_{OW}$ are measure through aqueous phase.

Values of the critical capillary pressure ($P_{c}^{CR}$) can be directly related to the antifoam efficiency [64]. Table 2.1 shows that the presence of silica particles in silicone oil drops causes a significant decrease in $P_{c}^{CR}$ for both solutions of Sodium dioctysulfosuccinate (AOT) and octylphenol decaethylene glycol ether (Triton X-100). The results given in Table 2.1 show that presence of spread oil layers, also facilitates the emergence into the air-surfactant solution interface of oil droplets. The observation that particles facilitate rupture of air-water-oil pseudoemulsion films is consistent with the observations of Garrett et al. [17, 58, 62], Wasan et al. [69, 70], and Bergeron et al. [61]. That the presence of a spread oil layer can further reduce the entry barriers, enhancing the antifoam efficiency has been attributed by Denkov et al. [64] to accompanying changes in the wetting conditions experienced by particles at the air-water surface.
Table 2.1. Critical capillary pressure $P_{c}^{CR}$ for entry of silicone oil droplets into air-water surfaces of 10 mM AOT and 1 mM and Triton X-100 solutions in the presence and absence of hydrophobed silica particles (also in the presence and absence of spread layer of silicone oil) [64].

<table>
<thead>
<tr>
<th>Antifoam</th>
<th>Spread layer</th>
<th>$P_{c}^{CR}$, Pa</th>
</tr>
</thead>
<tbody>
<tr>
<td>Silicone oil</td>
<td>No</td>
<td>28 ± 1</td>
</tr>
<tr>
<td></td>
<td>Yes</td>
<td>19 ± 2</td>
</tr>
<tr>
<td>Silicone oil / hydrophobed</td>
<td>No</td>
<td>20 ± 5</td>
</tr>
<tr>
<td>silica</td>
<td>Yes</td>
<td>4 ± 1</td>
</tr>
</tbody>
</table>

It is believed that the sebum soil present in washing processes is also an oil-particle synergistic antifoam [71, 72]. This soil contains fatty acids which may form calcium soaps due to a reaction between $\text{Ca}^{2+}$ ions present in wash water at the prevailing high pH derived from the presence of $\text{Na}_2\text{CO}_3$ buffer in detergent formulations. The soil also contains triglycerides. Zhang et al. [34, 35] showed that there is a synergistic antifoam effect between a triglyceride oil (triolein) and calcium soap particles, once the later are formed at pH 9, and in the presence of $\text{Ca}^{2+}$. Results for an antifoam mixture of triolein/oleic acid are present in Fig. 2.26. The foam height decreased significantly once calcium soap formed (Fig. 2.26 (a)). These soap particles formed at the triolein-water surface as revealed by optical microscopy and shown in Fig. 2.26 (b).
Fig. 2.26. (a) Foam stability profile of 0.01 wt% C\textsubscript{12}-C\textsubscript{15} EO\textsubscript{3} sulphate with triolein/oleic acid mixture, ♦ in the absence of Ca\textsuperscript{2+}, ■ in the presence of Ca\textsuperscript{2+} at pH 9; (b) An image taken after around 5 minutes of a drop of triolein and oleic acid reacted with 300ppm hardness at 0.01 wt% N25-3S at pH = 9; Droplet diameter 160 µm [34].

2.4 Deactivation of Antifoams

In a continuous foam generation experiment, the effectiveness of oil/hydrophobic particle antifoam may deactivate gradually (so called deactivation). This behaviour has been described in several studies [58, 61, 73, 74], especially for silicone/silica mixed antifoams.

Pouchelon and Araud [73] studied the deactivation of silicone oil/silica particle mixtures in AOT solutions using a mechanical shake test with up to 60000 shake cycles. Inactive large white agglomerates of a size up to several millimetres were found to form after continuous
shaking. These agglomerates contained a much higher level of silica particles than that of the original antifoam droplets. Koczo et al. [70] and Racz et al. [75] also observed deactivation of silicone oil / silica particle antifoams. Koczo et al. [70] attributed the effect to reduction of droplet sizes which meant that the droplets would not accumulate in Plateau borders where the antifoam action was supposed to occur. Racz et al. [75] on the other hand attributed the deactivation to emulsification of the spreading antifoam. Neither of these hypotheses seems to be supported by later careful work of Denkov and co-workers [68, 74] concerning antifoam deactivation.

Using an automated shake test, Marinova et al. [68] showed for example that the defoaming efficiency of a PDMS / hydrophobed silica particle mixed antifoam in sodium dioctyl sulfosuccinate (AOT) solution continuously decreases. In this experiment, foam was generated in cycles, each of which consists of shaking for a fixed period, followed a quiescent period. After each cycle the time taken for the foam to collapse is measured. Results are shown in Fig.2.27.

![Image](image.png)

**Fig.2.27.** Deactivation of poly-dimethylsiloxane oil / silica particle antifoam (10 μl) in AOT solution (10 mM) in an automated shake test measurement [74].

Marinova and Denkov et al. [68, 74] have shown that the deactivation is accompanied by an increase in the critical capillary pressure $P_{c}^{CR}$ for entry into the air-water surface. Results are shown in Table 2.2. Observed changes of the antifoam properties include: a
decrease of the number of deformable drops with a slight change in the size distribution; formation of large non-deformable silica-rich agglomerates, shown in Fig. 2.28; and disappearance of the oil layer at the air-water surface.

Table 2.2. Entry barrier measurement and change of properties of PDMS / hydrophobic silica antifoam drops in AOT solution by a continuous automated shaking measurement [68].

<table>
<thead>
<tr>
<th>Number of shaking cycles</th>
<th>Deformable droplets / %</th>
<th>Diameter of deformable droplets / μm</th>
<th>Critical entry pressure $P_{c}^{CR}$ / Pa</th>
<th>Large agglomerates / %</th>
<th>Large agglomerates size / μm</th>
<th>Thickness of spread oil layer / nm</th>
</tr>
</thead>
<tbody>
<tr>
<td>3</td>
<td>100</td>
<td>6 - 24</td>
<td>3 ± 2</td>
<td>0</td>
<td>-</td>
<td>250</td>
</tr>
<tr>
<td>30</td>
<td>100</td>
<td>7 - 25</td>
<td>4 ± 2</td>
<td>0</td>
<td>-</td>
<td>11</td>
</tr>
<tr>
<td>70</td>
<td>45</td>
<td>6 - 25</td>
<td>9 ± 1</td>
<td>55</td>
<td>6 - 26</td>
<td>8</td>
</tr>
<tr>
<td>95</td>
<td>26</td>
<td>5 - 12</td>
<td>7 ± 2</td>
<td>74</td>
<td>4 - 50</td>
<td>2</td>
</tr>
<tr>
<td>300</td>
<td>26</td>
<td>3 – 7</td>
<td>18 ± 2</td>
<td>74</td>
<td>5 – 100</td>
<td>&lt; 0.5</td>
</tr>
</tbody>
</table>

Fig. 2.28. Formation of large silica-rich agglomerates after 95 shaking cycles of 0.01% PDMS / hydrophobic silica antifoams in 10 mM AOT solution [68].
They concluded, based on the above results, that this antifoam deactivation behaviour is mainly correlated with: 1) formation of silica-enriched and silica-free droplets after a disproportionation by splitting/coalescence during the shaking process; and 2) disappearance of the spread oil layer at the air-water surface, which adversely alters the emergence of oil droplets.

Fig.2.29. A scheme of the process of silicone oil-silica particle antifoam exhaustion and reactivation of emulsion [74].

The whole process is summarized in Fig.2.31 [74]. When a fresh antifoam sample is emulsified, a layer of PDMS oil is formed at the air-water surface (Fig.2.29(a)), the presence of which, as shown in Table 2.1, facilitates emergence of silicone drops into the air-water surface. During deactivation, droplets gradually segregate into two inactive groups: silica-rich and silica-free ones (Fig.2.29(b)). This is accompanied by a disappearance of the spread oil layer due to the inability of particle-free drops to emerge and also to reduced rates of supply of oil by spreading from particle-rich droplets and
agglomerates. As observed by Pouchelon and Araud [73], the silica-rich agglomerates were of millimetre size as shown in Fig.2.29 (e). Addition of more PDMS oil results in a restoration of the spread oil, redistribution of silica, and reactivation of the antifoams.

Besides this polydimethylsiloxane/silica antifoam, the deactivation behaviour of hexadecane/silica antifoam has also been observed by Wicks [76]. Results are shown in Fig.2.30 where no spread oil layers form at the air-water surface. Antifoam deactivation is probably similar to that of PDMS/silica particle antifoam in that separation into particle-free droplets and large silica-rich agglomerates occurs, but without any role for spread layer because the latter is absent in this system.

![Graph](image)

**Fig.2.30.** $F$ versus number of cylinder shaking test plots for 2 g dm$^{-3}$ hydrophobed silica/hexadecane antifoam in 3×10$^{-2}$ M Triton X-100, NaCl 1.55×10$^{-3}$ M at 25±2 °C; ♦ without shaking ($t = 0$ seconds) before measurement, ■ after shaking for $t = 600$ seconds [76].
2.5 Summary

Here we have been concerned with the relevance of the existing of knowledge of the foam behaviour of aqueous surfactant solutions both in the absence and presence of antifoam to foam generation in a practical high foam washing context. In that context, surfactant concentration may be markedly reduced in the absence of chelating agent by the effect of metal ions, such as Ca\(^{2+}\) and Mg\(^{2+}\). Precipitation of surfactant will lower the effective rates of transport to air-water surfaces both because the precipitated particles are expected to be relatively large with low diffusion coefficients and because of low rates of breakdown to form molecularly dispersed surfactant. Such particles may also potentially function as antifoams. We will establish the extent to which these effects are present in the case of sodium alkyl benzene sulphonate solutions, arguably the most commonly used surfactant in laundry detergent formulations.

Sebum body soil is a mixture containing different fatty acids, triglycerides, cholesterol and hydrocarbons. It is a highly viscous turbid liquid where the turbidity implies the presence of solid particulate materials. The defoaming effect of sebum soil in detergent solutions may therefore be caused by oil-particle synergy. The effect of a triolein/oleic acid mixture as an antifoam in alkaline solutions has been reported by Zhang et al. [34]. This model however is not representative enough to simulate the antifoam behaviour of sebum soil, because unlike the soil, it is a clear liquid – particles are only present as a result of reaction of the fatty acids with Ca\(^{2+}\) in a wash liquor. We must therefore establish not only the role of the reaction of the fatty acid components in sebum with Ca\(^{2+}\) but also the role of the particulate material intrinsic to the composition of sebum. In order to simplify the problem of establishing the mode of action of sebum, we will attempt to reproduce its behaviour using model compositions of greater simplicity – ideally consisting of a triglyceride oil containing particles of a single compound which is sparingly soluble in the oil. Understanding the antifoam effect of such a model antifoam will require in turn a detailed study of hydrophobicity (by measuring the contact angles) and geometry (by measuring the crystalline structure) of the relevant particles present in the oil. The study should extend to
measurement of the entry, spreading and bridging behaviour of the relevant oil phases; and effect of these particles in rupturing the air-water-oil pseudoemulsion film.

Deactivation of the antifoam effect of sebum soil during continuous washing or scrubbing could occur in much the same manner as found with silicone/silica antifoam mixtures. We will seek to establish the extent to which this happens and whether, if so, it functions by essentially the same deactivation mechanism as silica/silicone antifoam.

2.6 References

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Chapter 3 Materials and Methods

3.1 Introduction

This chapter includes two subsequent sections. The first describes the materials and their sources which are based on the current detergent formulations, as shown in Table 1.1. An electrolyte system is utilized to explore the effect of pH and Ca\textsuperscript{2+} on the foam behaviour of surfactant solutions (2.0×10\textsuperscript{-3} M in total) in the absence and presence of antifoams:

- NaCl (1.7×10\textsuperscript{-2} M) + CaCl\textsubscript{2} with pH adjustment using NaOH and HCl

Although Na\textsubscript{2}SO\textsubscript{4} is used as filler in laundry powder products it has been excluded in order to avoid precipitation of CaSO\textsubscript{4} (Ca\textsuperscript{2+} + Na\textsubscript{2}SO\textsubscript{4}) which may complicate the system unnecessarily - particularly in determination of the Ca\textsuperscript{2+}-Surfactant phase diagram. Sodium chloride (NaCl) at the same ionic strength as found in typical wash situations has been used as a substitute (i.e. 1.7×10\textsuperscript{-2} M NaCl was used to replace 5.69×10\textsuperscript{-3} M Na\textsubscript{2}SO\textsubscript{4}). The final part of this chapter discusses the experimental techniques used throughout the whole project.

3.2 Materials

3.2.1 Surfactants

The commercial Sodium Linear Alkyl Benzene Sulphonate paste from P&G is named as “NaLAS” in this thesis. It has been used in the foaming experiments to study the defoaming effect of different antifoams, including sebum soil and other pure antifoam models and their deactivation behaviour. The anionic surfactant content of this NaLAS is 84.1% by weight with a specified chain length and phenyl isomer distribution, shown in
Table 3.1. Impurities in the surfactant pastes are 15.13% water, 0.75% \( \text{Na}_2\text{SO}_4 \) and \( \text{Na}_2\text{CO}_3 \) with equal alkalinity as 0.02% NaOH by weight.

Table 3.1 Chain length and phenyl isomer distribution of commercial NaLAS sample from P&G

<table>
<thead>
<tr>
<th>Alkyl chain length</th>
<th>( \geq 6 ) phenyl (mol%)</th>
<th>5 Phenyl (mol%)</th>
<th>4 Phenyl (mol%)</th>
<th>3 Phenyl (mol%)</th>
<th>2 Phenyl (mol%)</th>
<th>Total (mol%)</th>
</tr>
</thead>
<tbody>
<tr>
<td>&lt; C10</td>
<td>0.000</td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>C10</td>
<td>---</td>
<td>3.025</td>
<td>2.308</td>
<td>2.178</td>
<td>2.472</td>
<td>9.983</td>
</tr>
<tr>
<td>C12</td>
<td>8.377</td>
<td>7.968</td>
<td>5.991</td>
<td>6.260</td>
<td>5.996</td>
<td>34.592</td>
</tr>
<tr>
<td>&gt; C13</td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td>0.000</td>
</tr>
<tr>
<td>Total (%)</td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td>100.00</td>
</tr>
</tbody>
</table>

A pure sample of sodium dodecyl 4-phenyl sulphonate (\( \text{C}_{12} \) 4-phenyl \( \text{SO}_3\text{Na} \)) was also supplied by P&G, with a purity of 99.0% by weight. The molecular structure of \( \text{C}_{12} \) 4-phenyl \( \text{SO}_3\text{Na} \) is shown in Fig. 3.1. Sodium Dodecyl Sulfate (SDS) at a purity of 99.0% was purchased from Sigma-Aldrich UK and used as received.

![Molecular structure of \( \text{C}_{12} \) 4-phenyl \( \text{SO}_3\text{Na} \)](image)

Fig. 3.1 A molecular structure of \( \text{C}_{12} \) 4-phenyl \( \text{SO}_3\text{Na} \)

3.2.2 Electrolytes and Water

Sodium chloride (NaCl), at a minimum purity of at least 99.5% for maintaining the ionic
strength in solution, and calcium chloride dihydrate (CaCl₂.2H₂O), at a purity of at least 99%, for adjusting the hardness levels were obtained from Sigma-Aldrich UK. Sodium hydroxide (NaOH) at a purity of 97% and hydrochloric acid (HCl) with an activity of 37% were also purchased from Sigma-Aldrich. They were diluted to 1.0 M concentrated solutions for pH value adjustment in each experiment. Doubly distilled de-ionised water was used throughout.

3.2.3 Antifoams

Sebum soil antifoam, a mixture of triglycerides, fatty acids and hydrocarbons, is supplied by P&G. The recipe of P&G for preparation of this sebum soil is given in Appendix 3.1. The composition, inferred from the usual composition of the constituent ingredients such as coconut oil etc., is given in Appendix 3.2. All the other ingredients used in pure antifoam models are purchased from Sigma-Aldrich UK, including the triglycerides: triolein (glyceryl trioleate) with a purity of ≥ 99.0% and tristearin (glyceryl tristearate), ≥ 99.0%; the fatty acids: oleic acid, ≥ 99.0% and stearic acid, ≥ 99.0%; the hydrocarbons: squalene, ≥ 98.0% and hexadecane, ≥ 99.0%; and cholesterol, ≥ 99.0%.

3.2.4 Cleaning of Glassware

All the glassware was cleaned before use to ensure there was no surface active contaminant. A cleaning procedure was followed by first soaking the vessels in Decon 90 solution (an emulsion of anionic and non-ionic surface active agents, stabilizing agents, non-phosphate detergent builders, alkalis and sequestering agents, in an aqueous base, supplied by Decon Laboratories Ltd., UK) for at least 12 hours, then rinsing by using doubly distilled de-ionised water. After that, the vessels were soaked in APS solutions (2 wt% solution of ammonium persulphate in 97.5% sulphuric acid) for 1 hour, then rinsed under distilled de-ionized water again for several minutes, and dried in air before using.
3.3 Experimental Techniques

This section describes the preparation of antifoams and surfactant solutions, the measurement of Ca$^{2+}$-surfactant phase diagram and the techniques used for the measurement of: air-water surface tensions at equilibrium and dynamic conditions; oil-water interfacial tensions; contact angles of antifoam particles at air-water and oil-water interfaces; foamability and foam stability of surfactant solutions; size distribution of antifoam droplets in solution and that of crystalline particles in antifoam oils; crystal structure of antifoam particles; viscosities of oil/particle synergistic antifoams; vertical thin film draining behaviour in the presence and absence of antifoams and the entry behaviour of antifoams at air-water surfaces.

3.3.1 Foamability and Foam Stability Measurement

3.3.1.1 Tumbling Tube Method

The tumbling tube method is used in P&G for foamability measurement of detergent products. As shown in Fig.3.2, each tube is made of polymethyl methacrylate which has a total volume of 1875 cm$^3$. Foamability was measured as the volume of air entrained in the foam immediately after generation by rotating the 500 cm$^3$ mixed surfactant solutions at a frequency of 0.47 Hz for 10 rotations and at 25±1$^\circ$C. The foam stability was measured as the volume of air in foams after the tubes are allowed to stand for 10 minutes. This tumbling tube method was also used to measure the deactivation behaviour of antifoams using a continuous rotation mode. All the measurements were replicated twice. The error measured by this method is ± 62.5 cm$^3$. 

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3.3.1.2 Cylinder Shaking Method

In each measurement, 25 cm$^3$ of the mixed surfactant solutions were added in 100 cm$^3$ graduated cylinders which were standing in a thermostat water bath at 25 °C. The temperature of the solutions was then equilibrated to 25 °C after 5 minutes. The foamability was measured as the volume of air entrained in foam immediately by shaking the equilibrium solutions at a frequency about 3 Hz in cylinders for 10 seconds. The height of the cylinders is ~ 18 cm and the diameter is ~ 2.7 cm. Foam stability was measured as volume of air in the foam after the cylinders were allowed to stand for 10 minutes in the thermostat water bath at 25 °C. All the measurements were replicated twice. The error measured by this method is ± 1.5 cm$^3$.

3.3.1.3 Ross-Miles Method for Measuring Bubble Size Distribution

Neither tumbling tube nor cylinder shaking methodologies for foam generation are convenient for the measurement of bubble sizes. The well-known Ross-Miles method can however be readily modified to provide for images of foam, so that bubble size distribution
can be estimated. It is less convenient than cylinder shaking (especially with respect to the consumption of expensive pure antifoam materials). It also apparently involves less rapid generation of air-water surfaces than the cylinder shaking method (see for example Garrett et al. [1]).

A schematic of the Ross-Miles foam generation apparatus [2] used is shown in Fig.3.3. Foamability and foam stability measurement by this method requires two reservoirs. Equal volumes (200 ml) of surfactant solution were added to both the upper reservoir (Fig.3.3 (a)) and the lower reservoir (Fig.3.3 (b)). A capillary of 3 mm in diameter and 90 mm in length allowed the solution to flow from the upper reservoir, forming a jet which impinges upon the air-water surface of the lower reservoir to cause air entrainment and foam generation.

An optical prism (Fig. 3.3 (c)) with a standard scale disk was attached to the front surface of the lower reservoir by silicone oil (DC 200 from Sigma-Aldrich, UK) starting from the scale line of 400 ml in order to facilitate imaging of the foam. Images of bubbles in the plane of the front inner walls of this lower reservoir were made using a cool light source for illumination and a Canon EOS digital camera. The camera and light source were placed at 90° with respect to each other. Images were analyzed by suitable software (ImageJ software developed by National Institute of Health, US). However, correction for statistical sampling bias was not applied [3].
3.3.2 Preparation of Antifoams and Surfactant Solutions

3.3.2.1 Antifoam Preparation

Three types of oil/particle synergistic antifoams (twelve models in total) are prepared with the various oil components. They have been used in the foaming experiments at a room temperature of $25^\circ C$.

A. Hydrocarbon-based antifoams

1. Hexadecane (90% by weight, liquid at $25^\circ C$) + Stearic Acid (5% by weight, solid at 25
2. Squalene (90%, liquid) + Stearic Acid (5%, solid)

B. Triolein-based antifoams
3. Triolein (90%, liquid) + Oleic acid (5%, liquid)
4. Triolein (90%, liquid) + Stearic acid (5%, solid)
5. Triolein (90%, liquid) + Stearic acid (10%, solid)
6. Triolein (85%, liquid) + Stearic acid (15%, solid)
7. Triolein (90%, liquid) + Oleic acid (5%, liquid) + Stearic acid (5%, solid)
8. Triolein (90%, liquid) + Stearic Acid (5%, solid) + Cholesterol (5%, solid)
9. Triolein (90%, liquid) + Tristearin (5%, solid)
10. Triolein (90%, liquid) + Tristearin (5%, solid) + Stearic acid (5%, solid)

C. Triolein/Hydrocarbon/fatty acid antifoams
11. Triolein (60%, liquid) + Squalene (30%, liquid) + Stearic Acid (5%, solid)
12. Triolein (30%, liquid) + Squalene (60%, liquid) + Stearic Acid (5%, solid)

Antifoam model 3 is prepared by simply mixing the triolein and oleic acid according to the quantity ratio at 25 °C because both components are simple liquid. For other antifoams which contain stearic acid particles, before each test, they were freshly prepared by first mixing and heating at a constant temperature of around 70°C (melting point of stearic acid: 69.6°C) in a thermostatically-controlled water bath (GD 120, Grant Instrument Ltd.) until the solid particles were dissolved. Triolein/tristearin antifoams were heated to 55°C in order to completely dissolve the solid (melting point of tristearin is 55°C). In both cases, the liquid mixtures were quickly cooled and remixed in an iced ultrasonic water bath (from Guyson International Ltd.) at the temperature of 0°C for 5 minutes. Use of fast cooling and ultrasonics was intended to ensure reproducibility, homogenization and decrease of the size of stearic acid and tristearin crystalline particles in the oil phase. Decreasing the sizes of the particles was intended to increase the probability of insertion of solid particles into oil droplets after dispersal in solution. Before use, the sebum soil was prepared following the
same procedure (the sebum soil of composition given in Appendix 3.1 becomes completely liquid at 72^0C).

3.3.2.2 Antifoam Dispersion

(A). Antifoam Dispersion in NaLAS and C_{12} 4-phenyl SO_3Na solutions

Two different solutions were prepared for each foaming test: 250 ml solution X with double-concentrated NaLAS (or C_{12} 4-phenyl SO_3Na) at 4.0 \times 10^{-3} M in the presence of NaCl 1.7 \times 10^{-2} M adjusted at pH 7 and 250 ml solution Y with double-concentrated Ca^{2+} in 1.7 \times 10^{-2} M NaCl (after adjustment for the desired pHs: pH 3, 7 and 10.5 by addition of the appropriate amount of NaOH or HCl solutions). For foaming measurements in the presence of antifoam, double-concentrated antifoam (sebum soil for example) was dispersed in solution X with a high speed emulsifier (ULTRA – TURRAX T25 basic, IKA - WERKE) at a rotation frequency of 270 Hz for 1 min in a 500 ml beaker. This ensures that the soil antifoam is dispersed under exactly the same conditions and in the same solution for each experiment (because the reaction of Ca^{2+} with NaLAS and fatty acids could otherwise significantly change the dispersion state of antifoam which could cause variations in foam behaviour). Foam measurements were made on equal volume mixtures of solutions X and Y.

One disadvantage of this dispersion method is, in each foaming experiment, at least 0.5 g antifoams were required when they were added at 2 g l^{-1} into a double-concentrated 250 ml NaLAS solution. It would not be affordable for this project to use such high amounts of pure antifoam materials, if this dispersion method is strictly followed. Therefore, pure antifoams were generally only used in cylinder shaking foaming experiments. In this method antifoams were weighed on a microscope cover slip and added together at 2.0 g l^{-1} directly into 12.5 ml double-concentrated NaLAS solutions at pH 7, then dispersed in the ultrasonic water bath (from Guyson International Ltd.) at 25^0C for 5 minutes. After that, another half volume of solution (12.5 ml) at the adjusted pH levels (pH 10.5 and pH 3) in
the absence or presence of Ca\textsuperscript{2+} (double-concentrated) is mixed to reach the final desired compositions. Only 0.025 g of antifoam was used for each experiment which compares with 1 g for the method employing a high-speed emulsifier. Optical microscopy (see section 5.4.4) reveals that the two methods produced essentially the same droplet size of antifoam dispersal in solution. A consistent condition for the study of foam behaviour is therefore ensured.

Some agglomerates were found floating at the air-water interface in the case of antifoams containing fatty acid particles after dispersion by both methods. By contrast no agglomerates formed in the antifoam containing tristearin particles. Those agglomerates containing large fatty acid crystals (images by microscopy shown in section 5.5.2) were removed before each foaming experiment. Their removal was not expected to have a significant consequence for the overall defoaming profile because they were too large to be present in foam films, and could not therefore be expected to be effective as antifoams. However, their presence implies some deactivation of the antifoam as described by Pouchelon et al. [4] and Marinova et al. [5, 6]. The concentration of effective antifoam is in fact therefore reduced by the process of dispersion in the case of antifoams containing fatty acid particles.

(B). Antifoam Dispersion in C\textsubscript{12} 4-phenyl SO\textsubscript{3}Na / SDS solutions

Three different solutions were prepared for foaming tests at pH 3 and 10.5 under all the hardness conditions (Ca\textsuperscript{2+} from 0 to 40×10^{-4} M): 250 ml Solution I with double-concentrated C\textsubscript{12} 4-phenyl SO\textsubscript{3}Na (4.0×10^{-3} M) in 1.7×10^{-2} M NaCl; 250 ml Solution II with double-concentrated Ca\textsuperscript{2+} in 1.7×10^{-2} M NaCl (after adjustment for the desired pHs by HCl and NaOH) and 250 ml Solution III with double-concentrated SDS (4.0×10^{-3} M) in 1.7×10^{-2} M NaCl.

For measurement of foaming behaviour of C\textsubscript{12} 4-phenyl SO\textsubscript{3}Na/SDS mixed system, antifoams were first dispersed by ULTRA – TURRAX in Solution I at 2.5 gl\textsuperscript{-1}. Solution I
was then mixed with Solution III at a volume ratio of 4:1 to attain the binary surfactant Solution IV with 2.0 g\textsuperscript{-1} antifoam. This ensures that the antifoams are dispersed under exactly the same solutions for each experiment. Foam measurements were made on equal volume mixtures of Solutions IV and II for \(C_{12}4\text{-phenyl SO}_3\text{Na/SDS}\) system.

### 3.3.2.3 pH Adjustment

The level of HCl or NaOH needed to obtain the required pHs in the Ca\textsuperscript{2+} or surfactant solutions (originally at pH 7) was calculated first. Then twice this level was added into Ca\textsuperscript{2+} solution. Ca\textsuperscript{2+} solution was then mixed with surfactant solution to form a mixed dispersion of antifoams with desired initial pHs and composition. Using this procedure the pHs may however subsequently decrease after mixing because of the reaction of OH\textsuperscript{-} and Ca\textsuperscript{2+} with fatty acids presence in some antifoams. Foam behaviour at a constant pH was also studied. For this measurement, we first mixed the two solutions containing antifoams, then used HCl or NaOH to adjust the pH to the target levels till these are constant after 20 minutes.

### 3.3.3 Measurement of Ca\textsuperscript{2+}-Surfactant Phase Diagram

The Ca\textsuperscript{2+}-Surfactant phase diagram is composed of a CMC boundary, a monomer-precipitate boundary and a micellar-precipitate boundary. The precipitation boundaries represent the onset of turbidity, which is defined in our study as the minimum Ca\textsuperscript{2+} concentration required to cause visible turbidity due to formation of Ca(LAS)\textsubscript{2} or Ca(\(C_{12}4\text{-phenyl SO}_3\text{)}\textsubscript{2} precipitates at a constant surfactant concentration.

In each measurement, ten sample solutions of a given surfactant concentration were prepared in 50 ml standard glass flasks at pH 10.5. Ca\textsuperscript{2+} concentrations were increased by 0.5\times10\textsuperscript{-4} M from the first sample where no precipitation happens to the tenth where the solution is turbid. These various sample solutions are then allowed to sit in a 25\textdegree\textsuperscript{0}C water bath for 24 hours to ensure complete precipitation. At the precipitation boundary, there is
usually a significant change from transparent to turbid between two samples based on observation by eye. The middle value of the Ca$^{2+}$ concentration between a clear solution and a turbid solution is taken as the concentration at the precipitation boundary, and the error measured by this method is therefore ± 0.25×10^{-4} M. An example of the turbidity measurement of 2.0×10^{-3} M NaLAS solution is shown in Fig. 3.4.

![Image](image.png)

**Fig.3.4.** A turbidity measurement of 2.0×10^{-3} M NaLAS with an increase of Ca$^{2+}$ concentration from left to right: 6.5×10^{-4} M, 6.0×10^{-4} M, 5.5×10^{-4} M, 5.0×10^{-4} M, 4.5×10^{-4} M, 4×10^{-4} M, at 1.7×10^{-2} M NaCl, pH 10.5 and Temperature of 25 °C.

### 3.3.4 Equilibrium Interfacial Tension Measurement

#### 3.3.4.1 Measurement of Air-Liquid Surface Tensions by the Wilhelmy Plate Method

The Wilhelmy plate method (CDCA-100 Commercial Surface Tensiometer, Camtel Ltd., UK) [7] is used to measure the air-liquid surface tensions of both aqueous surfactant solutions and triolein. The method is shown schematically in Fig.3.5. It involves measurement of the force $F$ on the plate due to the meniscus, so that:

$$\gamma_{AL} = \frac{F}{l \cos \theta}$$  \hspace{1cm} (3.1)

where $\gamma_{AL}$ is the air-liquid surface tension, $l$ is the wetted perimeter of the Wilhelmy plate.
and $\theta$ is the contact angle.

**Fig. 3.5.** A scheme of the Wilhelmy plate method

In this case, the plate is made from platinum and roughened to ensure a zero contact angle (as indicated by the Wenzel equation [8]). This technique permitted measurement of the change of the surface tension with time. The values of surface tensions measured after one hour were used to make Gibbs plots from which the CMC could be inferred. All the measurements were made at $25^\circ$C.

### 3.3.4.2 Measurement of Oil-Water Interfacial Tensions by the Pendant Drop Method

The pendant drop method involves measurement of the shape of a drop suspended from a capillary. The shape of drop is determined by the balance of hydrostatic and capillary pressure where the latter is in turn described by the Laplace equation. The relevant equation for the shape of the drop is [9]:

$$\gamma_{ow} \left( \frac{1}{R_1} + \frac{1}{R_2} \right) = \gamma_{ow} \frac{d(x \sin \theta)}{dx} = \Delta \rho g \gamma + \frac{2 \gamma_{ow}}{b}$$  \hspace{1cm} (3.2)

where $\gamma_{ow}$ is the interfacial tension, $R_1$ and $R_2$ are the principal radii of the curvature, $\Delta \rho$ is the difference in densities ($\Delta \rho = \rho_2 - \rho_1$) and $\Delta \rho g \gamma$ is the hydrostatic head. $b$ is
the radius of curvature at the bottom of the drop and $\theta$ is the angle made at the tangent to the oil-water surface, as illustrated in Fig. 3.6 (a).

![Fig. 3.6. (a) A schematic drop shape; (b) An image of water drop hanging from a capillary tip in triolein, NaLAS: 2.0×10$^{-3}$ M, Ca$^{2+}$: 5.25×10$^{-4}$ M, NaCl: 1.7×10$^{-2}$ M, at pH 10.5.](image)

Equation (3.2) can be written in dimensionless form as:

$$\frac{d\bar{x}\sin \theta}{\bar{x}d\bar{x}} = 2 + \beta \bar{y}$$  \hspace{1cm} (3.3)

where $\bar{x} = \frac{x}{b}$ and $\bar{y} = \frac{y}{b}$. The dimensionless parameter $\beta$ is thus given by:

$$\beta = \frac{\Delta \rho g b^2}{\gamma_{ow}}$$  \hspace{1cm} (3.4)

For a pendant drop, the parameter $\beta$ is negative in the Equation (3.3).

Tables giving the correlation among $\theta$, $x/b$ and $y/b$ at different $\beta$ values were calculated by Bashforth and Adams and validated later by Fordham [10] and Stauffer [11].
These have been used in the software program purchased from First Ten Angstroms, Ltd., UK in our measurement. By using this pendant drop method (the equipment is purchased from Camtel Ltd., UK), interfacial tensions of triolein-surfactant solutions (and water) at different pHs and Ca\(^{2+}\) concentrations were measured. Equilibrium for one hour allowed for slow adsorption of surfactants at the oil-water interface. Densities of these liquids were measured in a suitable density bottle at 25 °C. For each measurement, oil samples and surfactant solutions were first mixed to stock at 25 °C for one week to reach equilibrium and separated by centrifuge (EBA12, Hettich Zentrifugen Ltd.).

### 3.3.5 Dynamic Air-Water Surface Tension Measurement

The maximum bubble pressure method for measurement of the dynamic surface tension has been applied in many different research fields recently, such as agriculture, pharmacy, detergency [12-14]. This technique allows the study of the change of surface tension for short times down to a millisecond scale. Here we used the latest version of the maximum bubble pressure tensiometer (BPA-1S) developed by SINTERFACE Technologies, Germany. The facility has the advantages of high accuracy, reproducibility of surface tension measurement and can reach a time range of 0.1ms to 100s (see in Table 3.2) [15-17]. This equipment is fully automated and controlled by a computer program.

#### Table 3.2 Technical parameters of BPA-1S

<table>
<thead>
<tr>
<th>Technical Parameters</th>
<th>Values</th>
</tr>
</thead>
<tbody>
<tr>
<td>Surface tension range</td>
<td>10 to 100mN/m</td>
</tr>
<tr>
<td>Reproducibility of measured values</td>
<td>+/- 0.1mN/m</td>
</tr>
<tr>
<td>Accuracy of surface tension</td>
<td>+/- 0.25mN/m</td>
</tr>
<tr>
<td>Dynamic time range</td>
<td>0.1ms to 100s</td>
</tr>
<tr>
<td>Temperature range</td>
<td>10°C to 90°C</td>
</tr>
</tbody>
</table>

A photograph of BPA-1S is shown in Fig. 3.7. Surfactant solutions were contained in a
flask (80ml) which can fit tightly into the cell of the device. The temperature was maintained at 25°C during the measurement by connecting the cell with a water thermostat bath. Gas flow is through a capillary which is connected to a gas pump through a pressure sensor which measures the pressure during the accompanying bubble formation. The position of the capillary can be controlled automatically by the program itself.

Fig. 3.7 (a) An image of BPA-1S; (b) Changes of the capillary pressure $P$ during the bubble formation process

This method measures the maximum pressure of a meniscus formed in a capillary immersed into the liquid phase (for example NaLAS solutions in the presence and absence of antifoams in our experiments) during gas flow through the capillary. The maximum bubble pressure is measured when the meniscus forms as a hemispherical shape at the tip of the capillary in this process (see in Fig. 3.7 b). The surface tension $\gamma_{AW}^d$ can then be calculated by the Laplace-Young equation:

$$\gamma_{AW}^d = f \frac{rP}{2}$$

where $r$ is the radius of the capillary; $f$ is a correction factor which is needed only when the capillary radius $r$ is higher than 0.2 mm. Considering the excess maximum pressure in the measuring system is $P_S$, the hydrostatic liquid pressure $P_H = \Delta \rho g H$ ($\Delta \rho$ is the
difference between the density of liquid and gas; \( g \) is the gravity, and \( H \) is the immersion depth of capillary into the liquid) and the excess pressure \( P_V \), which arises as a result of dynamic effects during fast bubble formation, the measured capillary pressure \( P \) is given by:

\[
P = P_S - P_H - P_V
\]  

(3.6)

Then the surface tension can be obtained by:

\[
\gamma_{AW}^d = f \left( \frac{r(P_S - P_H)}{2} \right) - \Delta\gamma_a - \Delta\gamma_v
\]  

(3.7)

where \( \Delta\gamma_a \) is a correction due to the aerodynamic resistance of the capillary, and \( \Delta\gamma_v \) is a correction due to the viscosity of the liquid [18, 19].

3.3.6 Contact Angle Measurement using Sessile Drop Method

Drops formed at the solid-air interface satisfy the Young-Laplace equation at equilibrium between the three phases: the aqueous phase \((W)\), the solid phase \((S)\) and the air \((A)\):

\[
\gamma_{SA} = \gamma_{SW} + \gamma_{AW} \cos \theta
\]  

(3.8)

where \( \gamma_{SA} \) is the solid-air interfacial tension, \( \gamma_{SW} \) is the solid-water interfacial tension, \( \gamma_{AW} \) is the air-water surface tension and \( \theta \) is the contact angle. The drop should be symmetric about a central vertical axis. Contact angles can therefore be calculated by fitting the shape of the drop by equation 3.8. Figure 3.8 gives an example of an image showing air-water contact angle on the surface of a compressed disk of stearic acid crystals. In our study, both the advancing angle and receding angles were measured.
Fig. 3.8. An image showing air-water contact angle measurement of water drop on a compressed disk of stearic acid; Average angle: 91 degrees (Angle left: 92 degrees; Angle right: 90 degrees) measured through the aqueous phase.

The sessile drop shape was imaged by using the same equipment as that used for the pendant drop method (from Camtel Ltd., UK). Both stearic acid and tristearin disks were made by compressing the crystals using evacuable pellet dies from Specac Ltd. at 20 Pas. To measure the oil-water contact angles, the disks were placed at the bottom of a glass cuvette, and soaked in the triolein which is saturated by stearic acid or tristearin, at 25 °C. The shape of equilibrated water or surfactant solution drops formed at the oil-solid interface was then analyzed, so that the contact angles are then determined. The solutions were the same as those used in the pendant drop interfacial tension measurements described in section 3.3.1.2 except that sufficient stearic acid or tristearin was added to ensure saturation and prevent dissolution of the surface of the disks.

3.3.7 Particle Size Analysis

3.3.7.1 Measurement of Antifoam Droplet Size Distribution by Laser Diffraction

A laser diffraction technique (Mastersizer 1000 from Malvern Instrument Ltd.) was used to measure the size distribution of antifoam droplets dispersed in surfactant solutions. The principle of this technique is based on the Mie theory [20]. Particles (with a diameter higher than 50 nm) passing through a laser beam will scatter light at an angle that is
directly related to their size. The scattering intensity observed is determined by particle sizes and dimensions. This means that large particles scatter light at narrow angles with high intensity. Small particles, in contrast, scatter at wider angles but with low intensity. Particle size distribution can therefore be calculated from measurements of the intensities of scattered light as a function of angle. According to the Mie theory, only particles in a size range from 1 micron to several millimeters can be detected by the Mastersizer 1000. The volumes of particles are measured by this technique and the particle diameters are calculated by assuming the particles adopt a spherical shape.

A typical particle-sizing instrument employing the Mie theory is illustrated in Fig.3.9., which mainly contains: 1) A laser, providing a source of coherent, intense light of fixed wavelength; 2) A sample presentation system to ensure that the material under test passes through the laser beam as a homogeneous stream of particles in a known, reproducible state of dispersion; 3) A series of detectors to measure the light pattern produced over a wide range of angles.

In each measurement, the concentration of antifoam droplets in surfactant solutions is diluted to 0.1 g/l. This concentration is low enough to allow the scattered radiation to be directly measured by the detector and avoid the multi scattering of other particles. The measurement is conducted at a room temperature of 25°C.

![Fig.3.9. A scheme of a typical particle-sizing measurement based on the Mie theory](image)
3.3.7.2 Measurement of Crystalline Particles Size Distribution Using Dynamic Light Scattering (DLS)

The particle sizes of tristearin (and a proportion of stearic acid dispersed in triolein) in the antifoam mixtures, are all less than 1 micron. Laser diffraction cannot therefore be used. Instead Dynamic Light Scattering (DLS, Zetasizer Nano from Malvern Instrument Ltd.) was used.

Dynamic Light Scattering measures the random movement of particles in solutions due to Brownian motion, which is dependent upon the size of particles [21]. This Brownian motion is caused by the random movement of solvent molecules surrounding the particles. The larger the particles, the slower the movement will be. The velocity of particles subject to Brownian motion is determined by the translational diffusion coefficient $D$. The method permits determination of $D$ which can be related to the hydrodynamic diameter $d(H)$ of an equivalent spherical particle using the Stokes-Einstein equation, so that:

$$d(H) = \frac{kT}{3\pi\eta D}$$

(3.9)

where $k$ is the Boltzmann’s constant, $T$ is the absolute temperature and $\eta$ is the viscosity of the continuous medium. The actual dimensions of the non-spherical crystalline particles considered here are not therefore obtained. Only the dimensions of an equivalent spherical particle with the same diffusion coefficient are determined.

As with the laser diffraction technique, this measurement is also based on the Mie theory, seen in Fig 3.8. However, due to the movement of these particles, the intensity of the light scattered will fluctuate. Obviously, smaller particles result in faster intensity fluctuations because of their more rapid movement. A digital auto-correlator is required to measure the similarity of signals scattered by particles at different time intervals. The shorter the time interval, the higher the similarity. The decay of the correlation reveals an indication of
The sizes of particles of tristearin and stearic acid dispersed in triolein were measured using dynamic light scattering at a concentration of about $5.0 \times 10^{-3}$ g l$^{-1}$ at a scattering angle of 90°. It was however necessary first to remove large particles from the stearic acid dispersion using a one micron hydrophobic fluoropore membrane (purchased from Millipore Ltd.). All the measurements are made at 25 °C.

3.3.8 Measurement of Antifoam Crystal Behaviour

3.3.8.1 Polarizing Optical Microscopy

An optical polarizing microscope (Jenaval from Carl Zeiss Ltd.) was used to investigate the optical properties of specimens, exemplified by crystalline fatty acid and tristearin particles and Ca(LAS)$_2$ liquid crystalline precipitates in our study [22, 23]. As illustrated in Fig.3.10, for this measurement, the sample is placed on the stage between a polarizer and an analyzer. Transmitted light passes through the polarizer, where the vibration direction of light is filtered to occur in only one linear direction. If the sample is isotropic, meaning there is only one single index of refraction, the polarized light cannot pass through the analyzer. This type of sample therefore will not be seen through the eyepiece of the microscope. If the light passes through a crystal (or liquid crystal) sample (or any birefringent specimen), a double refraction or birefringence will occur owing to their anisotropic structure. One of these two refracted rays is called an ordinary ray, while the other is called an extraordinary ray. This birefringent property of crystals (or liquid crystals) lets the light travel through the analyzer, rendering visible crystalline and liquid crystalline entities.
3.3.8.2 Scanning Electron Microscopy (SEM)

A scanning electron microscope (SEM, Quanta 200 ESEN by FEI Ltd.) was used to study crystal morphology and structure. A schematic diagram is shown in Fig.3.11. A high-energy beam of electrons in a raster scan pattern is generated by an electron gun. This electron path is controlled by using electromagnetic lenses which are made of a coil of wire around the outside of a tube.

Compared with the optical microscopy, this technique can reach a much higher resolution, thus allowing us to observe much smaller sizes of objects. The potential resolution of the electron microscope is dependent on the wavelength of the electrons, which can be varied by adjusting the voltage of the electron beams. The shorter their wavelength (meaning the faster the electrons travel), the higher the resolution of the microscope. When the primary electron beam is scanned across the surface of the specimen, it will produce signals that contain information about the sample's surface topography, composition and electrical conductivity in the X-rays, backscattered electrons and secondary electrons emitted. The detector will map these signals with beam position and build up images.
was used, the column was always maintained at a vacuum. This is to ensure the stability in the beam, because the reaction between any gas and electrons could cause ionization of the gas molecules and degradation of the images.

Antifoam samples before measurement were spread on the stage and sputter coated with a gold/palladium alloy so they were electrically conductive. A vacuum environment in the sample chamber was also required in sample preparation. This avoided an uneven coating caused by the gas molecules.

**Fig. 3.11.** A schematic diagram of a scanning electron microscopy

### 3.3.9 Antifoam Viscosity Measurement

Viscosity is a measure of the resistance of fluid to an applied stress [24]. Bohlin CVOR rheometer (from Malvern Instrument Ltd) is used to measure the viscosities of our
antifoam samples, including sebum soil, triolein/stearic acid, triolein/tristearin and triolein. This rheometer is connected to a compressed air source to maintain a pressure at 2 bar, which ensures a continuous rotation rate. A cone plate, as shown in Fig.3.12, was used in our measurement having geometry of 40 mm in diameter and 4° opening angle. There is a gap of 150 μm employed during the rotation. The cone geometry ensures a constant shear across the sample despite changes in the angular component of rheology. An automatic controlled rate mode is used to measure the forces in a shear rate range from 0.1 to 100 s⁻¹ in a consistent temperature of 25 °C.

Samples are transported slowly from the glass vessels to the cell by a spatula in order to avoid an introduction of extra shear forces. The minimum amount of samples should be enough to fill the cell, so no air bubbles are entrained during the measurement.

![Fig.3.12. A scheme of cone plate used to measure the viscosity of samples operated by a Bohlin CVOR rheometer](image)

3.3.10 Vertical Thin Film Draining Behaviour

This apparatus was constructed and modified based on the original version described by Garrett [25]. A diagram of this device is shown in Fig.3.13. A glass frame was fully
covered with the surfactant solutions (in the absence and presence of antifoam) initially and the system was allowed to be equilibrated for 3 hours before the frame was raised vertically by a computer-controlled system connected through a polymer fiber to form a thin film. The moving speed (from 0.015 cm/s to 45 cm/s) and the position of the glass frame (0cm to 10cm) can be varied by changing the settings of a controlling computer program developed by the University of Manchester (by Anthony Diggle) [26]. The thermostat jacket surrounds the whole device to maintain a constant temperature at 25 °C. A moistened cotton wool pad is inserted into the top of the cell to prevent evaporation during the measurement.

Foam films of different heights formed at different speeds were imaged by a Canon EOS SLR camera using red monochromatic incident light generated by a LED source (wavelength of the red light: 619 to 629 nm) in order to permit estimation of film thickness as function of film height from the position of interference fringes.

![Fig.3.13. A scheme of the apparatus for observing vertical thin film draining behaviour](image-url)
3.3.11 Measurement of Antifoam Entry Behaviour by the Film Trapping Technique (FTT)

The film Trapping Technique (FTT) has been developed at the University of Sofia [27] and is used in our research work in an attempt to measure the critical capillary pressure for emergence of antifoam drops into the air-water surface. This method is illustrated in Fig.3.14. The FTT device has three main components, as shown in Fig.3.14 (A): A vertical glass capillary of several microns in radius and ~10 centimeters in length, which is connected to a pressure transducer by silicone rubber tubes; a glass vessel for carrying the sample solutions; an inverted microscope (IM 7100 from MEIJI TECHNO, Ltd.) for observing the entry behaviour of antifoam drops [28]. All the glassware was cleaned before use according to the procedure described in section 3.2.3.

Sample solutions were prepared by dispersing the antifoams in surfactant solutions (with a concentration range of antifoam from 100µl to 1ml in 30ml of aqueous phase). For each measurement, the capillary was adjusted to a vertical position above the vessel, after that, it was gradually moved down to the air-water surface until antifoam drops trapped in the layer between the air-water meniscus and the glass substrate, as illustrated in Fig.3.14 (B). Newton’s rings around the antifoam globules can be observed by the microscope at the initial stage [27]. During the measurement, the pressure $P_d$ is increased and after each step, around 10 minutes interval was needed to ensure the completion of liquid drainage between the antifoam droplets and the air-water interface. The shape of meniscus changes with the increase of $P_d$ until the pseudoemulsion film is ruptured to form a lens, as shown in Fig.3.14 (C). The pressure was recorded as the critical capillary pressure $P_c^{CR}$.

The normal FTT has a limitation in that only critical capillary pressures greater than 20 Pa can be measured. This is because the pressure caused by the air-water meniscus which is formed initially between the film layer and oil surface is about 20 Pa ($P_c$). Therefore, the entry behaviour of antifoams which have critical capillary pressures less than 20 Pa cannot be observed. To extend the measuring capability for $P_c^{CR} \leq 20$ Pa, a gentle FTT is
available. This involves placing a sapphire disk in the middle of the vessel to control the shape of the meniscus during the experiment, seen Fig.3.14 (D) [29]. When the antifoam oil droplet is captured in the capillary, a flat interface can be created with a nearly zero $P_C$ by adjusting the wettability of the capillary. The rest of operation is identical to that with the normal FTT arrangement.

**Fig.3.14.** A Film Trapping Technique (FTT) apparatus scheme; (A) Components of a FTT equipment: a vertical glass capillary, a glass vessel and an inverted microscope; (B) Antifoam droplet trapped by an air-water film; (C) Changes of the meniscus shape with the increase of $P_d$; (D) Modification for measurement by gentle FTT [28].
Appendix 3.1 Ingredients used by P&G for sebum soil preparation

<table>
<thead>
<tr>
<th>Ingredient</th>
<th>Weight (g)</th>
<th>Percentage (%)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Coconut oil</td>
<td>600</td>
<td>15</td>
</tr>
<tr>
<td>Oleic Acid</td>
<td>600</td>
<td>15</td>
</tr>
<tr>
<td>Paraffin Oil</td>
<td>600</td>
<td>15</td>
</tr>
<tr>
<td>Olive Oil</td>
<td>600</td>
<td>15</td>
</tr>
<tr>
<td>Cottonseed Oil</td>
<td>600</td>
<td>15</td>
</tr>
<tr>
<td>Squalene</td>
<td>200</td>
<td>5</td>
</tr>
<tr>
<td>Cholesterol</td>
<td>200</td>
<td>5</td>
</tr>
<tr>
<td>Myristic Acid</td>
<td>200</td>
<td>5</td>
</tr>
<tr>
<td>Palmitic Acid</td>
<td>200</td>
<td>5</td>
</tr>
<tr>
<td>Stearic Acid</td>
<td>200</td>
<td>5</td>
</tr>
</tbody>
</table>

Appendix 3.2 Composition of sebum soil antifoam inferred from the ingredients used by P&G

<table>
<thead>
<tr>
<th>Sebum soil</th>
<th>Percentage by weight (%)</th>
<th>Phase behaviour (25°C)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Triglycerides</td>
<td>24.57</td>
<td></td>
</tr>
<tr>
<td>Triolein</td>
<td>10.12</td>
<td>Liquid</td>
</tr>
<tr>
<td>Tricaprylin</td>
<td>0.39</td>
<td>Liquid</td>
</tr>
<tr>
<td>Tricaprin</td>
<td>0.37</td>
<td>Liquid</td>
</tr>
<tr>
<td>Trilinolein</td>
<td>7.49</td>
<td>Liquid</td>
</tr>
<tr>
<td>Trilaurin</td>
<td>2.48</td>
<td>Solid</td>
</tr>
<tr>
<td>Trimyristin</td>
<td>0.82</td>
<td>Solid</td>
</tr>
<tr>
<td>Tripalmitin</td>
<td>2.78</td>
<td>Solid</td>
</tr>
<tr>
<td>Tristearin</td>
<td>0.12</td>
<td>Solid</td>
</tr>
<tr>
<td>Fatty acids</td>
<td>30.47</td>
<td></td>
</tr>
<tr>
<td>Oleic acid</td>
<td>15.23</td>
<td>Liquid</td>
</tr>
<tr>
<td>Myristic acid</td>
<td>5.08</td>
<td>Solid</td>
</tr>
<tr>
<td>Palmitic acid</td>
<td>5.08</td>
<td>Solid</td>
</tr>
<tr>
<td>Stearic acid</td>
<td>5.08</td>
<td>Solid</td>
</tr>
<tr>
<td>Hydrocarbons</td>
<td>20.31</td>
<td></td>
</tr>
<tr>
<td>Paraffin oil</td>
<td>15.23</td>
<td>Liquid</td>
</tr>
<tr>
<td>Squalene</td>
<td>5.08</td>
<td>Liquid</td>
</tr>
<tr>
<td>Cholesterol</td>
<td>5.08</td>
<td>Solid</td>
</tr>
</tbody>
</table>
3.4 References

17. Fainerman, V.B., A.V. Makievski, and R. Miller, Accurate analysis of the bubble


Chapter 4 Foamability and Foam stability of NaLAS and C\textsubscript{12} 4-phenyl SO\textsubscript{3}Na Solutions in the Absence of Antifoam

4.1 Introduction

The tendency to precipitate from hard water (Ca\textsuperscript{2+}) is an important characteristic of anionic surfactants such as NaLAS [1]. Ca\textsuperscript{2+}-LAS\textsuperscript{-} precipitation phase diagrams have been measured by Smith et al. [2] and Matheson et al. [3] in order to define the interaction between NaLAS and hardness ions (Ca\textsuperscript{2+}) in solution. Cohen et al. [4, 5] have studied the effect of various concentrations of NaLAS and Ca\textsuperscript{2+} on the foam behaviour and suggested that the foamability correlates with Ca\textsuperscript{2+}-LAS\textsuperscript{-} precipitation as revealed by the precipitation phase diagram. However no studies have considered the possible antifoam effect of the precipitate and the possible correlation of both dynamic and equilibrium surface tensions with foam and precipitation behaviour.

In practical wash conditions, sebum soil antifoam is usually present. Here however we are concerned mainly with the effect of Ca\textsuperscript{2+} ions on foam behaviour. The effect of sebum soil is considered in Chapter 5.

This chapter describes measurement of Ca\textsuperscript{2+}-LAS\textsuperscript{-} and Ca\textsuperscript{2+}-C\textsubscript{12} 4-phenyl SO\textsubscript{3}\textsuperscript{-} precipitation phase diagrams (including measurement of monomer-micellar boundaries, monomer-precipitate boundaries and micellar-precipitate boundaries) at pH 10.5. We also consider the effects of Ca\textsuperscript{2+} and pH on the foam behaviour of micellar solutions of NaLAS and C\textsubscript{12} 4-phenyl SO\textsubscript{3}Na at surfactant and background electrolyte concentrations relevant for practical application. Of particular interest is the cause of the reduction in foamability of solutions upon formation of precipitates in the presence of Ca\textsuperscript{2+}.
4.2 Ca\(^{2+}\)-NaLAS and Ca\(^{2+}\)-C\(_{12}\) 4-phenyl SO\(_3\)\(^{-}\) Precipitation Phase Diagrams

4.2.1 Some Considerations Concerning the Relevance of the Ca\(^{2+}\)-LAS\(^{-}\) Precipitation Phase Diagram

Ca\(^{2+}\)-LAS\(^{-}\) precipitation is determined by the solubility product \(K_{sp} = [Ca^{2+}][LAS^{-}]^2\). The interaction between LAS\(^{-}\) and Ca\(^{2+}\) is quite complex and can be illustrated theoretically in a phase diagram which is shown in Fig. 4.1. This phase diagram contains four regions:

1). A clear submicellar region where concentrations of both monomeric LAS\(^{-}\) and Ca\(^{2+}\) are too low to satisfy the solubility product.

2). A turbid region where LAS\(^{-}\) monomer coexists with Ca(LAS)\(_2\) precipitate as the concentration of calcium increases so that the solubility product is satisfied. It is believed the precipitate consists of lamellar phase particles (probably multi-walled vesicles) [3].

3). A clear micellar region where no precipitate is present because inclusion of Ca\(^{2+}\) and LAS\(^{-}\) in micelles means that the free concentrations of these ions are too low to satisfy the solubility product.

4). A turbid micellar-precipitate region where, despite the presence of micelles, the solubility product is satisfied. Here micelles, monomeric LAS\(^{-}\) and Ca(LAS)\(_2\) precipitate coexist.

![Fig.4.1. A theoretical Ca\(^{2+}\)-LAS\(^{-}\) phase diagram](image-url)
It is possible to speculate about the likely consequences of increasing calcium concentration at constant LAS\(^-\) concentration on surface tension behaviour. We could consider two such hypothetical scans through the phase diagram. These are depicted in Fig. 4.2 as ABC and DEF. Scan ABC starts with a micellar solution of LAS\(^-\). In the clear micellar region AB the effect of calcium is to reduce the CMC and increase surface activity. Equilibrium surface tension will decrease as a result of increasing of surface activity. However the decrease in CMC will cause the rate of micelle breakdown to decline so the rate of surfactant transport to the air-water surface will also decline. This will mean that the difference between the dynamic surface tension and the equilibrium surface tension will increase with increasing calcium concentration in region AB. At sufficiently low surface ages this may mean that the dynamic surface tension actually increases in this region. As the calcium concentration is further increased we scan across region BC where we have an invariant system according to the phase rule (if the micellar state can be considered to be a phase). The equilibrium surface tension is therefore constant and equal to the value at the precipitation boundary B. However scanning from B to C means increasing proportions of Ca(LAS)\(_2\) which is likely to be present as particles with extremely low diffusion coefficients and slow breakdown rates. Dynamic surface tensions will be expected to rise markedly in consequence.

**Fig.4.2.** Equilibrium and Dynamic Surface Tension behaviour in Ca\(^{2+}\)-LAS\(^-\) theoretical phase diagram; \(\gamma_{AW}^e\) is the equilibrium air-water surface tension and \(\gamma_{AW}^d\) is the dynamic surface tension.
The scan DEF starts with a submicellar solution. In consequence equilibrium surface tensions will be high relative to those in the clear micellar region. Low monomer concentrations will also mean high dynamic surface tensions. Increasing calcium concentrations will increase surface activity and then reduce equilibrium surface tensions. Unfortunately increasing adsorption will also mean decreasing transport rates by diffusion (the characteristic time for diffusion is proportional to the square of the adsorption) and therefore increasing dynamic surface tensions. Removal of surfactant as Ca(LAS)$_2$ precipitates in the region EF will mean increasing equilibrium surface tensions and further increases in dynamic surface tensions. Strictly these considerations apply only to pure anionic surfactants. However it seems reasonable to expect the essential features of this behaviour to be retained, at least in a qualitative sense, with commercial blends of surfactants. We will show that this is a reasonable expectation.

Consideration of antifoam mechanism suggests that in some circumstances lowering the air-water equilibrium surface tension can diminish or even eliminate antifoam action [6]. This is of course a crude oversimplification – many other properties are necessarily involved. If nevertheless the effectiveness of soil antifoam is assumed to depend simply on the surface tension, it can be concluded that the optimum condition for generation of the highest foam volume in the presence of antifoam is in the region AB in any scan at constant LAS$^-$ concentration. In this region equilibrium air-water surface tensions will be minimal at B but dynamic surface tensions will be minimal at some point where calcium concentrations are lower than at B (as a consequence of the effect of calcium on micelle breakdown rates). Indeed at sufficiently low surface ages it is probable that the minimal dynamic surface tension in the region AB will occur at A. Alternatives such as scanning beyond B to C will mean large increases in dynamic surface tensions relative to those prevailing in the region BC. The scan DEF is everywhere submicellar so both equilibrium and dynamic and surface tensions will necessarily be higher.

Apart from the naivety of the assumption that the antifoam effectiveness is determined by the air-water surface tension another difficulty concerns the relevance of dynamic surface
tensions. Foam stability clearly concerns surface tensions at least approaching equilibrium. However foam generation involves rapid formation of new air-water surfaces so that dynamic surface tensions are likely to be relevant [7]. However, this begs the question of which surface age is “characteristic” of a given method of foam generation. Another complicating factor concerns the reaction of Ca\(^{2+}\) with fatty acids to form soaps which in turn may influence the effectiveness of the soil antifoams [8]. We can however eliminate this effect by making measurements at a sufficiently low pH. All those assumptions in the presence of antifoam are examined and discussed in Chapter 5.

4.2.2 Experimental Ca\(^{2+}\)-LAS\(^{-}\) Precipitation Phase Diagram

The commercial NaLAS sample supplied by P&G is a blend of phenyl isomers having a chain length distribution from C\(_{10}\) to C\(_{13}\), as described in section 3.2.1. This type of surfactant mixture usually contains some highly surface active minor components [9]. The slow transport behaviour of these components makes it difficult to measure the equilibrium surface tensions of NaLAS - equilibration at air-water surfaces taking at least 24 hours. In our study, surface tensions were measured by the Wilhelmy plate method after 1 hour as a compromise. This means the CMCs determined by this measurement are not strictly equilibrium values.

Surface tensions (at 1 hour surface age) results of NaLAS solutions were measured over a concentration range from 1.0×10\(^{-4}\) M to 1.0×10\(^{-3}\) M in 1.7×10\(^{-2}\) M NaCl. Results are shown in Fig. 4.3 where Surface Tension vs. \(\log_{10}\) (NaLAS concentration) Gibbs plots are presented. The CMCs and equilibrium surface tensions of micelle solutions tend to decrease with the increase of Ca\(^{2+}\) concentration, as shown in Fig 4.3 (a to c). CMC values of NaLAS solutions in 1.7×10\(^{-2}\) M NaCl calculated according to these Gibbs plots are 5.3×10\(^{-4}\) M in the absence of Ca\(^{2+}\), 4.7×10\(^{-4}\) M in the presence of 1.0×10\(^{-4}\) M Ca\(^{2+}\) and 3.9×10\(^{-4}\) M in the presence of 2.0×10\(^{-4}\) M Ca\(^{2+}\).
Fig. 4.3. Equilibrium Surface tensions of NaLAS solutions in 1.7×10⁻² M NaCl, at pH 10.5 and temperature of 25±1 °C; (a) in the absence of Ca²⁺, (b) in the presence of 1.0×10⁻⁴ M Ca²⁺, (c) in the presence of 2.0×10⁻⁴ M Ca²⁺.
The precipitation boundaries of Ca\(^{2+}\)-LAS\(^{-}\) can be determined by observation of the onset of turbidity in a NaLAS solution with increasing Ca\(^{2+}\) concentration, as described in section 3.3.3. Here Ca(LAS)\(_2\) precipitates form when the solutions become turbid. Below the CMC line, where NaLAS is present only as monomers, the Ca\(^{2+}\)-LAS\(^{-}\) precipitation boundary is linear, which implies that the boundary is determined by a constant solubility product where \(K_{sp} = [Ca^{2+}][LAS^{-}]^2\). We discusses this in detail in section 4.2.4 where we established that, within experimental error, a stoichiometric Ca(LAS)\(_2\) precipitate is formed. Above the CMC line, where the NaLAS micelles and monomers coexist, the precipitation boundary shows as a convex line, due to the inclusion of Ca\(^{2+}\) in surfactant micelles. Both sodium and calcium ions are bounded to the micelles in that circumstance. The measured precipitation phase diagram of log\(_{10}\)[LAS\(^{-}\)/M] vs. log\(_{10}\)[Ca\(^{2+}\)/M], including a CMC line and two precipitation boundaries is shown in Fig 4.4.

**Fig.4.4.** Ca\(^{2+}\)-LAS\(^{-}\) precipitation phase diagram measured in 1.7\times10^{-2} M NaCl at pH 10.5 and Temperature of 25±1 °C.
4.2.3 Experimental Ca$^{2+}$-C$_{12}$ 4-phenyl SO$_3^-$ Precipitation Phase Diagram

The Ca$^{2+}$-C$_{12}$ 4-phenyl SO$_3^-$ precipitation phase diagram for this pure compound was also measured. In order to determine the monomer-micellar boundary, three CMC values were obtained from measurements of the surface tensions (at 1 hour surface age) of C$_{12}$ 4-phenyl SO$_3$Na solutions at pH 10.5 and in the absence of Ca$^{2+}$, in the presence of 1.0×10$^{-4}$ M and 2.0×10$^{-4}$ M Ca$^{2+}$ respectively at 25 °C using the Wilhelmy plate method. Fig 4.5 presents a summary of the equilibrium surface tension measurements. Unfortunately this sample of C$_{12}$ 4-phenyl SO$_3$Na contained minor amounts of more surface active impurities, which meant impractically long equilibration times for surface tension measurements. Therefore again, the surface tension results were recorded after 1 hour to compare with those measured for NaLAS solutions.

The Ca$^{2+}$-C$_{12}$ 4-phenyl SO$_3^-$ precipitation boundaries were again measured at different concentrations of C$_{12}$ 4-phenyl SO$_3$Na at pH 10.5, in the presence of 1.7×10$^{-2}$ M NaCl at 25±1 °C. Only a slight difference is apparent when comparing a phase diagram of log$_{10}$ [C$_{12}$ 4-phenyl SO$_3^-$ / M] vs. log$_{10}$ [Ca$^{2+}$ / M], with that of log$_{10}$ [LAS$^-$ / M] vs. log$_{10}$ [Ca$^{2+}$ / M], as shown in Fig.4.6.
Fig. 4.5. Equilibrium surface tension of C₁₂ 4-phenyl SO₃Na in 1.7×10⁻² M NaCl, at pH 10.5 and temperature of 25±1 °C; (a) in the absence of Ca²⁺, (b) in the presence of 1.0×10⁻⁴ M Ca²⁺, (c) in the presence of 2.0×10⁻⁴ M Ca²⁺.
4.2.4 Effect of Ionic Activities on the Monomer Precipitation Boundaries and Solubility Product

Experimental measurements of the monomer-precipitate boundary may be used to verify the stoichiometry of the precipitate. It is however necessary to allow for the effect of ionic strength on the solubility product. Here we calculated the solubility products for the experimental results assuming that stoichiometry is Ca(LAS)$_2$ (where in this case LAS represents LAS$^-$ or C$_{12}$ 4-phenyl SO$_3^-$). A constant value for the solubility product as a function of Ca$^{2+}$ concentration would then confirm the stoichiometry. We therefore write for the solubility product:

$$K_{sp} = f_\pm C_{Ca^{2+}} C_{LAS^-}^2$$  \hspace{1cm} (4.1)

where $f_\pm$ is the mean activity coefficient, $C_{Ca^{2+}}$ is the calcium ion concentration and $C_{LAS^-}$ is the LAS$^-$ (or C$_{12}$ 4-phenyl SO$_3^-$) ion concentration.
The mean ion activity coefficient can be estimated using the Debye-Huckel limiting law [10] for dilute electrolytes, which means we can write

$$\log_{10} f_z = -0.5092 z_+ z_- \sqrt{s}$$

(4.2)

where \(s\) is the ionic strength and \(z_+\) and \(z_-\) are the charges on the ions. The ionic strength in this case, where we have \(\text{Na}^+, \text{Ca}^{2+}, \text{LAS}^-,\) and \(\text{Cl}^-\) ions present, is given by

$$s = 0.5(C_{\text{Na}^+} + C_{\text{Cl}^-} + C_{\text{LAS}^-} + 4C_{\text{Ca}^{2+}})$$

(4.3)

Since \(C_{\text{Cl}^-} = C_{\text{Na}^+} + 2C_{\text{Ca}^{2+}} - C_{\text{LAS}^-}\) we can write

$$s = (C_{\text{Na}^+} + 3C_{\text{Ca}^{2+}})$$

(4.4)

Combining Equations (4.1), (4.2) and (4.4) and taking logs we have

$$\log_{10} K_{sp} = \log_{10} f_z + \log_{10} C_{\text{Ca}^{2+}} + 2\log_{10} C_{\text{LAS}^-}$$

$$= -(1.0184 \sqrt{C_{\text{Na}^+} + 3C_{\text{Ca}^{2+}}}) + \log_{10} C_{\text{Ca}^{2+}} + 2\log_{10} C_{\text{LAS}^-}$$

(4.5)

We can now calculate \(K_{sp}\) as a function of \(C_{\text{Ca}^{2+}}\) at the monomer-precipitate boundary using the values of \(C_{\text{Na}^+}\) and \(C_{\text{Ca}^{2+}}\) for each of the experimental points available.

Results are shown in Table 4.1. Values of \(K_{sp}\) are seen to be essentially constant as a function of \(\text{Ca}^{2+}\) concentration with some deviation at higher concentration of \(\text{Ca}^{2+}\) which corresponds to higher ionic strength. It seems likely that such deviation is due to the limitations of the Debye-Huckel law at high ionic strength rather than significant deviation from the stoichiometry of \(\text{Ca(LAS)}_2\).
**4.3 Effects of pH and Calcium on Foam Behaviour of NaLAS Solutions in the Absence of Antifoam**

Here we measured the foam behaviour of micellar solutions at a constant concentration of NaLAS with increasing concentrations of Ca\(^{2+}\) using both tumbler and cylinder shaking methodologies. This represents the hypothetical scan ABC shown in Fig.4.2. A concentration of 2.0×10\(^{-3}\) M NaLAS was used as representative of that used in practical hand washing detergency. Solutions were prepared at a constant background electrolyte condition of 1.7×10\(^{-2}\) M NaCl and at pH 3, 7 and 10.5. The cause of the well-known decrease in foamability, accompanying precipitation at high levels of Ca\(^{2+}\), was a particular interest. Dynamic surface tensions were therefore measured to establish whether slow transport of surfactant to air-water surfaces represented a cause. In addition, the possible role of the Ca\(^{2+}\)-LAS\(^{-}\) precipitate as an antifoam was also explored.

**4.3.1 Foamability and Foam Stability Measurement**

Ca\(^{2+}\)-LAS\(^{-}\) precipitation plays a decisive role in determining the foam behaviour of NaLAS solutions in the absence of builders and antifoams. Increase in Ca\(^{2+}\) concentration beyond the micellar-precipitate boundary results in progressive precipitation of NaLAS as Ca(LAS)\(_2\) and a reduction in foamability. Results for both cylinder shaking and tumbler...
Methodologies are presented in Fig. 4.7 and 4.8 respectively. Both methodologies reveal a reduction in foamability at Ca\textsuperscript{2+} concentrations above the precipitation boundary.

**Fig. 4.7.** Foamability and foam stability by cylinder shaking of 2.0×10\textsuperscript{-3} M NaLAS at 1.7×10\textsuperscript{-2} M NaCl, and Temperature of 25±1 °C. (a) immediately after shaking for 10s; (b) after standing for 10 min; □ pH 3; ◊ pH 7; Δ pH 10.5.
In the case of both methodologies, the effect of pH on foamability is negligible when compared with that of Ca\(^{2+}\) concentration (see Fig. 4.7a and 4.8a). Foam volumes decrease only slightly after 10 minutes (as is clear if Fig. 4.7a is compared with Fig. 4.7b and Fig.4.8a with Fig.4.8b respectively). This means the aqueous films in the foams generated by these NaLAS solutions are quite stable in the absence of antifoams over that time (see in Fig. 4.7b and Fig. 4.8b).

**Fig.4.8.** Foamability and foam stability by tumbling tube rotation of 2.0×10\(^{-3}\) M NaLAS at 1.7×10\(^{-2}\) M NaCl and Temperature of 25±1 °C. (a) immediately after 10 rotations; (b) after standing for 10 min; □ pH 3; ◇ pH 7; △ pH 10.5.
One possible explanation for the decreasing foamability at Ca$^{2+}$ concentrations above the micellar-precipitate boundary could be that the precipitate acts as an antifoam. To explore this possibility, the foamability of 2.0×10$^{-3}$ M NaLAS solution at 40×10$^{-4}$ M Ca$^{2+}$ and pH 10.5 was measured after removal of the precipitate by filtration using a Millipore filter (0.2 μm purchased from Millipore Corporation, USA). No significant difference was noticed in the foamability and foam stability by cylinder shaking of sample solutions before and after filtration. Results are shown in Fig.4.9. This indicates that the decrease in foamability accompanying precipitation of Ca(LAS)$_2$ is not due to any antifoam behaviour by the precipitate.

![Graph showing foam behaviour](image)

**Fig.4.9.** Foam behaviour by cylinder shaking of surfactant solutions before and after filtration of Ca(LAS)$_2$ precipitate in 2.0×10$^{-3}$ M NaLAS, at 40×10$^{-4}$ M Ca$^{2+}$, 1.7×10$^{-2}$ M NaCl, pH 10.5 and Temperature of 25±1°C.

Smith *et al.* [2] have shown that Ca(LAS)$_2$ precipitates are in fact liquid crystalline. This was verified for the Ca(LAS)$_2$ precipitates formed in this study. Thus the Ca(LAS)$_2$ precipitate collected by centrifugation was confirmed as lamellar phase by direct observation with microscopy using crossed-polarizers. The relevant images are shown in Fig. 4.10. Absence of an antifoam effect is likely to be due to the hydrophilic nature of the surfaces of the lamellar phase particles where the surfactant head groups will dominate exposure to the aqueous phase.
Fig. 4.10. Photomicrographs with a crossed polarizer of Ca(LAS)$_2$ precipitates formed in 2.0×10$^{-3}$ M NaLAS at 40×10$^{-4}$ M Ca$^{2+}$, 1.7×10$^{-2}$ M NaCl, pH 10.5. The scale bar represents 100.0μm.
4.3.2 Dynamic Surface Tension Behaviour of NaLAS Solutions

Measurement of dynamic surface tensions by the Maximum Bubble Pressure Tensiometer [8] was used to establish the effect of calcium on the dynamic surface tension of NaLAS solutions at pH 10.5. Results are shown in Fig.4.11 for three different surface ages. It is obvious from the figure that presence of up to ~ 6.0×10^{-4} M calcium causes a decrease in surface tension at surface ages ≥ 1s. This is presumably due to enhanced surface activity in this clear micellar region of the phase diagram (region AB in Fig 4.2). However this decrease in surface tension is essentially absent at a surface age of 0.1s. This effect is presumably a consequence of the expected reduction in micelle breakdown rates due in turn to the reduction of the CMC by calcium as discussed in section 4.2.1.

At calcium concentrations > ~ 6.0×10^{-4} M, the solutions become turbid due to precipitation of Ca(LAS)_2 as lamellar phase particles (as shown in Fig. 4.10). This is the region BC in Fig.4.2. At the relatively high surface age of 10s the surface tension is almost constant with increasing calcium ion concentration. As we have seen (in section 4.2.1) consideration of the phase rule suggests that for a pure surfactant in this region of the phase diagram (where micelles, precipitated liquid crystal phase and monomer coexist) the system should be invariant at equilibrium. Here we have non-equilibrium measurements and impure surfactant. However there appears to be an echo of the equilibrium behaviour of a pure surfactant in these measurements. Low and near constant (with increasing calcium concentration) surface tensions at a surface age of 10s suggests significant surfactant adsorption. That foam is stable after standing for up to 10 minutes is not therefore surprising.
At the low surface age of 0.1s and calcium concentrations of $> 6.0 \times 10^{-4}$ M, dynamic surface tensions increase markedly. This is presumably a consequence of an increase of precipitation of NaLAS in this region from a micellar state to form liquid crystalline particles (see Fig.4.10). Such particles are likely to have extremely low diffusion coefficients, slow breakdown rates and no tendency to adhere to air-water surfaces. The effect is particularly striking at $40 \times 10^{-4}$ M calcium. Here after 10s of aging the surface tension is $\sim 32$ mN m$^{-1}$. However the surface is almost denuded of surfactant after 0.1s of aging as indicated by a dynamic surface tension only about 5-6 mN m$^{-1}$ below that of pure water. Low foamability (as shown in Fig. 4.7 (a) and Fig. 4.8 (a)) in this region clearly correlates with these slow rates of transport to air-water surfaces. These effects of Ca$^{2+}$ on dynamic surface tensions are not specific to pH 10.5. Changing the pH to 3 had negligible effect in these systems as shown in Fig. 4.12, which correlated with the absence of any
difference in foamability in a pH range 3 - 10.5. These dynamic surface tensions suggest that if we were to define a characteristic time for foam generation by for example cylinder shaking it would be < 1s.

![Graph](image)

**Fig.4.12.** The effect of pH on Dynamic Surface Tensions of $2.0 \times 10^{-3}$ M NaLAS at $1.7 \times 10^{-2}$ M NaCl, $8.0 \times 10^{-4}$ M Ca$^{2+}$, and Temperature of 25±1 °C; ◆ pH 3; ◇ 10.5.

4.4 Effects of pH and Calcium on Foam Behaviour of C$_{12}$ 4-phenyl SO$_3$Na Solutions in the Absence of Antifoam

The foamability of “pure” C$_{12}$ 4-phenyl SO$_3$Na was measured using the cylinder shaking methodology only. Results are shown in Fig.4.13. As with NaLAS solutions, the foamability of the “pure” C$_{12}$ 4-phenyl SO$_3$Na solution is also dependent upon Ca$^{2+}$-C$_{12}$ 4-phenyl SO$_3^-$ precipitation in the absence of builders and antifoam. In the micellar-precipitate region (where Ca$^{2+} \geq 5.25 \times 10^{-4}$ M at $2.0 \times 10^{-3}$ M C$_{12}$ 4-phenyl SO$_3$Na), foamability decreases with increasing Ca$^{2+}$ concentration. The foams were however stable for at least 10 minutes. There was no effect of pH (pH 3 vs. pH 10.5) on both foamability and foam stability.
Fig. 4.13. Foamability and foam stability by cylinder shaking in $2.0 \times 10^{-3}$ M C$_{12}$ 4-phenyl SO$_3$Na, at $1.7 \times 10^{-2}$ M NaCl and Temperature of 25±1 0C. (a) immediately after shaking for 10s; (b) after standing for 10 min; □ pH 3; ◇ pH 10.5.

As with NaLAS, removal of the Ca(C$_{12}$ 4-phenyl SO$_3$)$_2$ precipitate by filtration using a Millipore filter (0.2 μm purchased from Millipore Corporation, USA) produced no significant change in foamability. Again therefore there was no indication of antifoam behaviour by the precipitate.
Fig. 4.14. Foam behaviour by cylinder shaking of surfactant solutions before and after filtration of Ca(C_{12} 4-phenyl SO_3)_2 precipitate in 2.0 \times 10^{-3} \text{ M} \ C_{12} 4-phenyl SO_3Na at 40 \times 10^{-4} \text{ M} \ Ca^{2+}, 1.7 \times 10^{-2} \text{ M} \ NaCl, \text{ pH } 10.5 \text{ and Temperature of } 25 \pm 1 \text{ ^oC}.

The Ca(C_{12} 4-phenyl SO_3)_2 precipitate, not surprisingly, is found to be present in solutions as lamellar phase liquid crystals by observation with microscopy using crossed-polarizers. The relevant image is shown in Fig. 4.15.

Fig. 4.15. Photomicrographs with a crossed polarizer of Ca(C_{12} 4-phenyl SO_3)_2 precipitates formed in 2.0 \times 10^{-3} \text{ M} \ C_{12} 4-phenyl SO_3Na at 40 \times 10^{-4} \text{ M} \ Ca^{2+} \text{ and } 1.7 \times 10^{-2} \text{ M} \ NaCl, \text{ pH } 10.5. \text{ The scale bar represents } 100.0 \mu \text{m}.
The corresponding dynamic surface tensions were also measured. Results are shown in Fig.4.16. The dynamic surface tensions of C$_{12}$ 4-phenyl SO$_3$Na solutions, measured at 0.1s, 1s and 10s are seen to decrease up to the precipitation boundary, at 5.25×10$^{-4}$ M Ca$^{2+}$, as a result of enhanced surface activity with an increase of Ca$^{2+}$ concentration. This decrease of surface tension does not however correlate with any change in foam behaviour.

**Fig.4.16.** Dynamic surface tensions at various surface ages of solution of 2.0×10$^{-3}$ M C$_{12}$ 4-phenyl SO$_3$Na at 1.7×10$^{-2}$ M NaCl, pH 10.5 and Temperature of 25±1 °C; ◆ 0.1 s; ■ 1 s; ▲ 10 s.

The marked increase in dynamic surface tension at the precipitation boundary is qualitatively similar to the behaviour shown by the NaLAS/Ca$^{2+}$ system. Again this increase in dynamic surface tension after that boundary correlates with the decrease in foamability which suggests that slow transport of surfactant to air-water surfaces is responsible. This is particularly striking at surface ages of 0.1s where dynamic surface tensions approach those of pure water, implying negligible surfactant adsorption. Low adsorption levels will mean no positive (or even negative) disjoining pressures, high
Plateau border capillary pressures and low surface tension gradients, all of which will contribute to low foamability.

Comparison of C\textsubscript{12} 4-phenyl SO\textsubscript{3}Na with that of commercial NaLAS reveals higher dynamic surface tensions and lower foamabilities in the micellar-precipitate region (compare Fig 4.7 and 4.11 with respectively Fig.4.13 and Fig.4.16). This is presumably due to fractionation of precipitation in the case of the commercial NaLAS with means higher concentrations of dissolved surfactant at given concentrations of Ca\textsuperscript{2+} despite similar values of the solubility product.

4.5 Summary

Foamability of NaLAS and C\textsubscript{12} 4-phenyl SO\textsubscript{3}Na solutions in the absence of antifoam is essentially independent of pH and declines markedly in the micellar-precipitate region of the phase diagram due to diminished rates of transport of surfactant to the rapidly generated air-water surfaces formed during foam generation. Ca(LAS)\textsubscript{2} and Ca(C\textsubscript{12} 4-phenyl SO\textsubscript{3})\textsubscript{2} precipitates are liquid crystalline particles which have shown no significant antifoam effect. The relatively large size of these precipitates compared with micelles implies much smaller diffusion coefficients. Moreover, it is known, for example, that precipitation of lamellar phase particles from micellar LAS solution by excess NaLAS produces from 2 to 4 orders of magnitude reduction in breakdown rates compared to micelles [11]. It seems that low diffusion coefficients and slow breakdown rates of the liquid crystalline precipitates will combine to produce a relatively small contribution to the overall transport of surfactant monomers to air-water surfaces. Transport will be due mainly to the monomer and the much diminished residual micellar surfactant present.

Comparison of the dynamic surface tensions and foamabilities in the micellar-precipitate region implies that the age of surfaces during foam generation with the methodologies used here is less that 1s. An objective assessment of the characteristic surface age of the
air-water surfaces during foam generation cannot be given.

Measurement of dynamic surface tensions at surface ages greater than 10s indicates a small dependence upon Ca$^{2+}$ concentration in the micellar-precipitate region. This implies that significant adsorption has taken place by that time. It is not therefore surprising that any foam produced is relatively stable on a time scale of several minutes.

### 4.6 References

Chapter 5 Foamability and Foam Stability of NaLAS and C_{12} 4-phenyl SO_{3}Na Solutions in the Presence of Antifoam

5.1 Introduction

Here we explore the antifoam behaviour of sebum soil under a variety conditions in order to provide a basis for establishing its mode of action. As we have shown in Appendix 3.2, sebum soil is mainly a complex mixture of triglycerides, hydrocarbons and fatty acids. The presence of the latter means that conversion of fatty acids to soaps may occur in-situ. We therefore explore the effect of pH and Ca^{2+} concentration in surfactant solution on the antifoam behaviour of sebum soil.

Sebum soil is a viscous, turbid fluid mixture of particles and oils. The nature and geometry of particles will be almost impossible to ascertain because of its complexity. This could make a key aspect of the antifoam mechanism of sebum soil inaccessible to investigation. We will therefore seek to establish which of the pure components of this mixture could form oil/particle synergistic antifoams which have a similar antifoam performance to sebum soil. We will then use these mixtures as models for the latter. Here we will describe the selection of suitable models and present a comparison of their antifoam performance with that of sebum soil.

Again we will use micellar Sodium Alkyl Benzene Sulphonate (NaLAS and C_{12} 4-phenyl SO_{3}Na where appropriate) concentrations typical of that used in practical wash situations. The antifoam performance will be studied as a function of Ca^{2+} concentration at a constant micellar surfactant concentration representing a scan through the precipitation phase boundary ABC shown in Fig.4.2. The pH will be varied from 3 to 10.5. Use of pH 3 should suppress any tendency to form soaps from the fatty acid component of either sebum soil or any model antifoam. Comparison with foam behaviour at high pH will help elucidate any specific role for soap formation.
5.2 Effect of Sebum Soil Antifoam on Foamability and Foam Stability of NaLAS Solutions

Sebum soil is an effective antifoam which is always present under practical washing conditions with detergent solutions. Here we study the antifoam behaviour of sebum soil at two different concentrations 1.0 g l\(^{-1}\) and 0.25 g l\(^{-1}\). Foamability and foam stability of solution of \(2.0 \times 10^{-3}\) M NaLAS in the presence of sebum soil antifoam at different pHs (pH 3, 7 and 10.5) and Ca\(^{2+}\) concentrations are presented, which will be compared with those in the absence of antifoam.

5.2.1 Interaction of Sebum Soil, Ca\(^{2+}\) and pH

5.2.1.1 Effect of Sebum Soil Antifoam and Ca\(^{2+}\) on pH

Sebum soil antifoam contains various types of fatty acids, which can react in the absence of Ca\(^{2+}\) at high pH to form insoluble sodium soaps, acid soaps or even soluble carboxylate ions. At high pH and in the presence of Ca\(^{2+}\), however calcium soaps can form. These calcium soaps are generally of lower solubility than the corresponding sodium soaps. Under conditions of high pH and in the presence of Ca\(^{2+}\), any fatty acid present therefore tends to be converted to calcium soaps. This reaction can be represented by the equations:

\[
RCOOH + OH^- \leftrightarrow RCOO^- + H_2O
\]
\[
2RCOO^- + Ca^{2+} \leftrightarrow (RCOO)_2Ca
\]  
(5.1)

It has been reported that conversion of the fatty acid in triglyceride oil-fatty acid mixtures to calcium soaps may cause an enhancement of antifoam effects [1, 2]. However such enhancement concerns liquid fatty acids which are miscible with the relevant oil. Precipitation of calcium soap particles at the oil-water interface is then necessary before any synergistic oil-particle antifoam behaviour can become apparent. By contrast, sebum soil is a mixture of oil and particles at ambient temperature, so that oil-particle antifoam synergy may in principle occur irrespective of the formation of calcium soaps.
The extent to which calcium soap formation occurs is of course determined by the pH and calcium content of the foam generating solution. If the pH is low enough (for example pH = 3) any soap formation is suppressed. However at higher pHs, formation of sodium and calcium soaps from the fatty acids will cause a reduction of pH as indicated by Equation (5.1) and (5.2). These long-chain fatty acids are weak acids so that the reaction with hydroxide ions is driven by removal of carboxylate ions as the sodium or calcium soaps. The resultant changes in pH can be used to monitor, in a crude way, the extent of conversion of fatty acid to soaps.

The change of pH with time after mixing a prepared sebum soil antifoam dispersion by the Ultra–Turrax with a NaLAS solution containing sufficient alkali to give a nominal pH of 10.5 (mixing X with Y as described in section 3.3.2) before reaction with sebum soil is shown in Table 5.1. The pH declined significantly from 10.5 to 8.68 in the absence of Ca$^{2+}$ due to the formation of sodium soaps and from 10.5 to 6.96 in the presence of 40×10$^{-4}$ M Ca$^{2+}$. This indicates that the formation of calcium soaps causes a further decrease since more protons are released from fatty acids. The reaction of sebum soil antifoam with Ca$^{2+}$ is seen to be rapid – essentially complete after a couple of minutes.

**Table 5.1** pH measurement of 2.0×10$^{-3}$ M NaLAS, at 1.7×10$^{-2}$ M NaCl, originally at pH 10.5, and in the presence and absence of sebum soil antifoam and at Temperature of 25±1 °C.

<table>
<thead>
<tr>
<th>Time (min)</th>
<th>0 – 2</th>
<th>5 – 7</th>
<th>10 – 12</th>
<th>20 – 22</th>
</tr>
</thead>
<tbody>
<tr>
<td>In the absence of antifoam</td>
<td>Ca$^{2+}$: 40×10$^{-4}$ M</td>
<td>10.48</td>
<td>10.47</td>
<td>10.46</td>
</tr>
<tr>
<td>In the presence of 1.0 g l$^{-1}$ antifoam</td>
<td>Ca$^{2+}$: 0×10$^{-4}$ M</td>
<td>8.68</td>
<td>8.61</td>
<td>8.55</td>
</tr>
<tr>
<td></td>
<td>Ca$^{2+}$: 40×10$^{-4}$ M</td>
<td>6.96</td>
<td>6.86</td>
<td>6.78</td>
</tr>
<tr>
<td>In the presence of 0.25 g l$^{-1}$ antifoam</td>
<td>Ca$^{2+}$: 40×10$^{-4}$ M</td>
<td>9.04</td>
<td>9.03</td>
<td>9.01</td>
</tr>
</tbody>
</table>

Results for the corresponding change in pH in the case of a nominal pH of 7 are shown in
Table 5.2. Here the effect of sebum soil antifoam concentration is also given. In the absence of calcium, no significant change in pH is evident regardless of antifoam concentration (increased from 0.25 to 1.0 g l⁻¹). However in the presence of calcium some decline in pH is revealed implying the formation of calcium soap. Reduction in pH in the case of 0.25 g l⁻¹ antifoam is small and more or less independent of water hardness which implies that the reaction is essentially complete even at 8.0×10⁻⁴ M Ca²⁺ under the conditions studied.

Table 5.2 pH measurement of 2.0×10⁻³ M NaLAS after 30 minutes, at 1.7×10⁻² M NaCl, originally at pH 7, and in the presence of sebum soil antifoam and at Temperature of 25±1 °C.

<table>
<thead>
<tr>
<th>Ca²⁺ Concentration (1×10⁻⁴ M)</th>
<th>0</th>
<th>8</th>
<th>20</th>
<th>40</th>
</tr>
</thead>
<tbody>
<tr>
<td>In the absence of sebum soil antifoam</td>
<td>6.95</td>
<td>6.85</td>
<td>6.87</td>
<td>6.90</td>
</tr>
<tr>
<td>In the presence of 0.25 g l⁻¹ antifoam</td>
<td>6.98</td>
<td>6.55</td>
<td>6.54</td>
<td>6.55</td>
</tr>
<tr>
<td>In the presence of 1.0 g l⁻¹ antifoam</td>
<td>7.02</td>
<td>5.84</td>
<td>5.42</td>
<td>5.16</td>
</tr>
</tbody>
</table>

As expected, no significant changes in pH were found in surfactant solutions at pH 3.0 when sebum soil antifoam was added. Results are presented in Table 5.3. No calcium soap formation therefore has occurred. It should be noted however that, after mixing the solutions X and Y, the pH level slightly increased. This effect was probably caused by the presence of residual Na₂CO₃ in the NaLAS sample used. These results indicate that the pH of NaLAS solution should always be monitored and adjusted if necessary before use.

Table 5.3 pH measurement of 2.0×10⁻³ M NaLAS, at 1.7×10⁻² M NaCl, originally at pH 3, and in the presence of 1.0 g l⁻¹ sebum soil antifoam and at Temperature of 25±1° C.

<table>
<thead>
<tr>
<th>Time (min)</th>
<th>0 – 2</th>
<th>20 – 22</th>
</tr>
</thead>
<tbody>
<tr>
<td>Ca²⁺: 0 × 10⁻⁴ M</td>
<td>3.28</td>
<td>3.19</td>
</tr>
<tr>
<td>Ca²⁺: 40 × 10⁻⁴ M</td>
<td>3.28</td>
<td>3.26</td>
</tr>
</tbody>
</table>
Finally we should note that all pH measurements concerning foam behaviour in the presence of sebum soil reported here concern *initial* pH values. Actual values (except in the case of pH 3) will be lower as a result of conversion of fatty acids to soaps as reported here.

5.2.1.2 Effect of Ca\(^{2+}\) on Sebum Soil Antifoam Droplet Size Distribution

As we have shown reactions at high pH and in the presence of Ca\(^{2+}\) will result in all or part of the fatty acids present in sebum soil converting to sodium or calcium soaps (or even dissolving as carboxylate ions). Here we remember that the sebum soil was first dispersed in surfactant solution using an Ultra–Turrax before adjustment of pH and, where appropriate, addition of Ca\(^{2+}\). Details of the preparation of the dispersion are given in section 3.3.2.2.

A preliminary measurement of the size distribution of sebum soil antifoam droplets in NaLAS solutions before and after adding Ca\(^{2+}\) by optical microscopy shows slight difference. Calcium (or sodium) soaps are not found to be present as particles separated from the oil droplets in solutions, as shown in Fig.5.1, but probably form in the surface of oil droplets which cannot be seen by optical microscopy [1].

The size distribution of sebum soil antifoam droplets in these two NaLAS solutions has also been measured by the Laser Diffraction device Mastersizer 1000. Results as shown in Fig. 5.2 further confirm that the calcium soap formation has negligible effect in changing the sebum soil antifoam droplets sizes.
Fig. 5.1. Optical micrographs of 1.0 g l⁻¹ sebum soil antifoam droplets in 2.0×10⁻³ M NaLAS, at 1.7×10⁻² M NaCl, pH 10.5 dispersed by Ultra–Turrax at Temperature of 25±1 °C; (a) in the absence of Ca²⁺; (b) in the presence of 5.25×10⁻⁴ M Ca²⁺. The scale bar represents 5.0 μm.

Fig. 5.2. Laser Diffraction of a distribution of 0.1 g l⁻¹ sebum soil antifoam droplets dispersed in 2.0×10⁻³ M NaLAS at 1.7×10⁻² M NaCl, pH 10.5, and Temperature of 25±1 °C; ◊ in the absence of Ca²⁺; ◇ in the presence of 5.25×10⁻⁴ M Ca²⁺.
5.2.2. Foamability and Foam Stability in the Presence of 1.0 g l\(^{-1}\) Sebum Soil Antifoam

The foamability of NaLAS solutions declines significantly when 1.0 g l\(^{-1}\) sebum soil antifoam is added under all pH and hardness conditions studied. Results are presented in Fig. 5.3 (a) and should be compared with the corresponding Fig. 4.7 (a) where the foamability profile in the absence of antifoam is presented. In general, foamabilities in the presence of antifoam decline monotonically with increase in calcium concentration. There is no obvious indication of optimal high foam in the clear micellar region where the equilibrium surface tension is relatively lower than that in other regions. Differences in pH do not appear to cause marked differences in foamability with no clear trend associated with declining pH apparent.

Comparison of Fig. 5.3 (a) with Fig. 5.3 (b) reveals that in the presence of antifoam the foam is relatively unstable. The stability of foam at calcium concentrations up to the precipitation boundary appears to be lower for antifoam dispersions prepared at pH 10.5 than is found with those prepared at pH 3 or 7. This may indicate some adverse effect of calcium soap formation on foam stability.

The effect is made more obvious if plots of \(F\) values are considered. Here \(F\) is defined as [3, 4]:

\[
F = \frac{\text{Volume of air in foam in the presence of antifoam}}{\text{Volume of air in foam in the absence of antifoam}}
\]

This \(F\) ratio is therefore independent of the dimensions of the vessel used to measure the foam. \(F\) is useful in this context for separating the effects of antifoam action from those due to Ca(LAS)\(_2\) precipitation. Results of \(F\) values calculated based on the foam volume results in Fig. 4.7 and Fig. 5.3 are therefore presented in Fig. 5.4.
Fig. 5.3. Foamability and foam stability by cylinder shaking of $2.0 \times 10^{-3}$ M NaLAS, at $1.7 \times 10^{-2}$ M NaCl, in the presence of 1.0 g l$^{-1}$ sebum soil antifoam and at Temperature of 25±1 °C. (a) immediately after shaking for 10 s; (b) after standing for 10 min; ▲ pH 3; ■ pH 7; ◆ pH 10.5.
Fig. 5.4. $F$ profile by cylinder shaking of $2.0 \times 10^{-3}$ M NaLAS, at $1.7 \times 10^{-2}$ M NaCl, in the presence of 1.0 g l$^{-1}$ sebum soil antifoam and at Temperature of $25 \pm 1$ °C. (a) immediately after shaking for 10 s; (b) after standing for 10 min; ▲ pH 3; ■ pH 7; ◆ pH 10.5.

The $F$ value is seen to increase in the micellar-precipitate region of the phase diagram for antifoam dispersions prepared at pH 7 and 10.5. The effect appears to be real despite the large error bars. Absence of the effect at pH 3 suggests that it concerns reaction between fatty acids in the antifoam with calcium.
It could therefore suggest that a comparatively high concentration of sebum soil (1.0 g l\(^{-1}\)) containing \(~30\%\) long chain fatty acids by weight causes a removal of calcium from \(\text{Ca}(\text{LAS})_2\) to form calcium soaps (which have a much lower solubility product than \(\text{Ca}(\text{LAS})_2\) \((\sim 2.5 \text{ to } 3.0 \times 10^{-11} \text{ measured at ionic strength of } 0.17 \text{ at temperature of } 25 ^\circ \text{C})\) as shown in Table 5.4.

**Table 5.4** Solubility products \((K_{sp})\) of Calcium soaps measured at Temperature of 25±1 °C.

<table>
<thead>
<tr>
<th>Calcium soaps</th>
<th>Solubility Product measured at ionic strength of (/ M)</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>0.0</td>
</tr>
<tr>
<td>Oleate [5]</td>
<td>(\sim 3.8 \times 10^{-16})</td>
</tr>
<tr>
<td>Myristate [5]</td>
<td>(\sim 2.2 \times 10^{-15})</td>
</tr>
<tr>
<td>Palmitate [5]</td>
<td>(\sim 3.8 \times 10^{-18})</td>
</tr>
<tr>
<td>Stearate [6]</td>
<td>-</td>
</tr>
</tbody>
</table>

This effect can cause an increase of the micellar NaLAS concentration, thus a decrease of the dynamic surface tension, slightly enhancing the resistance to antifoam, which dominates over any slightly enhanced antifoam effectiveness due to calcium soap formation. This effect is of course not so obvious if overall foam volumes are considered because they are low even in the absence of antifoam because of \(\text{Ca}^{2+}\)-LAS\(^{-}\) precipitation. Measurements of dynamic surface tensions of NaLAS solutions in the presence of \(40 \times 10^{-4}\) M \(\text{Ca}^{2+}\) and 1.0 g l\(^{-1}\) sebum soil antifoam dispersion at low surface age (< 1 s) confirms this effect. As shown in Fig. 5.5, surface tensions measured at pH 10.5 are much lower than those measured at pH 3, the condition where the removal of \(\text{Ca}^{2+}\) from \(\text{Ca}(\text{LAS})_2\) precipitate is absent.
Fig. 5.5. The effect of pH on dynamic surface tensions of 2.0×10^{-3} M NaLAS, at 1.7×10^{-2} M NaCl, 40×10^{-4} M Ca^{2+}, in the presence of 1.0 g l^{-1} sebum soil antifoam and at Temperature of 25±1 °C; ◆ pH 3; ◇ 10.5.

The reduction in dynamic surface tension as the calcium concentration approaches the precipitation boundary (at Ca^{2+} concentration approaching 5.25×10^{-4} M) at surface ages ≤ 1s indicates enhanced surfactant adsorption without the concomitant decrease in transport efficiency associated with the micellar-precipitate region, as shown in Fig.4.12. This could be expected to increase resistance to antifoam action to produce optimally enhanced foamability and foam stability as the precipitation boundary is approached. However no such effect is apparent in either foam volume or the ratio $F$. Indeed foamability and foam stability appear to decrease in this region at all pH values which implies that absence of an optimal high foam volume does not concern calcium soap formation. Also it cannot simply concern the effect of calcium on surfactant transport in NaLAS solutions (due to decreases in micelle breakdown kinetics) because antifoam action is also apparent in measurements of foam stability at high surface ages where the rapid transport is less relevant.
5.2.3 Foamability and Foam Stability in the Presence of 0.25 g l⁻¹ Sebum Soil Antifoam

When the concentration of sebum soil antifoam is reduced to 0.25 g l⁻¹ in NaLAS solutions, slight changes in pH levels with an increase of Ca²⁺ concentration will mean that less calcium soap forms compared to that at 1.0 g l⁻¹ sebum soil antifoam (see Table 5.2). This also means that any tendency for calcium soap precipitation to remove calcium from Ca(LAS)₂ precipitate will be diminished.

Foamabilities and foam stabilities as a function of pH and calcium concentration are presented in Fig.5.6. The corresponding $F$ ratios are presented in Fig.5.7. Differences in foamabilities with changes in pH are more marked than found at higher sebum soil concentrations but are still not striking. Under all conditions the foam is unstable with this level of sebum soil. However in contrast to the situation with higher levels of antifoam the ranking of foamability follows pH with the highest foam volumes found at pH 3 at most calcium concentrations. This is consistent with enhanced antifoam effects accompanying formation of calcium soap. It is perhaps surprising however that even in the absence of calcium relatively low foam is also found with dispersions prepared at pH 10.5. It would seem that long chain sodium soaps (of limited solubility under these conditions) may further enhance the antifoam efficiency in this context.

That the effect of pH on foamability is more pronounced at 0.25 g l⁻¹ than at 1.0 g l⁻¹ antifoam concentration is probably due to the method of preparation of these dispersions. Thus acid or alkali was added to solutions to give the nominal pH. Any reaction with sebum soil caused a reduction in pH which was most pronounced for the case of pH 10.5 where the pH dropped three units in the presence of 1.0 g l⁻¹ soil antifoam and 40×10⁻⁴ M calcium (see in section 5.2.1.1). Lowering the concentration of sebum soil will reduce this effect and will drive the conversion to calcium soap closer to completion. A more effective
antifoam effect will therefore be produced if that effect is determined by formation of calcium soaps (or even sodium soaps) in this context.

![Graph showing foamability and foam stability](image)

Fig.5.6. Foamability and foam stability by cylinder shaking of $2.0 \times 10^{-3}$ M NaLAS, at $1.7 \times 10^{-2}$ M NaCl, in the presence of $0.25$ g l$^{-1}$ sebum soil antifoam and at Temperature of $25 \pm 1$ °C. (a) immediately after shaking for 10 s; (b) after standing for 10 min; ▲ pH 3; ■ pH 7; ◆ pH 10.5.

Plots of $F$ against calcium concentration at various pH values shown in Fig. 5.7 reveal that the increase in $F$ with increasing concentrations of calcium in the micellar-precipitate region of the precipitation phase diagram found at $1.0$ g l$^{-1}$ is absent. Nevertheless at high
calcium concentrations (Ca$^{2+}$: 40×10$^{-4}$ M) in this region $F$ is higher for pH 7 and 10.5 than at pH 3 as is found for 1.0 g l$^{-1}$ sebum soil antifoam (as shown in Fig.5.7 (a)). It seems probable that this behaviour may also be attributable to removal of calcium from Ca(LAS)$_2$ precipitate to form calcium soap. Such an effect will be less significant of course with lower sebum soil antifoam levels so that, although $F$ does not increase at high calcium concentrations for dispersions prepared at pH 7 and 10.5, the order of $F$ with respect to dispersions at pH 3 is reversed.

**Fig.5.7.** $F$ profile by cylinder shaking of 2.0×10$^{-3}$ M NaLAS, at 1.7×10$^{-2}$ M NaCl, in the presence of 0.25 g l$^{-1}$ sebum soil antifoam and at Temperature of 25±1 °C. (a) immediately after shaking for 10 s; (b) after standing for 10 min; ▲ pH 3; ■ pH 7; ◆ pH 10.5.
Foamability and foam stability of $2.0 \times 10^{-3}$ M NaLAS in the presence of 0.25 g l$^{-1}$ sebum soil antifoam was also measured using the tumbling tube rotation method. Results are presented in Fig. 5.8 and the corresponding $F$ values are shown in Fig. 5.9. A marked antifoam effect of sebum soil is seen under all pH and Ca$^{2+}$ concentration conditions. The effect of pH has little effect on foamability. However foam stability is seen to be relatively strongly dependent upon pH. Low foam stability in the presence of sebum soil at pH 7 and 10.5 again suggests a role for calcium soap precipitation under these conditions.

Fig. 5.8. Foamability and foam stability by tumbling tube rotation of $2.0 \times 10^{-3}$ M NaLAS, at $1.7 \times 10^{-2}$ M NaCl, in the presence of 0.25 g l$^{-1}$ sebum soil antifoam and at Temperature of 25±1 °C. (a) immediately after 10 rotations; (b) after standing for 10 min; ▲ pH 3; ■ pH 7; ♦ pH 10.5.
Fig.5.9. $F$ profile by tumbling tube rotation of $2.0 \times 10^{-3}$ M NaLAS, at $1.7 \times 10^{-2}$ M NaCl, in the presence of $0.25$ g l$^{-1}$ sebum soil antifoam and at Temperature of $25 \pm 1$ °C. (a) immediately after 10 rotations; (b) after standing for 10 min; ▲ pH 3; ■ pH 7; ◆ pH 10.5.
5.2.4 Foam Behaviour in the Presence of Antifoam at Constant pH

As described in section 5.2.1.1, the addition of sebum soil antifoam under alkaline conditions will cause a decrease of pH in the absence of Ca\(^{2+}\), because of reaction of fatty acids in the sebum soil with hydroxylate ions. The decrease is more marked in the presence of Ca\(^{2+}\) because the equilibrium is driven by removal of carboxylate as calcium soap. Detergent powder formulations usually contain sodium carbonate as buffer to maintain the pH level at around 10 to 10.5 during the washing process, mainly for enhancing the overall cleaning performance [7]. This condition was simulated by adjusting the pH to 7 and 10.5 after mixing sebum soil antifoam into solutions until it became constant for 20 minutes. It is believed that under this condition conversion to calcium soap will if anything be increased.

Foamability and foam stability of 2.0\(\times\)10\(^{-3}\) M NaLAS in the presence of 0.25 g l\(^{-1}\) sebum soil antifoam were for example measured by cylinder shaking at constant pHs of 7 and 10.5. Results are presented in Fig.5.10 and Fig.5.11 respectively, where they are compared with these obtained where the pH was adjusted before addition of sebum soil. No significant difference in the foam behaviour is observed in this comparison. It seems that the antifoam efficiency of sebum soil is only slightly changed, even when more calcium soap is expected to form at this constant pH. This observation implies that essentially complete conversion to soap of the fatty acid present in the sebum soil was achieved by a procedure which did not involve maintaining a constant pH during dispersion of the soil.
**Fig.5.10.** Foamability and foam stability by cylinder shaking of 2.0×10⁻³ M NaLAS at 20×10⁻⁴ M Ca²⁺, 1.7×10⁻² M NaCl, and 0.25 g l⁻¹ sebum soil antifoam at pH 7 and Temperature of 25±1 °C. (a) immediately after shaking for 10 s; (b) after standing for 10 min; □ pH adjusted before mixing with sebum soil antifoam; ■ pH adjusted after mixing with sebum soil antifoam.
Fig.5.11. Foamability and foam stability by cylinder shaking of $2.0 \times 10^{-3}$ M NaLAS at $20 \times 10^{-4}$ M Ca$^{2+}$, $1.7 \times 10^{-2}$ M NaCl, and 0.25 gl$^{-1}$ sebum soil antifoam at pH 10.5 and Temperature of $25 \pm 1$ °C. (a) immediately after shaking for 10 s; (b) after standing for 10 min; □ pH adjusted before mixing with sebum soil antifoam; ■ pH adjusted after mixing with sebum soil antifoam.
5.3 Behaviour of Sebum Soil as Antifoam

5.3.1 Antifoaming Behaviour of Oil or Particles Alone

To understand the defoaming mechanism of sebum soil, we started by investigating the antifoaming behaviour of each potential particulate and oil component in sebum soil respectively. Table 5.5 presents the foamability and foam stability results of NaLAS solution at pH 3 and 10.5 in the presence of these oils and particles when used alone. The $F$ value which is independent of the dimensions of the vessel and allows us to cancel out any difference of foam volumes in the absence of antifoam is used to represent the antifoaming efficiency of these oils and particles. The lower the $F$ values, the more effective the antifoams.

Table 5.5 $F$ profile in cylinder shaking measurement of $2.0 \times 10^{-3}$ M NaLAS, at $1.7 \times 10^{-2}$ M NaCl, in the absence and presence of $5.25 \times 10^{-4}$ M Ca$^{2+}$, at 1.0 g l$^{-1}$ oils or particles dispersed ultrasonically at Temperature of $25 \pm 1$ °C. The error of $F$ is ± 0.01.

<table>
<thead>
<tr>
<th>Antifoam</th>
<th>$F$ after 10s</th>
<th></th>
<th></th>
<th>$F$ after 10 min</th>
<th></th>
<th></th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>pH = 3</td>
<td>pH = 10.5</td>
<td>pH = 3</td>
<td>pH = 10.5</td>
<td></td>
<td></td>
</tr>
<tr>
<td></td>
<td>nil Ca$^{2+}$</td>
<td>with Ca$^{2+}$</td>
<td>nil Ca$^{2+}$</td>
<td>with Ca$^{2+}$</td>
<td>nil Ca$^{2+}$</td>
<td>with Ca$^{2+}$</td>
</tr>
<tr>
<td>Sebum soil</td>
<td>0.2</td>
<td>0.2</td>
<td>0.2</td>
<td>0.2</td>
<td>0.2</td>
<td>0.2</td>
</tr>
<tr>
<td>Hexadecane</td>
<td>1.0</td>
<td>1.0</td>
<td>1.0</td>
<td>1.0</td>
<td>1.0</td>
<td>1.0</td>
</tr>
<tr>
<td>Squalene</td>
<td>1.0</td>
<td>1.0</td>
<td>1.0</td>
<td>1.0</td>
<td>1.0</td>
<td>1.0</td>
</tr>
<tr>
<td>Triolein</td>
<td>1.0</td>
<td>1.0</td>
<td>1.0</td>
<td>1.0</td>
<td>1.0</td>
<td>1.0</td>
</tr>
<tr>
<td>Stearic acid (5%)</td>
<td>1.0</td>
<td>0.9</td>
<td>0.9</td>
<td>1.0</td>
<td>1.0</td>
<td>0.9</td>
</tr>
<tr>
<td>Tristearin (5%)</td>
<td>0.9</td>
<td>0.8</td>
<td>0.8</td>
<td>0.8</td>
<td>0.8</td>
<td>0.8</td>
</tr>
<tr>
<td>Cholesterol (5%)</td>
<td>0.9</td>
<td>0.8</td>
<td>0.9</td>
<td>0.8</td>
<td>0.8</td>
<td>0.8</td>
</tr>
</tbody>
</table>

Sebum soil obviously has a marked antifoam effect under all these conditions. By contrast, none of these oils or particles behaves as an efficient antifoam. In fact, most of them do not function at all as the $F$ values are almost equal to 1.0. This means that there are negligible
changes in the foamability in the presence of these ingredients in NaLAS solutions. That oils alone are not effective concerns the stability of the relevant air-water-oil pseudoemulsion film [8, 9]. Absence of significant antifoam effects by particles of, for example, stearic acid or tristearin suggests that the contact angles at the air-water surfaces are too low. Since all these pure oils and particulate solids are representative of the materials present in sebum soil, it strongly suggests that the latter exhibits typical oil-particle synergy where neither oils nor particulate components are effective alone [3, 10-12].

5.3.2 Oil-Particle Antifoam Synergy

We now sought to find the combination of oils and particles of materials present in sebum soil which give similar antifoam behaviour. In selecting oils we used pure hydrocarbons, a pure triglyceride (triolein) and mixed hydrocarbon and triglyceride. As particulate components, we selected stearic acid as the fatty acid and tristearin as the triglyceride, where the former would simulate the sensitivity to pH and Ca$^{2+}$ found with sebum soil. We also included triolein/oleic acid mixtures where the particles are only formed in situ as calcium oleate. The preparation of the relevant mixtures is described in section 3.3.2.1. Antifoam behaviour was measured using cylinder shaking with ultrasonic dispersal of the antifoam (see section 3.3.2.2).

Table 5.6 below presents the $F$ values measured after cylinder shaking for 10 seconds (foamability) and after standing for 10 minutes (foam stability) in the presence of antifoams in $2.0 \times 10^{-3}$ M NaLAS at different pHs and Ca$^{2+}$ concentrations. Results concern the clear micelle region, so effects of Ca(LAS)$_2$ precipitation on surfactant transport are absent. Comparison of results at pH 3 and pH 10.5 illustrates any effect of calcium or sodium soap formation on antifoam effectiveness.
Table 5.6 $F$ profile in cylinder shaking measurement of 2.0×10^{-3} M NaLAS, at 1.7×10^{-2} M NaCl, in the absence and presence of 5.25×10^{-4} M Ca^{2+}, at 1.0 g l^{-1} oil/particle synergistic antifoams dispersed ultrasonically at Temperature of 25±1 °C. The error of $F$ is ± 0.01.

<table>
<thead>
<tr>
<th>Antifoam</th>
<th>(F) after 10s</th>
<th>(F) after 10 min</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>(pH = 3)</td>
<td>(pH = 10.5)</td>
</tr>
<tr>
<td></td>
<td>nil Ca^{2+}</td>
<td>with Ca^{2+}</td>
</tr>
<tr>
<td>Sebum soil</td>
<td>0.2</td>
<td>0.2</td>
</tr>
<tr>
<td>Hexadacane/ Stearic acid (90/5)</td>
<td>0.9</td>
<td>0.7</td>
</tr>
<tr>
<td>Squalene/ Stearic acid (90/5)</td>
<td>0.4</td>
<td>0.6</td>
</tr>
<tr>
<td>Triolein/Oleic acid (90/5)</td>
<td>1.0</td>
<td>1.0</td>
</tr>
<tr>
<td>Triolein/ Stearic acid (90/5)</td>
<td>0.6</td>
<td>0.6</td>
</tr>
<tr>
<td>Triolein/ Stearic acid (90/10)</td>
<td>0.5</td>
<td>0.7</td>
</tr>
<tr>
<td>Triolein/ Stearic acid (85/15)</td>
<td>0.5</td>
<td>0.6</td>
</tr>
<tr>
<td>Triolein/ Stearic acid/Oleic acid (90/5/5)</td>
<td>0.4</td>
<td>0.5</td>
</tr>
<tr>
<td>Triolein/ Stearic acid/Cholesterol (90/5/5)</td>
<td>0.4</td>
<td>0.4</td>
</tr>
<tr>
<td>Triolein/ Tristearin (90/5)</td>
<td>0.3</td>
<td>0.2</td>
</tr>
<tr>
<td>Triolein/ Tristearin/ Stearic acid (90/5/5)</td>
<td>0.1</td>
<td>0.2</td>
</tr>
<tr>
<td>Triolein/ Squalene/Stearic acid (60/30/5)</td>
<td>0.5</td>
<td>0.6</td>
</tr>
<tr>
<td>Triolein/ Squalene/Stearic acid (30/60/5)</td>
<td>0.5</td>
<td>0.7</td>
</tr>
</tbody>
</table>
In general, the antifoam effect of oil/particle mixtures was observed under all pH and hardness conditions with either triolein/stearic acid or triolein/tristearin mixtures. The antifoam behaviour of these mixtures was qualitatively similar to that of sebum soil. However, the tristearin proved to be more effective than stearic acid in promoting the antifoam behaviour of triolein.

Hydrocarbon/fatty acid mixtures were represented by hexadecane/stearic acid and squalene/stearic acid. It is clear from Table 5.6 that the former was weakly effective in diminishing foamability over most conditions. However, curiously foam stabilities in the presence of Ca$^{2+}$, regardless of pH were higher. This may well represent the expected enhancement of resistance to antifoam effects by the reduction in air-water surface tension due to the presence of Ca$^{2+}$ (so that any enhancement of antifoam performance due to calcium soap formation at high pH is eliminated by the effect of changes in surface tension, and therefore contact angle of soap particles). By contrast, squalene/stearic acid was only effective at low pH.

Triglyceride/fatty acid mixtures were represented by triolein/oleic acid and triolein/stearic acid. We found that triolein/oleic acid (90/5) behaves as an antifoam only at pH 10.5 in the presence of Ca$^{2+}$, because calcium oleate soap particulates are expected to form in the surface of triolein, as shown in Fig.5.12 (b). The particles are then able to rupture the air-water-triolein pseudo-emulsion film to promote the emergence of triolein droplets into the air-water surface to break the liquid foam films. This result is consistent with the earlier findings of Zhang, et al. [1, 2].
Fig. 5.12. Images of triolein/oleic acid (90/5) droplets formed in $1.7 \times 10^{-2}$ M NaCl at pH 10.5 and Temperature of 25±1 °C, (a) In the absence of Ca$^{2+}$, (b) In the presence of $5.25 \times 10^{-4}$ M Ca$^{2+}$.

Triolein/stearic acid (90/5) exhibits antifoam effects under all the conditions studied. This antifoaming effect is qualitatively the same as that of sebum soil, but less efficient. Increasing the weight ratio of stearic acid in triolein from 5/90 to 10/90 or 15/85 has negligible impact on the overall antifoam efficiency. This reveals that the synergistic effect between triglyceride oil and the fatty acid particle is realized even at low pH. The effect at pH 3 would appear to be dominated by the crystal habits of the fatty acids and the configurations adopted at the oil-water surface, but not by the amount of particles in the oil droplets at the concentrations studied [8]. Foam volumes or $F$ values are relatively lower at high alkalinity, indicating that the formation of sodium stearate and calcium stearate may make the triolein/stearic acid antifoam more effective by altering the properties of the original stearic acid particle, such as its hydrophobicity, geometry or roughness.

The overall antifoam behaviour was not changed significantly by addition of oleic acid to a triolein/stearic acid (90/5) mixture, except at pH 10.5 and in the absence of Ca$^{2+}$. Higher foamabilities are then generated. A possible reason is a supposed decrease of equilibrium
air-water surface tension due to the presence of oleate ions. The solubility of oleic acid in $2.0\times10^{-3} \text{ M NaLAS}$ at pH 10.5 and $25^\circ\text{C}$ was measured as 0.43 g l$^{-1}$. This means 0.05 g l$^{-1}$ sodium oleate formed from the triolein/oleic acid (90/5) antifoam would be dissolved in solution in the absence of Ca$^{2+}$. However, measurements by Wihelmy plate method showed that the direct addition of 0.05 g l$^{-1}$ oleic acid had no impact on the equilibrium surface tension of NaLAS solution ($2.0\times10^{-3}$ M) at pH 10.5. The reason for this effect in the absence of Ca$^{2+}$ should be further investigated, but one conclusion at least can be made is that triolein/oleic acid/stearic acid (90/5/5) will be no more representative of sebum soil than the binary mixture of triolein/stearic acid alone. Effects of cholesterol on antifoam efficiency of the triolein/stearic acid mixture were negligible.

Triolein/tristearin (90/5) antifoam, among all these options, is seen to best represent sebum soil. Not only does it show an antifoam effect regardless of pH and hardness level, but it also behaves as effectively as sebum soil. In other words, extremely low foam volumes (and low $F$ values) are generated by NaLAS solutions in the presence of both sebum soil and triolein/tristearin mixtures. However, addition of stearic acid to triolein/tristearin further improves the antifoam activity mainly at low pH.

Mixed hydrocarbon/triolein oils with fatty acid could in principle also represent sebum. We therefore selected squalene/triolein mixtures the ratios of 30/60 and 60/30 in combination with stearic acid. However, the presence of squalene produced no improvement in the antifoam efficiency relative to that of triolein/stearic acid. Compared to triolein/stearic acid, squalene/stearic acid only shows an antifoam effect in solutions at pH 3. Stearic acid particles seem to be more effective when they locate in triolein than in the squalene droplets, probably because their oil-water contact angle $\theta_{OW}$ measured through the oil phase in triolein are lower than that measured in squalene. This may make triolein/stearic acid a more efficient oil-particle antifoam.

In summary, hydrocarbon/fatty acid antifoams are not representative of sebum soil due to a lack of overall antifoam effectiveness. Both triolein/stearic acid (90/5) and
triolein/tristearin (90/5) do represent sebum oils in that significant antifoam effects are seen under all pH and Ca$^{2+}$ concentration conditions. The antifoam effect of triolein/stearic acid (90/5) is independent of (i) the oil/particle quantity ratios (no change from triolein/stearic acid 90/5 to 90/10 and 85/15); (ii) the presence of oleic acid; (iii) the presence of cholesterol (5%) and (iv) the modification of the oil phase by introducing hydrocarbon. However, triolein/tristearin (90/5) is more effective than triolein/stearic acid, giving an apparent antifoam effect close to that of sebum soil. The higher efficiency of tristearin particles with respect to fatty acids (or the resulting sodium or calcium soaps formed at high pH) probably concerns their relative effectiveness in rupturing air-water-triolein pseudoemulsion films.

We therefore conclude that mixtures of triolein/stearic acid and triolein/tristearin appear to have many of the antifoam performance characteristics of sebum soil without the complexity of the latter. They therefore represent suitable model systems to establish aspects of the mode of action of sebum soil.

5.4 Effect of Triolein/stearic acid and Triolein/tristearin Antifoams on Foamability and Foam Stability of C$_{12}$ 4-phenyl SO$_3$Na Solutions

Triolein/stearic acid (90/5) and triolein/tristearin (90/5) at 1.0 g l$^{-1}$ were dispersed by Ultra–Turrax in C$_{12}$ 4-phenyl SO$_3$Na solutions (2.0×10$^{-3}$ M). The foamabilities and foam stabilities of these surfactant solutions at pH 3 and 10.5 and in the presence of Ca$^{2+}$ (at a concentration range from 0 to 40×10$^{-4}$ M) were measured by the cylinder shaking method. The addition of both antifoams caused a noticeable decrease in foamability under all pH and Ca$^{2+}$ concentrations. This antifoaming effect of triolein/stearic acid and triolein/tristearin in C$_{12}$ 4-phenyl SO$_3$Na is qualitatively similar to that of sebum soil in NaLAS solutions. A comparison of the foamability and foam stability results of C$_{12}$ 4-phenyl SO$_3$Na solutions in the absence and presence of these antifoams is given by Fig.4.12 vs. Fig.5.13 (in the presence of triolein/stearic acid); and Fig.4.12 vs. Fig. 5.14 (in
the presence of triolein/tristearin).

Triolein/stearic acid antifoam is more effective at pH 10.5 than at pH 3, presumably due to the formation of sodium and calcium stearate soaps at high pH. At Ca$^{2+}$ concentrations up to the precipitation boundary, foam volumes generated by C$_{12}$ 4-phenyl SO$_3$Na at pH 3 are ~15 to 20 cm$^3$ higher than those generated at pH 10.5, as shown in Fig. 5.13 (a). As the Ca$^{2+}$ concentration increases, for example, at 40$\times$10$^{-4}$ M, where Ca$^{2+}$-C$_{12}$ 4-phenyl SO$_3^{-}$ precipitation dominates the foam behaviour, differences in the foamability caused by the changes in antifoam due to increasing of Ca$^{2+}$ concentrations are less significant. No increase in $F$ values in the micellar-precipitate region at pH 10.5 as shown in Fig.5.14 means that this level of fatty acid (5% in triolein comparing 30% in sebum soil) cannot affect the extent of precipitation of Ca(C$_{12}$ 4-phenyl SO$_3$)$_2$ and therefore the intrinsic foamability (unlike the effect of sebum soil on NaLAS foamability under the same conditions (see section 5.2.2)).

Triolein/tristearin has much higher antifoaming efficiency than triolein/stearic acid antifoam at both pH conditions (compare Fig.5.15 with Fig.5.13 and Fig.5.16 with Fig.5.14). Varying the pH from 3 to 10.5 does not cause any change in its antifoaming behaviour because this does not change the properties of the tristearin particles. The foam volumes decrease only slightly 10 minutes later after generation in the presence of both antifoams. This means the antifoams are less efficient under the near-equilibrium conditions where adsorption of surfactants at air-water surfaces is approaching equilibrium levels.
Fig.5.13. Foamability and foam stability by cylinder shaking of $2.0 \times 10^{-3}$ M $\text{C}_{12}$ 4-phenyl $\text{SO}_3\text{Na}$ at $1.7 \times 10^{-2}$ M NaCl, in the presence of 1.0 g l$^{-1}$ triolein/stearic acid antifoam and Temperature of 25±$1$ °C. (a) immediately after shaking for 10 s; (b) after standing for 10 min; ◆ pH 3; ▲ pH 10.5.
Fig. 5.14. $F$ profile by cylinder shaking of $2.0 \times 10^{-3}$ M $C_{12}$-4-phenyl $SO_3Na$, at $1.7 \times 10^{-2}$ M NaCl, in the presence of 1.0 g l$^{-1}$ triolein/stearic acid antifoam and at Temperature of 25±1 $^0C$. (a) immediately after shaking for 10 s; (b) after standing for 10 min; ◆ pH 3; ▲ pH 10.5.
Fig.5.15. Foamability and foam stability by cylinder shaking of 2.0×10⁻³ M C₁₂ 4-phenyl SO₃Na at 1.7×10⁻² M NaCl, in the presence of 1.0 g l⁻¹ triolein/tristearin antifoam and at Temperature: 25±1 °C. (a) immediately after shaking for 10 s; (b) after standing for 10 min; ♦ pH 3; ▲ pH 10.5.
Fig. 5.16. $F$ profile by cylinder shaking of $2.0 \times 10^{-3}$ M C$_{12}$ 4-phenyl SO$_3$Na, at $1.7 \times 10^{-2}$ M NaCl, in the presence of 1.0 g l$^{-1}$ triolein/tristearin antifoam and at Temperature of 25±1°C. (a) immediately after shaking for 10 s; (b) after standing for 10 min; ◆ pH 3; ▲ pH 10.5.
5.5 Discussion and Summary

Sebum soil is an efficient antifoam in NaLAS solutions under all pH and hardness conditions. No optimal high foamability or stability was found at or near the precipitation boundary despite optimally low equilibrium and dynamic surface tensions. This behaviour therefore clearly concerns other properties in the system, ranging from the stability of pseudoemulsion films to the contact angles of particles at the relevant oil-water and air-water surfaces.

Formation of calcium (or even sodium) soaps in sebum soil appears to enhance antifoam effectiveness in some limited cases. However improvements in foam performance accompanying suppression of soap formation at low pH were not striking. That the effectiveness of sebum soil as an antifoam does not therefore apparently require the formation of soaps suggests that the essential physical nature of sebum soil is determined by the presence of solid particles (fatty acids, triglycerides or cholesterol) dispersed in liquid oils (triglycerides, hydrocarbons or mixtures of both). This hypothesis was tested by the use of model antifoams prepared from well-characterized (pure) materials.

Triolein/stearic acid and triolein/tristearin mixtures appear to model much of the basic antifoam behaviour of sebum soil. Both mixtures behave as effective antifoams under all the pH and hardness conditions studied. Trilolein/tristearin is however a more efficient antifoam than triolein/stearic acid. The antifoam performance of triolein/tristearin under the conditions studied appear to be similar to that of sebum soil. We find that the two antifoams triolein/stearic acid and triolein/tristearin appear to exhibit a performance sufficiently close to that of sebum soil to merit their use as model systems in helping to illuminate the mode of action of sebum soil.

Both sodium and calcium soaps will form under conditions of high pH in the mixtures containing fatty acids. This enhances the antifoam effectiveness of triglyceride/fatty acid mixtures, such as triolein/oleic acid and triolein/stearic acid, as shown in Table 5.5. For
triolein/stearic acid mixtures, this enhancement is observed at high pH even in the absence of Ca\(^{2+}\) which means that both sodium and calcium soap formation may be involved. The latter is expected to result in changes in contact angles, surface roughness or even crystal habit of the relevant particles. The exact reason for any change in the antifoam effectiveness of triolein/stearic acid antifoam with increasing pH or Ca\(^{2+}\) concentration is however not clear. By contrast in the case of triolein/oleic acid mixtures, antifoam effects are only observed at high pH and in the presence of Ca\(^{2+}\). Calcium oleate particles which are then formed are able to contribute to oil/particle synergy. Particles would be absent when Ca\(^{2+}\) is absent because oleic acid and triolein are completely miscible liquids.

The antifoam effects of sebum soil in NaLAS solutions, triolein/stearic acid and triolein/tristearin in C\(_{12}\) 4-phenyl SO\(_3\)Na solutions are less pronounced under the near-equilibrium conditions prevailing during foam stability measurements. This suggests that these antifoams function better under the conditions prevailing during foam generation where effective surface ages are low, air-water surface tensions are significantly higher and surfactant adsorption levels lower than equilibrium values.

5.6 References

Chapter 6 Comparison of Foam Measurement Methodologies

6.1 Introduction

The foam measurement technique favoured by P&G is the tumbling tube method. Unfortunately this technique uses 500 cm$^3$ samples of liquid for each measurement as described in section 3.3.1.1. Use of this technique with pure ingredients, such as pure surfactants and antifoam ingredients would become prohibitively expensive. It is therefore desirable to have an alternative technique which requires less material. Here we have selected the cylinder shaking method which requires only 25 cm$^3$ samples for each measurement as described in section 3.3.1.2. This cylinder shaking method has been used to make the foaming profile measurements reported before [1, 2]. However it is clearly necessary to establish whether both methods give similar results and, if not, in which way they differ. Any differences are of relevance for other aims of the project concerning the need for understanding the nature of foam generation by various means so that realistic models and simulations can be made.

In this chapter, we compared the foamability and foam stability of NaLAS solutions in the absence and presence of sebum soil antifoam measured by tumbling tube rotation method with those measured by cylinder shaking method. All the corresponding foam volume and $F$ results can be found in Chapter 4 and 5. Here we have examined the extent to which these methodologies correlate with one and another.

6.2 Comparison of Foam Measurement Methodologies in the Absence of Antifoam

A comparison between foam generation by cylinder shaking and the tumbling tube method is shown in Fig.6.1 for NaLAS solutions (2.0×10$^{-3}$ M) in the absence of antifoam at pH 3,
7 and 10.5 and at calcium concentrations from 0 to $40 \times 10^{-4}$ M.

Fig.6.1. Foamability and foam stability correlation between cylinder shaking and tumbling tube techniques of $2.0 \times 10^{-3}$ M NaLAS in the absence of antifoam, at 0, 8, 20 and $40 \times 10^{-4}$ M Ca$^{2+}$, and $1.7 \times 10^{-2}$ M NaCl and at Temperature of 25±1 °C. Foam volume Results in □ clear micellar region and ■ micellar-precipitate region; (a) immediately after foam generation ceased (b) after standing 10 min.
The correlation appears to lie on two lines. One line has a reasonable correlation coefficient of 0.91 and approximately extrapolates to the origin – all these results lie in the micellar-precipitate region. The other line is vertical and in fact concerns points measured with solutions in which precipitation is absent and for which foamability is maximal. For such solutions the tumbling tube method had no discrimination – all gave essentially the same foam height. By contrast cylinder shaking did discriminate hence the vertical line on plot in Fig. 6.1.

The lack of discrimination with the tumbling tube method concerns the rate of aeration relative to the size of the tubes. If the probability of foam film collapse is relatively low (because of high rates of surfactant transport and/or absence of antifoam), then the whole tube rapidly fills with foam so that aeration ceases. In this circumstance, any discrimination would have to be confined to the number of rotation required before the tubes become full. Here however we used a standard number of rotations throughout and therefore lost discrimination with certain solutions.

Foam volume was stable for at least 10 minutes for most solution conditions. It is not therefore surprising that the correlation between the two foam generation methods in the case of solutions in the micellar-precipitate region remains good for foam stability (after 10 minutes).

6.3 Comparison of Foam Measurement Methodologies in the Presence of Sebum Soil Antifoam

The same comparison has been made for NaLAS solutions containing 0.25 g l⁻¹ sebum soil antifoam in all pH and hardness conditions investigated, measured by both tumbling tube and cylinder shaking techniques (in both the clear micellar region and micellar-precipitate region of the Ca²⁺-LAS⁻ phase diagram). Results are presented in Fig. 6.2.
Fig. 6.2. Foamability and foam stability correlation between cylinder shaking and tumbling tube techniques of $2.0 \times 10^{-3}$ M NaLAS at 0, 8, 20 and $40 \times 10^{-4}$ M Ca$^{2+}$, and $1.7 \times 10^{-2}$ M NaCl and in the presence of 0.25 g l$^{-1}$ sebum soil antifoam and at Temperature of 25±1 °C. (a) immediately after foam generation ceased (b) after standing 10 min.

A linear correlation for foam volume, measured immediately after foam generation ceased, is seen to be reasonable with a correlation coefficient of ~0.94 and an intercept near the origin. However a similar plot for foam volumes measured after the foam has been
standing for 10 minutes reveals a marked deterioration in the correlation – with the correlation coefficient decaying to ~0.65 and a linear plot intercepting the cylinder shaking foam axis. Foams standing in the tumbling tubes would appear to be less stable in the presence of antifoam, especially at pH 7 and 10.5, as shown in Fig.5.8 (b). The origin of this discrepancy could concern differences in the capillary pressure in the foam, differences in bubble sizes and even the surfaces of the vessels (glass for the measuring cylinders and polymethyl methacrylate for the tumbling tubes). Establishing the cause could be instructive for foam evaluation in general and for comparison with consumer habits in particular.

To complete this study, a plot of all foam volume results (in the absence and presence of antifoams) is summarized in Fig.6.3. However, results for foam in the absence of antifoam in the clear micellar region of the precipitation phase diagram are excluded due to the relative absence of discrimination using the tumbling tube method as shown in Fig.6.1.

A good linear correlation is obtained again for foam volumes measured immediately after generation, with a correlation coefficient of ~0.96 and an intercept close to the origin. However when foam volumes after standing for 10 minutes are plotted the correlation coefficient decays to only ~0.82 with an intercept on the cylinder shaking axis. Again then we find that foam volumes are apparently less stable in the tumbling tubes when sebum soil antifoams are present which tend to diminish the correlation.
Fig. 6.3. Foamability and foam stability correlation between cylinder shaking and tumbling tube techniques of 2.0×10^{-3} M NaLAS at 0, 8, 20 and 40×10^{-4} M Ca^{2+} and 1.7×10^{-2} M NaCl, and at Temperature of 25±1 °C. (a) immediately after foam generation ceased (b) after standing 10 min.; ■ in the absence of antifoam; ◆ in the presence of 0.25 g l^{-1} sebum soil antifoam; ▲ in the presence of 1.0 g l^{-1} sebum soil antifoam

The ratio $F$ is calculated as the ratio of the volume of air in foam with antifoam to the volume of air in the foam in the absence of antifoam. If both the foam volume in the absence of antifoam and the foam volume in the presence of antifoam are closely correlated for the two methodologies then $F$ should be also.
Fig.6.4. Correlation of the ratio $F$ for $2.0 \times 10^{-3}$ M NaLAS at 0, 8, 20 and $40 \times 10^{-4}$ M Ca$^{2+}$ and $1.7 \times 10^{-2}$ M NaCl, in the presence of 0.25 g l$^{-1}$ sebum soil antifoam and at Temperature of $25 \pm 1$ $^0$C. (a) immediately after foam generation ceased; (b) after standing 10 min.

Two factors will however cause the correlation with $F$ to weaken. The first simply concerns the accumulation of random errors in estimation of $F$. The second concerns the existence of a limit on foam volume found for the tumbling tube method – a linear correlation with cylinder shaking breaks down at that point (see results for foam volumes in the absence of sebum soil antifoam in the clear micellar region in Fig. 4.8). Calculation of $F$ will clearly not correlate with those obtained by cylinder shaking for situations which
give this behaviour. A plot of $F$ for all surfactant solutions in the presence of 0.25 gl$^{-1}$ sebum soil antifoam is shown in Fig.6.4 (derived from all the results given in Fig.4.8 and Fig.5.8). The correlation of $F$ estimated for both methodologies is seen to be not unexpectedly poor with a correlation coefficient of only $\sim$0.6 as a consequence of these two factors. When $F$ is calculated from foam volumes remaining after standing for 10 minutes the correlation further deteriorates with a correlation coefficient of only 0.5. This deterioration is of course a consequence of superimposition of the effect of lower foam stability in the tumbling tube on the other factors which reduce the correlation coefficient.

6.4 Poor Correlation Between Methodologies in Foam Stability Measurement

Comparison of foamability measurements by cylinder shaking and tumbling tube revealed a good correlation, both in the absence and presence of sebum soil antifoam. Comparison of foam stability measurements in the presence of sebum soil antifoam by the two chosen methods however revealed a marked deterioration in the correlation. This is attributable to differences in the effect of sebum soil antifoam on the stability of foam films generated by the two different methodologies.

6.4.1 Effect of Capillary Pressure on Antifoam Behaviour

A possible reason for this difference concerns different Laplace pressures in the Plateau border of the foam column, which could impact the antifoam effectiveness (if the critical capillary pressure for emergence of antifoam droplets is not achieved). According to Equation (2.14), the capillary pressure in the Plateau borders at equilibrium (after drainage has ceased) is given by the hydrostatic head, $\rho g H$, where $H$ is height of the foam column measured from the bottom layer of bubbles. We have therefore measured $H$ as a function of time for both cylinder shaking and tumbling tube methodologies.

The solution selected was $2.0 \times 10^{-3}$ M NaLAS in $1.7 \times 10^{-2}$ M NaCl and $8.0 \times 10^{-4}$ M Ca$^{2+}$.
pH 10.5 with 0.25 g l\(^{-1}\) sebum soil antifoam. The foam of this solution is stable in the absence of antifoam when generated by either tumbling tube or cylinder shaking. However, the presence of 0.25 g l\(^{-1}\) sebum soil antifoam reduces foam stability with both methodologies, but the effect is more marked with tumbling tubes than with cylinder shaking as reviewed by comparison of Fig 5.7 with Fig.5.9.

Changes in foam height with both cylinder shaking and tumbling tube methodologies were followed for 2 hours after foam generation ceased. With the tumbling tube, the amount of solution in the tube was varied using both 250 ml and 500 ml of solution (where the latter has been used for most of the work described here).

![Fig.6.5.](image)

**Fig.6.5.** (a) Measurement of foam height in tumbling tubes and cylinders; (b) Comparison between foam heights for cylinder shaking and tumbling tube methodologies with \(2.0 \times 10^{-3}\) M NaLAS at \(1.7 \times 10^{-2}\) M NaCl, \(8.0 \times 10^{-4}\) M Ca\(^{2+}\) at pH 10.5 and in the presence of 0.25 g l\(^{-1}\) sebum soil antifoam and Temperature of 25±1 °C; ▲ after cylinder shaking of 25 ml solution for 10s; ■ after 10 rotations of 500 ml solution in tumbling tubes; ♦ after 10 rotations of 250 ml solution in tumbling tubes.

Foam heights as a function of time are presented in Fig.6.5. With cylinder shaking, the foam height declines for 30 minutes from a starting point of \(~7.5\) cm until it reaches an
equilibrium height of ~5 cm. With the tumbling tube method, the height of foam generated by 500 ml surfactant solution was double that with 250 ml solution. Foam with the latter was stable – no changes of foam height at ~2 cm for the next 2 hours after the generation. Foam with 500 ml solution immediately started collapsing after generation and reached the same equilibrium height of ~2 cm after 40 minutes. The hydrostatic head corresponding to the equilibrium height with the cylinder (~400 Pa for foam height ~ 4.0 cm) is higher than that in the tumbling tube, which is around 200 Pa (foam height ~ 2.0 cm). The higher capillary pressure with the foam in the cylinder shaking method should mean a less stable foam if this is the cause of the apparent difference in foam stability with the two methodologies. However, it seems possible that the convergence on the same foam height after prolonged standing in the case of the two tumbling tube experiments (with different volumes of solution) does suggest an effect due to differences in capillary pressure. Foam is stable at a height of 2 cm (~ 200 Pa) but unstable at 4 cm (~ 400 Pa). Foam collapse as a result of antifoam action then occurs at capillary pressure greater than 200 Pa and ceased at capillary pressure ≤ 200 Pa.

### 6.4.2 Effect of Antifoam on Bubble Size Distribution

Another possible explanation for this difference in foam stability between tumbling tube and cylinder shaking technique concerns differences in sizes of bubbles generated by these two methodologies. Bubble sizes formed in the tumbling tubes are in fact significantly larger than those in the cylinders, especially at the top of the foam column as shown in Fig.6.6. The presence of a greater proportion of larger bubbles will mean a higher probability of the sebum soil antifoam droplets being trapped in foam films. Not only will the total number of antifoam droplets initially present be greater, the larger the film, but the rate of decrease due to drainage will be slower. Thus the rate of drainage of a foam film is slower the larger the film – in the case of Reynolds flow for example, the rate of drainage is inversely proportional to the square the film radius of a cylindrical film [3]. Therefore larger bubbles will experience a higher probability of rupture by antifoam droplets [4]. This factor is of course of greater importance as foam films drain during foam stability
measurement. If then the bubble sizes in a foam are greater, then it should tend to mean a lower stability in the presence of antifoam.

Fig. 6.6. Foams formed by shaking and rotation of $2.0 \times 10^{-3}$ M NaLAS at $1.7 \times 10^{-2}$ M NaCl, $8.0 \times 10^{-4}$ M Ca$^{2+}$ and in the presence of 0.25 g l$^{-1}$ sebum soil antifoam at pH 10.5 and Temperature of $25 \pm 1$ °C; (a) 25 ml solution immediately after shaking in cylinders for 10s; the scale bar represents 2.5 cm; (b) 500 ml solution immediately after 10 rotations in tumbling tubes; the scale bar represents 9 cm; (c) Comparison of bubbles in the upper layer of foam in the tumbling tube and cylinder; the scale bar represents 2.5 cm.

Quantification of bubble size distributions with both cylinder shaking and tumbling tube rotation methodologies was not possible because of the difficulty of obtaining images of the necessary high quality for use by image analysis software. However we can at least establish whether the sebum soil can preferentially rupture larger bubbles by utilizing the specially designed Ross-Miles facility described in section 3.3.4.3. A comparison of size distribution of bubbles formed by generation of $2.0 \times 10^{-3}$ M NaLAS solution, at pH 3 in the absence of antifoam vs. that in the presence of 1.0 g l$^{-1}$ sebum soil antifoam has been made.
The results are presented in Fig. 6.7, where the bubble radii ($R$) are calculated from the apparent areas, $A$, subtended by bubbles at the surface of observation by assuming $R = \sqrt{A/\pi}$. A Log-normal size distribution is presented in Fig. 6.7. Bubbles formed in the absence of antifoam mainly distribute in a radius range from 0.33 to 1.8 mm. These large-size bubbles, however, are not found in the presence of sebum soil antifoam, and the size distribution is skewed towards smaller radii of between 0.03 to 0.33 mm. This obviously indicates that larger bubbles are more vulnerable to rupture by antifoam.

**Fig. 6.7.** Bubble size distribution measured by Ross-Miles method in $2.0 \times 10^{-3}$ M NaLAS, at $1.7 \times 10^{-2}$ M NaCl, in the absence of Ca$^{2+}$, at pH 3 and Temperature of 25±1°C; (a) in the absence of antifoam; (b) in the presence of 1.0 g l$^{-1}$ sebum soil antifoam.
6.5 Summary

The foamabilities (i.e. initial foam volumes) measured by cylinder shaking and tumbling tube methods correlate with a coefficient of $\geq 0.95$ for many systems both in the absence and presence of sebum soil antifoam. These two methodologies differ significantly in dimensionality, but are both characterised by high Reynolds numbers ($>10^5$).

This correlation deteriorates with foam stability measurement using these two methodologies as indicated by a correlation coefficient of only $\sim 0.82$. The reason cannot be related to differences in hydrostatic head with these methodologies. It is possible however that the deterioration in correlation concerns differences in bubble sizes. Larger bubbles in the case of the tumbling tube methodology mean larger concentrations of antifoam in film during drainage and therefore a greater probability of foam film rupture and lower overall foam stability.

6.6 References

Chapter 7 Antifoam Mechanism of Triolein/Stearic acid and Triolein/Tristearin Mixtures

7.1 Introduction

As concluded in Chapter 5, triolein/stearic acid and triolein/tristearin are found to be the best oil/particle antifoam models to simulate the antifoam behaviour of sebum soil as both of them show an antifoam effect at all pH conditions studied in both the absence and presence of Ca\(^{2+}\). However, neither of these fatty acid and triglyceride crystalline particles or triolein oil can cause any foam film rupture when used alone. This suggests a synergistic effect between the oil and the particles, which determines the overall antifoam effectiveness of sebum soil. Elucidation of the possible antifoam mechanisms of triolein/stearic acid and triolein/tristearin mixtures will provide some indication of why sebum soil behaves as an efficient antifoam.

In this chapter, we first present a study of the role of the triolein oil in these two oil/particle synergistic antifoams. This includes the measurement of the spreading behaviour of sebum soil, triolein/stearic acid and triolein/tristearin mixtures at air-water surfaces under both equilibrium and dynamic conditions together with the equilibrium entry, spreading, and bridging coefficients of triolein oil at air-water surfaces for comparison with antifoam behaviour.

Studies of the role of stearic acid and tristearin crystalline particles in oil/particle synergistic antifoams are also presented here. Of special interest is the role of these two types of crystalline particles in rupturing the air-water-air foam films and air-water-oil pseudoemulsion films. This has been facilitated by observation of crystal habits and measurement of relevant contact angles.
7.2 Role of Oils in Oil/Particle Synergistic Antifoams

As we have shown in Chapter 5, presence of triolein oil droplets alone in NaLAS solutions does not cause any antifoam effect. Triolein droplets need to enter the air-water surfaces in order to rupture an air-water-air foam film by for example the “bridging-stretching” mechanism described in Chapter 2. The ineffectiveness of triolein droplets in foam film rupture could be attributed to a condition where the equilibrium entry coefficient $E_e = 0$. However, even if $E_e > 0$, the probable metastability of the air-water-oil pseudoemulsion film may prevent entry of the droplets. Rupture of such films is the main role of the particulate component of these mixed antifoams [1]. We have therefore determined the equilibrium entry coefficient for the triolein component of the model antifoams in the relevant surfactant solutions under different conditions of pH and Ca$^{2+}$ concentrations. This requires knowledge of any tendency of the surfactant solution to spread over the oil-air surface.

Once the oil has entered, the air-water surface may cause foam film rupture by either Marangoni spreading or by the bridging-stretching mechanism. In order to establish whether the former mechanism plays a role, we have directly measured the spreading behaviour of these antifoams on the air-water surfaces of relevant surfactant solutions. In addition, we have determined the equilibrium spreading and bridging coefficients of the oil component of these model antifoams – triolein. The equilibrium bridging coefficient gives indication of whether the bridging-stretching mechanism can prevail under equilibrium conditions (which are likely to be approached as a foam ages during foam stability determination).

7.2.1 Spreading Effect of Surfactant Solutions at Oil-Air Surfaces

The spreading behaviour of surfactant solutions at the oil-air surface has been studied. In this experiment, a drop of aqueous solution was added to the air-oil surface of triolein. The effect on the air-oil surface tension was monitored by the Wilhelmy plate technique. This
may provide some indication of the entry behaviour of triolein droplets into air-water surfaces under equilibrium conditions. If $E > 0$, no spreading over the oil by the surfactant solution will be found; if however $E = 0$, a stable duplex air-water-oil pseudoemulsion film will form, which would imply that the oil is perfectly wetted in by surfactant solution.

Results of oil-air equilibrium surface tensions after the addition of NaLAS and C_{12} 4 phenyl-SO_3Na droplets are presented in Fig.7.1 and Fig.7.2 respectively. In both cases, negligible changes of oil-air surface tensions were seen in the absence of Ca^{2+}. However, surfactant solutions containing 5.25×10^{-4} M calcium ions tend to spread on the oil-air surfaces, reducing the surface tensions by ~4 mN m^{-1}. This means that calcium ions, which increase the surface activity of surfactant solutions, may cause a decrease of the equilibrium entry coefficient of triolein droplets from positive to close to zero, where the latter implies that the triolein will be perfectly wetted by the solution. Varying the pH did not change the spreading behaviour of surfactant solution droplets at the oil-air surface, as shown in Table 7.1 and Table 7.2.
Fig. 7.1. Oil-air equilibrium surface tension after the addition of NaLAS solution droplets at $2.0 \times 10^{-3}$ M, in the presence of $1.7 \times 10^{-2}$ M NaCl, and at Temperature of $25 \pm 1$ °C; (a) pH 3, in the absence of Ca$^{2+}$; (b) pH 10.5, in the presence of $5.25 \times 10^{-4}$ M Ca$^{2+}$. 
**Fig. 7.2.** Oil-air equilibrium surface tension after the addition of C₁₂₄ phenyl-SO₃Na solution droplets at 2.0×10⁻³ M, in the presence of 1.7×10⁻² M NaCl, and at Temperature of 25±1 °C; (a) pH 3, in the absence of Ca²⁺; (b) pH 10.5, in the presence of 5.25×10⁻⁴ M Ca²⁺.
7.2.2 Spreading Effect of Antifoam Oils at Air-Water Surfaces

One possible explanation for the antifoam effect of oils concerns Marangoni spreading in foam films, giving rising to foam film collapse by the so-called “spreading-fluid entrainment” antifoam mechanism (see Fig. 2.18.). Such spreading has however been shown to be an unnecessary requirement for antifoam action [2]. Indeed unequivocal evidence that it does represent a mode of action of such oils is lacking [1, 3, 4]. Nevertheless we must explore the possibility that it plays a role in the case of the oil-based antifoams considered here.

The spreading behaviour of sebum soil antifoam under dynamic conditions prevailing in the foamability measurement was first studied. A comparison of the dynamic surface tensions of NaLAS solutions measured in the absence and presence of sebum soil antifoam is shown in Fig. 7.3. Results for NaLAS solution at pH 3 in the absence of Ca$^{2+}$ and pH 10.5 in the presence of Ca$^{2+}$ are presented in Fig 7.3 (a) and (b) respectively. If the sebum soil spreads under the dynamic condition, a decrease of air-water surface tension should be seen at a given surface age. Only slight increase in dynamic surface tension caused by the presence of antifoam in both conditions as measured reveals that the spreading behaviour of antifoam is absent.

Under the near-equilibrium condition prevailing in the foam stability measurement, the addition of sebum soil droplets does not cause any significant decrease of the air-water surface tension by spreading either. Results of equilibrium surface tensions for NaLAS solution at pH 3 in the absence of Ca$^{2+}$ and pH 10.5 in the presence of Ca$^{2+}$ are presented in Fig.7.4 (a) and 7.4(b) respectively. Marangoni spreading would therefore not appear to be an aspect of the mode of action of sebum soil antifoam in either foamability or foam stability measurement.
Fig. 7.3. Dynamic surface tension of $2.0 \times 10^{-3}$ M NaLAS, at $1.7 \times 10^{-2}$ M NaCl and Temperature of $25 \pm 1$ °C; (a) pH 3, in the absence of Ca$^{2+}$; (b) pH 10.5, in the presence of $5.25 \times 10^{-4}$ M Ca$^{2+}$; ◇ in the absence of antifoam; ◆ in the presence of 1.0 g l$^{-1}$ sebum soil antifoam.
Fig. 7.4. Equilibrium surface tension after the addition of sebum soil antifoam at 1.0 g l⁻¹ onto the air-water surface in the conditions of 2.0×10⁻³ M NaLAS, at 1.7×10⁻² M NaCl, and Temperature of 25±1 °C; (a) pH 3, in the absence of Ca²⁺; (b) pH 10.5, in the presence of 5.25×10⁻⁴ M Ca²⁺.

The spreading behaviour of triolein/stearic acid and triolein/tristearin under dynamic conditions was measured by comparing the dynamic surface tension of a dispersion of the antifoam in surfactant solution with the solution in the absence of antifoam. Results for NaLAS solution at pH 3 in the absence of Ca²⁺ and pH 10.5 in the presence of Ca²⁺ are
given in Fig. 7.5 and Fig. 7.6 for triolein/stearic acid and triolein/tristearin respectively. The dynamic surface tension is seen to be unaltered by the presence of antifoam in both cases. A decrease in the dynamic surface tension would at a given surface age be expected if the antifoam spread under this condition.

![Graph](image)

**Fig. 7.5.** Dynamic surface tension of $2.0 \times 10^{-3}$ M NaLAS, at $1.7 \times 10^{-2}$ M NaCl, and Temperature of $25 \pm 1$ °C; (a) pH 3, in the absence of Ca$^{2+}$; (b) pH 10.5, in the presence of $5.25 \times 10^{-4}$ M Ca$^{2+}$; ◇ in the absence of antifoam; ● in the presence of 1.0 g l$^{-1}$ triolein/stearic acid antifoam.
**Fig. 7.6.** Dynamic surface tension of $2.0 \times 10^{-3}$ M NaLAS, at $1.7 \times 10^{-2}$ M NaCl and Temperature of $25 \pm 1^\circ C$; (a) pH 3, in the absence of Ca$^{2+}$; (b) pH 10.5, in the presence of $5.25 \times 10^{-4}$ M Ca$^{2+}$; ◇ in the absence of antifoam; ◆ in the presence of 1.0 g l$^{-1}$ triolein/tristearin antifoam.

Addition of droplets of triolein/stearic acid and triolein/tristearin to the equilibrium air-water surfaces of surfactant solution was done to establish whether spreading could occur under the near-equilibrium condition prevailing during foam stability measurement. Results for NaLAS solution at pH 3 in the absence of Ca$^{2+}$ and pH 10.5 in the presence of
Ca$^{2+}$ are presented in Fig. 7.7 and 7.8 for triolein/stearic acid and triolein/tristearin respectively. No evidence of spreading is apparent. However we should note that, as described in section 7.1.1, in the presence of Ca$^{2+}$, the triolein cannot enter into the air-water surface because it is preferentially wetted by the surfactant solution. It therefore is difficult to see how these antifoams *could* spread in this circumstance.

**Fig. 7.7.** Equilibrium surface tension after the addition of triolein/stearic acid at 1.0 g l$^{-1}$ onto the air-water surface in the conditions of 2.0×10$^{-3}$ M NaLAS, at 1.7×10$^{-2}$ M NaCl, and Temperature of 25±1 °C; (a) pH 3, in the absence of Ca$^{2+}$; (b) pH 10.5, in the presence of 5.25×10$^{-4}$ M Ca$^{2+}$. 
Fig. 7.8. Equilibrium surface tension after the addition of triolein/tristearin at 1.0 g l\(^{-1}\) onto the air-water surface in the conditions of \(2.0 \times 10^{-3}\) M NaLAS, at \(1.7 \times 10^{-2}\) M NaCl, and Temperature of 25±1 °C; (a) pH 3, in the absence of Ca\(^{2+}\); (b) pH 10.5, in the presence of \(5.25 \times 10^{-4}\) M Ca\(^{2+}\).
7.2.3 Comparison of Antifoam Behaviour with Entry, Spreading and Bridging Coefficient Measurement

Equilibrium entry, spreading and bridging coefficients of triolein oil in NaLAS solutions (2.0×10⁻³ M) at pH 3, 7 and 10.5 in the absence and presence of Ca²⁺ can be calculated based on the air-water, oil-water and air-oil surface tension values by the equations of (2.19), (2.20) and (2.22) respectively. Here the final equilibrium air-water surface tension (γ_{AW}^e) should be equal to the initial value (γ_{AW}^i = γ_{AW}^e). This is revealed by the measurement with the Wilhelmy plate method in Fig. 7.9 that the presence of triolein oil droplets at the air-water surfaces does not cause any reduction of the equilibrium surface tensions. The oil-water and oil-air surface tensions are also measured after equilibration by pendant drop method and Wilhelmy plate method respectively as described in section 3.3.4. As shown in Fig. 7.1 and 7.2, the oil-air surface tension does not change after the saturation with NaLAS and C₁₂ 4 phenyl-SO₃Na solutions in the absence of Ca²⁺, but decreases in the presence of Ca²⁺.

Table 7.1 presents the equilibrium air-water, oil-water and air-oil surface tension values as measured at different pH and Ca²⁺ concentration conditions and their corresponding entry, spreading and bridging coefficients. In the presence of Ca²⁺, the oil-water, air-water and oil-air surface tensions are reduced because of an increase in surface activity [5]. The equilibrium entry coefficients calculated are positive in the absence of Ca²⁺ and close to zero in the presence of Ca²⁺. These entry coefficients correlate with the measurements shown in Fig.7.1 which imply entry coefficients of zero in the presence of Ca²⁺. Equilibrium spreading coefficients calculated under all conditions are negative. This is not surprising since there is no spreading effect caused by triolein droplets at the air-water surfaces as observed in the measurement shown in Fig. 7.9.
Fig. 7.9  Equilibrium surface tension after the addition of triolein droplet onto the air-water surface in the conditions of $2.0 \times 10^{-3}$ M NaLAS and at $1.7 \times 10^{-2}$ M NaCl, and Temperature of $25 \pm 1$ °C; (a) pH 3, in the absence of Ca$^{2+}$; (b) pH 10.5, in the presence of $5.25 \times 10^{-4}$ M Ca$^{2+}$.

Bridging coefficients calculated in all the conditions are negative. This means that the triolein/stearic acid and triolein/tristearin antifoams will be ineffective under near-equilibrium conditions. Absence of significant antifoam effects on foam stability with these antifoams shown in Fig.5.13 and Fig.5.15 is consistent with this expectation. However, under the dynamic conditions prevailing during foam generation, we could expect the dynamic surface tensions to be higher than the equilibrium values. If then the
dynamic surface tension is sufficiently high, we could find $B_d > 0$, so that foam film rupture by bridging-stretching becomes in principle possible. For example if we (unreasonably) suppose that an oil-water interfacial tension remains constant under dynamic condition, an increase in the air-water surface tension of greater than 0.2 mN m$^{-1}$ only is required to produce $B_d > 0$ in the absence of Ca$^{2+}$ and at pH 3. However, in the presence of Ca$^{2+}$, a surface tension of greater than 0.8 mN m$^{-1}$ is required.

Table 7.1 Equilibrium Entry, Spreading and Bridging coefficients of Triolein oil in 2.0×10$^{-3}$ M NaLAS, at 5.25×10$^{-4}$ M Ca$^{2+}$, 1.7×10$^{-2}$ M NaCl, and Temperature of 25±1 °C.

<table>
<thead>
<tr>
<th>NaLAS Solutions</th>
<th>$\gamma_{AW}^e$ (mN m$^{-1}$)</th>
<th>$\gamma_{OW}^e$ (mN m$^{-1}$)</th>
<th>$\gamma_{OA}^e$ (mN m$^{-1}$)</th>
<th>$E^e$ (mN m$^{-1}$)</th>
<th>$S^e$ (mN m$^{-1}$)</th>
<th>$B$ (mN$^2$ m$^{-2}$)</th>
</tr>
</thead>
<tbody>
<tr>
<td>pH 3</td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>nil Ca$^{2+}$</td>
<td>31.5</td>
<td>3.0</td>
<td>31.8</td>
<td>+2.8</td>
<td>-3.2</td>
<td>-9.99</td>
</tr>
<tr>
<td>with Ca$^{2+}$</td>
<td>27.8</td>
<td>1.4</td>
<td>28.6</td>
<td>+0.6</td>
<td>-2.2</td>
<td>-43.16</td>
</tr>
<tr>
<td>pH 7</td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>nil Ca$^{2+}$</td>
<td>31.2</td>
<td>4.0</td>
<td>31.6</td>
<td>+3.6</td>
<td>-4.4</td>
<td>-9.12</td>
</tr>
<tr>
<td>with Ca$^{2+}$</td>
<td>27.4</td>
<td>1.4</td>
<td>28.2</td>
<td>+0.6</td>
<td>-2.2</td>
<td>-42.52</td>
</tr>
<tr>
<td>pH 10.5</td>
<td></td>
<td></td>
<td></td>
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<td></td>
<td></td>
</tr>
<tr>
<td>nil Ca$^{2+}$</td>
<td>31.1</td>
<td>4.1</td>
<td>31.6</td>
<td>+3.6</td>
<td>-4.6</td>
<td>-14.54</td>
</tr>
<tr>
<td>with Ca$^{2+}$</td>
<td>27.4</td>
<td>1.3</td>
<td>28.6</td>
<td>+0.1</td>
<td>-2.5</td>
<td>-65.51</td>
</tr>
</tbody>
</table>

Triolein oil droplets however, do not cause any foam film rupture in foamability measurement either (as shown in the foamability results in Table 5.5). This suggests a high entry barrier for triolein droplets to emerge into the air-water surface. The role of stearic acid and tristearin particles in rupturing this air-water-oil pseudoemulsion therefore becomes important, as this would facilitate an emergence of oil droplets into the air-water surfaces allowing a possible bridging-stretching effect. This is discussed in section 7.5.

The air-water, oil-water and air-oil surface tensions of C$_{12}$ 4 phenyl-SO$_3$Na solutions (2.0×10$^{-3}$ M) at pH 3, 7 and 10.5 in the absence and presence of Ca$^{2+}$ (5.25×10$^{-4}$ M) are also measured respectively. Entry, spreading and bridging coefficients calculated based on
these surface tension values provide the same conclusions as those in NaLAS solutions, as shown in Table 7.2. This behaviour explains the relatively high foam stability of C₁₂₄ phenyl-SO₃Na solutions in the presence of triolein/stearic acid and triolein/tristearin at pH 3 and 10.5, as shown in Fig.5.13 and Fig. 5.15.

Table 7.2 Entry, Spreading and Bridging coefficients of Triolein oils at 2.0×10⁻³ M C₁₂₄ phenyl-SO₃Na, and 5.25×10⁻⁴ M Ca²⁺, 1.7×10⁻² M NaCl, and Temperature of 25±1 °C.

<table>
<thead>
<tr>
<th>C₁₂₄ phenyl-SO₃Na Solutions</th>
<th>γₐₜₜ</th>
<th>γₒₒ</th>
<th>γₒₐ</th>
<th>E⁺⁺</th>
<th>S⁺⁺</th>
<th>B</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>(mN m⁻¹)</td>
<td>(mN m⁻¹)</td>
<td>(mN m⁻¹)</td>
<td>(mN m⁻¹)</td>
<td>(mN m⁻¹)</td>
<td>(mN² m⁻²)</td>
</tr>
<tr>
<td>pH 3 nil Ca²⁺</td>
<td>30.9</td>
<td>3.0</td>
<td>31.6</td>
<td>+2.3</td>
<td>-3.7</td>
<td>-34.75</td>
</tr>
<tr>
<td>with Ca²⁺</td>
<td>27.4</td>
<td>1.4</td>
<td>28.2</td>
<td>+0.6</td>
<td>-2.2</td>
<td>-43.28</td>
</tr>
<tr>
<td>pH 7 nil Ca²⁺</td>
<td>30.9</td>
<td>3.8</td>
<td>31.4</td>
<td>+3.3</td>
<td>-4.3</td>
<td>-16.71</td>
</tr>
<tr>
<td>with Ca²⁺</td>
<td>27.4</td>
<td>1.4</td>
<td>28.2</td>
<td>+0.6</td>
<td>-2.2</td>
<td>-43.28</td>
</tr>
<tr>
<td>pH 10.5 nil Ca²⁺</td>
<td>31.2</td>
<td>4.1</td>
<td>31.6</td>
<td>+3.9</td>
<td>-4.3</td>
<td>-8.31</td>
</tr>
<tr>
<td>with Ca²⁺</td>
<td>27.4</td>
<td>1.4</td>
<td>28.3</td>
<td>+0.5</td>
<td>-2.3</td>
<td>-48.17</td>
</tr>
</tbody>
</table>

7.3 Characterization of Stearic Acid and Tristearin Crystals

Saturated long-chain fatty acids and triglycerides are crystalline particles adopting a regular straight-edged shape at room temperature [6]. The crystal structures of these fatty acids and triglycerides grown in the hydrocarbon and triglyceride oil mixtures in sebum soil may be different when compared with those grown in other media as described in the literature [7-10].

As described in 3.3.2.1, sebum soil antifoam received from P&G was prepared by first mixing and heating at a constant temperature of around 72 °C until the solid particles were dissolved. Then the liquid mixture was quickly cooled in an ice water bath with ultrasonic
agitation for 5 minutes. This was to ensure reproducibility, homogenization and decrease of the size of particulate components in the oil phase.

Fig 7.10 shows the image of sebum soil antifoam by optical microscopy with the crossed-polarizers. In this image, some large flake-like crystalline platelets (in a size range from around 100 to 200 microns) together with some small crystalline particles are found to coexist in the mixed oil and hydrocarbon liquid phases. Most of these large crystalline particles tend to grow as agglomerates (the sizes of these agglomerates are several hundred microns), which are possibly composed of a mixture of fatty acid, triglyceride and cholesterol particles (see in Appendix 3.2). Other small particles seem to be well dispersed in the oil/hydrocarbon mixed components.

![Image of sebum soil antifoam](image)

**Fig.7.10.** Optical micrograph of sebum soil antifoam with crossed-polarizers measured at Temperature of 25±1 °C; the scale bar represents 100.0µm; Antifoam was mixed and heated at 72 °C until the solid particles were dissolved, quickly cooled and remixed in an iced ultrasonic water bath for 5 minutes.
7.3.1 Determination of Stearic Acid Particle Size and Crystal Structure

Fig. 7.11 shows an image of stearic acid particles in triolein after rapidly cooling from a melt in ice water bath whilst subject to ultrasonic agitation. Most flake-like lozenge shaped particles tend to grow together to form large agglomerates in the absence of other fatty acid and triglyceride crystalline particles. The sizes of these stearic acid particles have a wide range of dimensions, distributing from 10 to 200μm. However, many small particles (more than 90% according to the particle number distribution, shown in Fig.7.12) are found well-dispersed in triolein. The average dimensions of these smaller particles vary from 1 up to 10μm as measured in this optical micrograph.

Fig.7.11. Optical micrograph of triolein/stearic acid (90/5) antifoam with crossed-polarizers measured at Temperature of 25±1 °C. The scale bar represents 100.0 μm. Antifoam was mixed and heated at 70 °C until the solid particles were dissolved, quickly cooled and remixed in an iced ultrasonic water bath for 5 minutes.
The sizes of stearic acid particles (including those agglomerates), which are larger than 1 micron, can be determined by a simple measurement based on the microscopic images. Here we defined the size of these particles as the average value of the longest dimension and the dimension drawn orthogonal the central point of the longest dimension.

A summary showing the size distributions of stearic acid particles > 1.0 μm is presented in Fig.7.12. Those having an average dimension smaller than 1μm cannot be imaged effectively by optical microscopy. Using a dynamic light scattering Zetasizer Nano (as described in section 3.3.5.2) can measure the size distribution of particles < 1 μm. Stearic acid particles which are smaller than 1 micron, however, are difficult to separate using a suitable one micron hydrophobic fluoropore membrane filter (from Millipore Ltd.). Most of these small particles tend to adhere on the walls of holes of the membrane during the filtration.

**Fig.7.12.** Size distribution of stearic acid particles (≥ 1.0 μm) in triolein oil at Temperature of 25±1 °C. Total number of particles counted > 1000.

As shown in Table 5.5, neither triolein nor stearic acid particles alone in NaLAS solutions have any antifoam effectiveness. Triolein/stearic acid mixtures however, cause a significant foam volume decrease under all pH and hardness conditions, as shown in Table 5.6. In the
case of spherical particles, this type of behaviour can be readily explained, as shown in section 2.2.3, in terms of the contact angles $\theta_{AW}$ and $\theta_{OW}$. Stearic acid particles are however revealed in Fig.7.11 to be clearly non-spherical. They are in fact crystalline particles with sharp edges. A detailed study of the crystal structure of stearic acid particles grown in triolein oil is necessary in order to understand their orientation adopted at the oil-water interface, which may in principle determine their efficiency in rupturing the air-water-oil pseudoemulsion films, and therefore antifoam effectiveness.

Fig.7.13. (a) Optical micrograph of a single stearic acid crystalline particle grown in triolein at 25±1 °C; (b) Electron micrograph of stearic acid crystalline particles grown in triolein at 25±1 °C; The scale bar represents 100.0 μm.
A large single stearic acid crystal has been grown in triolein at 25 °C for one month. An image, shown in Fig. 7.13 (a), was obtained by optical microscopy with crossed-polarizers. The morphology of large stearic acid crystals has also been studied by scanning electron microscopy as shown in Fig. 7.13 (b).

Using these images, it is possible to deduce the approximate crystalline morphology of stearic acid crystallized from triolein. That structure is represented in Fig. 7.14. The main uncertainty here concerns the detailed geometry of the edges of the crystal. Examination of Fig. 7.13 clearly reveals that the edge is not simply a right angle. We therefore approximate by supposing that it is represented by two angles – $90^\circ$ with respect to one crystal plane and $60^\circ$ with respect to the other plane (so that that angle $\gamma$ in Fig 7.14. is $30^\circ$) This will at least establish whether this crystalline particle with sharp edges can in principle give rise to the film destabilisation features exhibited by stearic acid in triolein, which will be discussed in section 7.4.

Fig.7.14. A hypothetical stearic acid crystalline particle growing in triolein at 25±1 °C, where $\alpha = 60^\circ$, $\beta = 120^\circ$, $\gamma = 30^\circ$ and $L = Z$, $H = L/10$. 
7.3.2 Determination of Tristearin Particle Size and Crystal Structure

Dynamic light scattering (DLS) methodology has also been used to measure the size distribution of tristearin particles in triolein. This triolein/tristearin mixed antifoam was again prepared from a melt by the same ultrasonic agitation method in an ice water bath as used for study of the relevant foam behaviour (see section 3.3.2.1). Tristearin particles formed by this method have an average size of < 1 micron, which cannot be measured by the optical microscope. Analytical results in Fig. 7.15, including three times replicated measurements, show that most particles have an equivalent spherical diameter in a range from 0.3 to 0.5μm.

**Fig. 7.15.** Dynamic Light Scattering of a distribution of 0.5% tristearin particles in triolein oil at Temperature of 25±1 °C; particle size as equivalent spherical diameter. Antifoam was mixed and heated at 55 °C until the solid particles were dissolved, quickly cooled and remixed in an iced ultrasonic water bath for 5 minutes.

Images of large tristearin crystals, obtained after the growth for one month in triolein at 25 °C are shown in Fig. 7.16, where Fig. 7.16 (a) is the image measured by the optical microscope and Fig. 7.16 (b) is the image measured by the scanning electron microscope. Unlike stearic acid, tristearin crystalline particles adopt more edges. A typical structure based on these measurements is shown in Fig 7.17.
Fig. 7.16. (a) Optical micrograph of tristearin crystalline particles grown in triolein at 25±1 °C; The scale bar represents 100.0 μm (b) Electron micrograph of tristearin crystalline particles grown in triolein at 25±1 °C; The scale bar represents 20.0 μm.

Fig. 7.17. A typical tristearin crystalline particle growing in triolein at 25±1 °C, where \( \alpha = \beta = \gamma = 130^0 \), \( \theta = 90^0 \) and \( L = Z \gg H \)
7.4 Oil-Particle Antifoam Behaviour

7.4.1 Determination of Size Distribution of Antifoam Droplets in NaLAS Solutions

Sebum soil, Triolein/stearic acid and Triolein/tristearin antifoams at 1.0 g l\(^{-1}\) were dispersed by Ultra–Turrax in NaLAS solution (2.0×10\(^{-3}\) M) at pH 7 and in the absence of Ca\(^{2+}\). Optical micrographs of these emulsified antifoam droplets samples from the surfactant solutions are shown in Fig.7.18 (a), (b) and (c) respectively. The size distribution of antifoam droplets based on optical microscopy is presented in Fig.7.19, which shows only slight differences between these three dispersions. Most droplets have a diameter in the range from 1 to 7 \(\mu\)m. In agreement with the measurement in 5.2.1.2, no changes in the size distribution are expected at pH 10.5, in the presence of Ca\(^{2+}\), where fatty acids are expected to covert to calcium (or sodium) soaps.
Fig. 7.18. Optical micrographs of antifoams (1.0 g l\(^{-1}\)) dispersed in the solution of 2.0×10\(^{-3}\) M NaLAS, in the presence of 1.7×10\(^{-2}\) M NaCl at pH 7 and Temperature of 25±1 °C by Ultra–Turrax. (a) in the presence of sebum soil antifoam; (b) in the presence of triolein/stearic acid (90/5) antifoam; (c) in the presence of triolein/tristearin (90/5) antifoam; The scale bar represents 5.0 μm.
Fig. 7.19. Antifoam droplet size distribution in $2.0 \times 10^{-3}$ M NaLAS, in the presence of $1.7 \times 10^{-2}$ M NaCl at pH 7 and Temperature of 25±1 °C; (a) sebum soil antifoam; (b) triolein/stearic acid (90/5) antifoam; (c) triolein/tristearin (90/5) antifoam. Number of droplets for each antifoam counted $> 300$. 
The large stearic acid crystalline particles are not found in the dispersion as shown in Fig. 7.18 (b). The dimensions of stearic acid particles in any case far exceed the dimensions of the droplets. Stearic acid particles actually formed large agglomerates floating at the air-water surface. These agglomerates were collected and examined using optical microscopy with crossed-polarizers. Relevant images are shown in Fig.7.20.

These large agglomerates are largely irrelevant with respect to foam behaviour – indeed they were often removed before making foam measurements. That they are irrelevant follows because their large size (> 100 μm) means they will be unlikely to be trapped in foam films not only because of their large size but also because of their low concentration. However, the formation of these agglomerates from triolein/stearic acid implies a significant deactivation of this antifoam [11, 12]. This is probably the cause of the lower antifoam efficiency of triolein/stearic acid when compared with that of triolein/tristearin. Smaller crystalline particles can be present in oil droplets of dimensions less than 10 μm without necessarily forming ineffective large agglomerates.

**Fig.7.20.** Stearic acid crystalline agglomerates collected in the solution of 2.0×10⁻³ M NaLAS, in the presence of 1.7×10⁻² M NaCl at pH 7 after dispersion by Ultra–Turrax; The scale bar represents 100.0 μm.
According to the measurement by optical microscopy and the DLS technique (shown in Fig. 7.12 and Fig. 7.15), a large number of small crystalline particles (<10.0 μm in the case of stearic acid; and < 1.0 μm in the case of tristearin) should be present in oil droplets dispersed in solution. It is probable that these stearic acid and tristearin particles are sitting at the oil-water interface or inside the oil droplets but are too small to be seen with optical microscopy. As suggested by the results of foamability in Table 5.5, if the oils and particles are present in the surfactant solutions separately, no antifoam effect should be seen. The fact that triolein/stearic acid and triolein/tristearin act as effective antifoams (see in Table 5.6) indicates the presence of oil/particle mixed droplets in the aqueous phase [1]. A Cryo-electron Microscopy technique has been used but failed to identify the particles at the oil-water interface where ice crystals formed during the sample preparation. These ice crystals were difficult to distinguish from the fatty acid and triglyceride particles.

In the study of antifoam effectiveness of triolein/particle antifoam models (in section 5.3.2), a different dispersion method - ultrasonic agitation was used. This generally has no impact on the droplet size distribution of antifoams compared to that by Ultra–Turrax methodology. An example of sebum soil antifoam droplets dispersed in NaLAS at pH 7 by ultrasonic agitation is shown in Fig. 7.21, where the droplet size distribution is seen to be similar to that shown in Fig. 7.19 (a).
Fig. 7.21. (a) Optical micrographs of sebum soil (1.0 g l⁻¹) dispersed in the solution of 2.0×10⁻³ M NaLAS, in the presence of 1.7×10⁻² M NaCl at pH 7 and Temperature of 25±1 °C by ultrasonic agitation; The scale bar represents 5.0 μm; (b) Sebum soil antifoam droplet size distribution. Number of antifoam droplets counted > 300.

7.4.2 Contact Angles and Emulsion Behaviour

From the previous foaming experiment results (in Table 5.5 and 5.6), we can conclude that both stearic acid and tristearin particles should sit at the oil-water interface when the antifoam mixtures are dispersed in surfactant solutions. Such particles should have the
property of rupturing the air-water-oil pseudoemulsion films which often prevent entry of oil droplets into the air-water surface despite positive entry coefficients. Foam films will only be ruptured only when this condition is satisfied.

Although we have not succeeded in obtaining the images of particles at the oil-water interface using the optical and cryo-electron microscopy techniques, we can still provide some other evidence to support this conclusion. Here we measured the oil-water contact angles on pressed stearic acid and tristearin disks with smooth surfaces using the sessile drop method. We also studied the effect of these two types of crystalline particles on the emulsion behaviour of triolein oil and surfactant solution. The presence of particles which destabilise the air-water-oil pseudoemulsion films should also destabilise the oil-water-oil films which will cause emulsion inversion from oil-in-water to water-in-oil [1].

The air-water contact angles are difficult to measure, as surfactant solution drops tend to spread rapidly at the air-solid surface (both stearic acid and tristearin) once they have been made until the air-solid surface is completely wetted. This indicates a condition of $\theta_{AW} < 90^\circ$ measured through the aqueous phase which is probably due to relatively low air-water surface tensions of these surfactant solutions. Under dynamic conditions, $\theta_{AW}$ would be higher than that measured at equilibrium as a consequence of the relatively high dynamic surface tensions then prevailing.

Table 7.3 and 7.4 present the advancing and receding oil-water contact angles measured through the aqueous phase in NaLAS and C_{12} 4 phenyl-SO_{3}Na solutions at 2.0×10^{-3} M respectively. The solution conditions include pH 3, 7, 10.5 in both the absence and presence of Ca^{2+} (5.25×10^{-4} M). Advancing and receding angles measured in all conditions are higher than 90°. This means that particles at the oil-water interface are preferentially wetted by the oil, as illustrated in the case of a spherical particle in Fig.2.24. The presence of Ca^{2+} causes some decrease of contact angle values generally, as it lowers the oil-water interfacial tensions. Formation of calcium or sodium stearate soaps from stearic acid at pH 10.5 seems to have no impact on the hydrophobicity of surfaces of particles, as only slight
changes of contact angle values are found with different pH conditions.

One disadvantage of this sessile drop method using compressed disks is that the air-water and oil-water contact angles are not measured on the actual surfaces of particles. However, neither a single stearic acid nor a tristearin crystalline particle which are large enough for this measurement can easily be obtained by crystal growth in triolein. However, indications given by the measurement technique here on whether an oil-water contact angle \( \theta_{ow} \) is > 90° or < 90° adopted by these particles are believed to be reliable [2].

**Table 7.3** Oil-water contact angles at 2.0×10⁻³ M NaLAS, in the presence of 5.25×10⁻⁴ M Ca²⁺, 1.7×10⁻² M NaCl, and at Temperature of 25±1 °C measured through the aqueous phase.

<table>
<thead>
<tr>
<th>Oil – NaLAS Solutions</th>
<th>Stearic acid</th>
<th>Tristearin</th>
</tr>
</thead>
<tbody>
<tr>
<td>Contact angle (deg)</td>
<td>Advancing</td>
<td>Receding</td>
</tr>
<tr>
<td>pH 3</td>
<td></td>
<td></td>
</tr>
<tr>
<td>nil Ca²⁺</td>
<td>124 ± 4</td>
<td>124 ± 4</td>
</tr>
<tr>
<td>with Ca²⁺</td>
<td>120 ± 4</td>
<td>120 ± 4</td>
</tr>
<tr>
<td>pH 7</td>
<td></td>
<td></td>
</tr>
<tr>
<td>nil Ca²⁺</td>
<td>122 ± 4</td>
<td>122 ± 4</td>
</tr>
<tr>
<td>with Ca²⁺</td>
<td>120 ± 4</td>
<td>120 ± 4</td>
</tr>
<tr>
<td>pH 10.5</td>
<td></td>
<td></td>
</tr>
<tr>
<td>nil Ca²⁺</td>
<td>130 ± 4</td>
<td>130 ± 4</td>
</tr>
<tr>
<td>with Ca²⁺</td>
<td>116 ± 4</td>
<td>116 ± 4</td>
</tr>
</tbody>
</table>
Table 7.4 Oil-water contact angles at 2.0×10^{-3} M C_{12} 4 phenyl-SO$_3$Na, in the presence of 5.25×10^{-4} M Ca$^{2+}$, 1.7×10^{-2} M NaCl, and at Temperature of 25±1 °C measured through the aqueous phase.

<table>
<thead>
<tr>
<th>pH 3</th>
<th>nil Ca$^{2+}$</th>
<th>124 ± 4</th>
<th>124 ± 4</th>
<th>122 ± 4</th>
<th>110 ± 4</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>with Ca$^{2+}$</td>
<td>120 ± 4</td>
<td>120 ± 4</td>
<td>110 ± 4</td>
<td>104 ± 4</td>
</tr>
<tr>
<td>pH 7</td>
<td>nil Ca$^{2+}$</td>
<td>122 ± 4</td>
<td>122 ± 4</td>
<td>116 ± 4</td>
<td>110 ± 4</td>
</tr>
<tr>
<td></td>
<td>with Ca$^{2+}$</td>
<td>120 ± 4</td>
<td>120 ± 4</td>
<td>116 ± 4</td>
<td>104 ± 4</td>
</tr>
<tr>
<td>pH 10.5</td>
<td>nil Ca$^{2+}$</td>
<td>130 ± 4</td>
<td>130 ± 4</td>
<td>124 ± 4</td>
<td>116 ± 4</td>
</tr>
<tr>
<td></td>
<td>with Ca$^{2+}$</td>
<td>116 ± 4</td>
<td>116 ± 4</td>
<td>125 ± 4</td>
<td>114 ± 4</td>
</tr>
</tbody>
</table>

More evidence that the particles adhere to the triolein/water interface is revealed by the emulsion behaviour. An oil-in-water emulsion, shown in Fig.7.22, is formed when equal volumes of triolein and NaLAS solution are mixed by hand-shaking.

Fig.7.22. Optical micrograph of an oil-in-water emulsion after the triolein is mixed with the solution of 2.0×10^{-3} M NaLAS at pH 3, in the presence of 1.7×10^{-2} M NaCl at equal volumes. The scale bar represents 20.0 μm.

The addition of stearic acid (at the ratio by weight of triolein/stearic acid: 90/5) alters the
emulsion behaviour from oil-in-water to water-in-oil, as shown in Fig. 7.23. This means that stearic acid crystalline particles adhered to the oil-water interface and ruptured the oil-water-oil film to cause an inversion of the emulsified system from oil-in-water to water-in-oil. Stearic acid particles sitting in the oil-water interface then also enhance the stability of this water-in-oil emulsion. This effect of surface active particles on emulsion stabilization was first described by Ramsden [13] and later by Pickering [14]. The same effect of stearic acid on inverting the oil/water to water/oil emulsion is found at alkaline conditions and in the presence of calcium ions, where the sodium or calcium stearate soaps form. This suggests that both stearic acid and stearate soaps can cause a rupture of the oil-water-oil emulsion films, so producing a water-in-oil emulsion.

![Fig. 7.23](image_url)

(a) Optical micrographs of a water-in-oil emulsion after the triolein/stearic acid (90/5) is mixed with the solution of $2.0 \times 10^{-3}$ M NaLAS at pH3, in the presence of $1.7 \times 10^{-2}$ M NaCl at equal volumes. The scale bar represents 20.0 μm. (a) before crossing the polarizer; (b) after crossing the polarizer.
The behaviour of tristearin particles at the oil-water interface was also studied using the same method. Triolein/tristearin (90/5) and NaLAS solution (2.0×10^{-3} M) in the presence of 1.7×10^{-2} M NaCl at pH 3 is mixed at equal volumes. Tristearin particles (< 0.5 \text{ μm}) in this mixture cannot be seen by using the optical microscope due to a limitation of resolution. The water-in-oil emulsion formed by triolein/tristearin mixture was identified by placing a drop of the emulsion against a drop of the aqueous NaLAS solution. Presence of a distinct interface between the two drops confirms that the emulsion was water-in-oil as shown in Fig.7.24. The behaviour of tristearin particles at the oil-water interface is obviously therefore analogous to that of stearic acid.

![Optical micrograph of a water-in-oil emulsion](image)

**Fig.7.24.** Optical micrograph of a water-in-oil emulsion after the triolein/tristearin (90/5) is mixed with the solution of 2.0×10^{-3} M NaLAS at pH 3, in the presence of 1.7×10^{-2} M NaCl at equal volumes. The scale bar represents 50.0 \text{ μm}.

### 7.4.3 Rupture of Single Films by Oil/Particle Antifoams

The behaviour of sebum soil, triolein/stearic acid and triolein/tristearin antifoam droplets in rupturing a vertical foam film was studied. Foam films were drawn from surfactant solution using the film pulling apparatus described in section 3.3.10. Three different speeds were used - 0.015 cm s^{-1}, 3.0 cm s^{-1} and 45 cm s^{-1}. The corresponding relative rates of surface area increase (dlnA/dt) are plotted against film height at these three pulling speeds.
in Fig 7.25. All films were pulled to exactly the same height under computer control.

**Fig. 7.25.** Plot of $\frac{d\ln A}{dt}$ against film height $h$; $\Delta$ at the pulling speed of 0.015 cm s$^{-1}$; $\Box$ at the pulling speed of 3.0 cm s$^{-1}$; $\Diamond$ at the pulling speed of 45 cm s$^{-1}$.

Fig. 7.26 for example, presents a plot of number distribution of films ruptured at different heights when they are drawn from the NaLAS solution at pH 3, in the absence of Ca$^{2+}$ and in the presence of 1.0 g l$^{-1}$ triolein/tristearin antifoam at the speed of 0.015 cm s$^{-1}$ (repeated 50 times).

**Fig. 7.26.** Number distribution of films ruptured at different height when they are drawn at the speed of 0.015 cm s$^{-1}$ from the NaLAS solution at pH 3, in the absence of Ca$^{2+}$ and in the presence of 1.0 g l$^{-1}$ triolein/tristearin antifoam, at Temperature of 25±1 $^\circ$C (measurement repeated 50 times).
Results of average foam film heights based on 50 times replicated measurements at each pulling speed are presented in Table 7.5. In the absence of antifoam, films formed are stable at these three rates of film pulling. In the presence of antifoam, however, films formed only when the rate was extremely low – at ~0.015 cm s\(^{-1}\). These films were not stable and ruptured when they were expanded at a height of ~1.0 to 2.0 cm above the bulk solution. No films could be made at all with the other two film pulling rates – 3.0 and 45 cm s\(^{-1}\). This means that antifoam effectiveness is more marked under dynamic conditions where equilibrium at air-water surfaces is not reached. Under this condition, the entry and bridging coefficient of triolein oil droplets are likely to be higher than the equilibrium values, as described in section 7.2.2. These results could tend to confirm the conclusions, derived from the foam measurements, that antifoam effects of triolein/stearic acid and triolein/tristearin mixtures are largely confined to the dynamic conditions prevailing during foam generation.

Table 7.5. Average heights of vertical foam films drawn from 2.0×10\(^{-3}\) M NaLAS, 1.7×10\(^{-2}\) M NaCl, at pH 3, in the absence and presence of 1.0 g l\(^{-1}\) antifoam and at Temperature of 25±1 °C for 50 times at different speeds of 0.015 cm s\(^{-1}\), 3.0 cm s\(^{-1}\) and 45 cm s\(^{-1}\) respectively.

<table>
<thead>
<tr>
<th>Pulling Speed / cm s(^{-1})</th>
<th>0.015</th>
<th>3.0</th>
<th>45</th>
</tr>
</thead>
<tbody>
<tr>
<td>In the absence of antifoam</td>
<td>5.7</td>
<td>5.7</td>
<td>5.7</td>
</tr>
<tr>
<td>In the presence of sebum soil</td>
<td>2.0</td>
<td>0</td>
<td>0</td>
</tr>
<tr>
<td>In the presence of triolein/stearic acid</td>
<td>1.0</td>
<td>0</td>
<td>0</td>
</tr>
<tr>
<td>In the presence of triolein/tristearin</td>
<td>1.6</td>
<td>0</td>
<td>0</td>
</tr>
</tbody>
</table>

As discussed in section 6.4.2, the antifoam effectiveness is not only determined by the surface tension behaviour at air-water surface, but also by the numbers of antifoam droplets trapped into the foam film. The probability of antifoam trapping is dependent upon the sizes of antifoam droplets and the foam film thickness. Most sebum soil,
triolein/stearic acid and triolein/tristearin antifoam droplets dispersed in NaLAS solutions have a diameter of \( \leq 7\mu m \), as shown in Fig.7.19. The thickness of vertical films (pulled from NaLAS solution in the absence of antifoam) can be estimated by measuring the position of interference fringes using a red monochromic incident light source as described in 3.3.10. At the film pulling rate of 0.015 cm s\(^{-1}\) for example, foam films were imaged when they were expanded at different heights (see in Fig.7.27).

**Fig.7.27.** Images of vertical foam films drawn from 2.0×10\(^{-3}\) M NaLAS, 1.7×10\(^{-2}\) M NaCl, at pH 3, in the absence of antifoam and at Temperature of 25±1 °C at the pulling speed of 0.015 cm s\(^{-1}\) to the heights of: (a) 0.96 cm; (b) 2.0 cm; (c) 3.12 cm; (d) 4.2 cm; (e) 5.27 cm; The scale bar represents 1.5 cm.

The thickness of the central position of the first order interference band is \( \sim 0.28 \mu m \), and of the second order band is \( \sim 0.55 \mu m \). Antifoam droplets < 1.0 \( \mu m \), which cannot be observed by optical microscopy, were detected by laser diffraction as shown in Fig.7.28, and could possibly be trapped in the film below the first band. The probability of antifoam droplets being trapped in films above this height is however likely to be negligible.
Fig. 7.28. Laser Diffraction Scattering of a number distribution of 0.1 g l\(^{-1}\) triolein/stearic acid antifoam droplets dispersed by Ultra-Turrax in 2.0\(\times\)10\(^{-3}\) M NaLAS at 1.7\(\times\)10\(^{-2}\) M NaCl, pH 3 and at Temperature of 25±1 °C.

We measured the heights of the first order interference band (H) in each image. As shown in Fig. 7.29, the height of this band increases during the pulling of the frame and gradually reaches the maximum of ~1.5 cm. This height approximates those at which the foam film rupture occurs in the presence of antifoam (see in Table 7.5). The foam film rupture is caused by those antifoams droplets trapped below the first order interference band. As we have shown in section 7.2.3, increases in air-water surface tension of > 0.2 mN m\(^{-1}\) only are necessary to reverse the sign of the bridging coefficient to positive for triolein at pH 3. It seems probable then that even at the relative rate of film pulling of only 3\(\times\)10\(^{-3}\) s\(^{-1}\) (roughly equivalent to a surface age of about 5 minutes) the air-water surface tension is higher by at least such an amount than that used in the calculation of the bridging coefficients given in Table 7.1. Here extremely slow equilibration was found with NaLAS, which is a complex blend of many isomers and homologs.
Fig. 7.29. Plot of the height (H) of the first order interference band plotted against the total pulling time of the film frame.

No interference fringes could however be found in the films during their expansion up to the maximum height of 5.7 cm at the pulling rates of 3.0 and 45.0 cm s\(^{-1}\). The film thickness could therefore not be estimated but films thickness are expected to increase with the rate of film pulling as a consequence of Frankel’s law [15]. A larger number of antifoam droplets would therefore be trapped in these two films. This will result in a higher probability of foam film rupture as revealed in Table 7.5. Therefore the enhanced effectiveness of the antifoam under these conditions concerns not only higher dynamic surface tensions but also enhanced probabilities of finding antifoam trapped in foam films.

### 7.4.4 Rupture of Air-Water-Oil Pseudoemulsion Films

The antifoam effect of sebum soil, triolein/stearic acid and triolein/tristearin mixtures is more marked under dynamic conditions. Presence of triolein droplet alone does not cause any foam film rupture, although both of its entry and bridging coefficients are probably greater than zero under dynamic conditions. This suggests the existence of a high entry barrier (or an extremely stable air-water-oil pseudoemulsion film). The emergence of triolein droplets there requires the application of a high critical capillary pressure \((P_{\text{C}^\text{CR}})\), which can be measured by using the FTT technique, as described in 3.3.11 [16].
To simulate dynamic conditions, where air-water surfaces tensions are relatively higher than those in equilibrium condition, a more dilute surfactant solution (i.e. $1.0 \times 10^{-4}$ M $\text{C}_{12} \text{phenyl-SO}_3\text{Na}$ at pH 3 and in the absence of $\text{Ca}^{2+}$) was used in measurement of $P_{C}^{CR}$. The equilibrium surface tension of this solution is $\sim 41$ mN m$^{-1}$, as shown in Fig.4.5 (a).

In this measurement, the triolein droplets and emerged oil lenses are difficult to differentiate, probably due to a relatively large dihedral angle of the oil lenses formed after the emergence of oil droplets into the air-water surface. Coalescence between the oil lenses however occurs more easily than that among the droplets. The $P_{C}^{CR}$ here required for triolein oil droplets to emerge into air-water surfaces was measured as the pressure required to cause emergence of droplets to form lenses, the presence which was indicated their ready tendency to coalesce. For triolein droplets alone, the $P_{C}^{CR}$ is $\sim 200$ Pa as measured using the FTT.

The role of these fatty acid and triglyceride crystalline particles in sebum soil is to destabilise the air-water-oil pseudoemulsion films. This means the presence of particles in triolein droplets should reduce the $P_{C}^{CR}$. To examine this assumption, the critical capillary pressure of triolein/tristearin mixed droplets was also measured in the $1.0 \times 10^{-4}$ M $\text{C}_{12} \text{phenyl-SO}_3\text{Na}$ solution by monitoring the coalescence among oil lenses. The $P_{C}^{CR}$ value is $\sim 40$ Pa, which is much lower than that for triolein droplets.

### 7.5 Role of the Particles in Rupture of Films

If we realistically suppose that stearic acid particles formed in triolein have a structure similar to that shown in Fig.7.14, and the particle has contact angles of $\theta_{AW} > 0^\circ$ and $\theta_{OW} > 90^\circ$ measured through the aqueous phase and $H = L/10$. In this case it may adopt at least six different configurations at the air-water surface [1].

One of the possible configurations adopted by stearic acid particle is shown in the Fig.7.30. This configuration can only occur if
$27.4^\circ < \theta_{AW} < 90^\circ$  \hspace{1cm} (7.1)

However if condition (7.1) is satisfied, such as particle could adopt a stable configuration in a plane-parallel aqueous film as shown in Fig. 7.30.

**Fig.7.30.** Stabilisation of air-water-air film by a hypothetical stearic acid particle with $27.4^\circ < \theta_{AW} < 90^\circ$, where is $\theta_{AW}$ measured through the aqueous phase.

We could now suppose that such a particle is present in an oil phase. It can then adopt the same six configurations at the air-water surface but with the contact angle condition expressed in terms of the angle at the oil-water interface. Therefore a similar configuration to that shown in Fig. 7.31 (a) will form at that interface if

$90^\circ < \theta_{OW} < 152.6^\circ$ \hspace{1cm} (7.2)

where the oil-water contact angle $\theta_{OW}$ is measured through the aqueous phase. Now as the air-water-oil film thins so that the particle bridges the film, rupture occurs at the sharp edge of the particle as shown in Fig.7.31 (b), if

$2.6^\circ < \theta_{AW}$ \hspace{1cm} (7.3)
Fig. 7.31. Rupture of air-water-oil pseudoemulsion film by a hypothetical stearic acid particle if $90^\circ < \theta_{OW} < 152.6^\circ$ and $\theta_{AW} > 2.6^\circ$, where $\theta_{OW}$ and $\theta_{AW}$ are measured through the aqueous phase. Rupture of oil-water-oil but not water-oil-water emulsion films if $\theta_{OW} > 90^\circ$.

Such a particle would sit at the oil-water surface to rupture a pseudoemulsion film if condition (7.3) is satisfied despite having nothing but a stabilizing effect if present in an air-water-air foam film. It would also stabilize a symmetrical water-oil-water film favouring water-in-oil emulsion stability. We then have the characteristics of a particle which meets the requirement of oil/particle antifoam synergy together with oil-in-water emulsion behaviour and which combines a reasonable interpretation of the salient features of actual lozenge shaped stearic acid crystalline platelets as revealed by optical and electron microscopy. The effect of the aggregation of such particles as implied by Fig. 7.13 (b) would be of course present more complex possibilities which are not explored here.

In comparison with the experimental contact angles shown in Table 7.3, it is clear that equation 7.2 is satisfied for all conditions. However the inequality 7.3 is so undemanding that it would be difficult to verify – such low contact angles would be easily realized but very difficult to measure.
Tristearin particles adopt a markedly different crystal habit to that of stearic acid. That habit is shown in Fig. 7.17. Tristearin particles alone do not rupture foam films generated by NaLAS solutions. A probable configuration which could be adopted by a tristearin particle at the air-water surface is then shown in the Fig. 7.32, where the air-water contact line hinges at the edge of the particle. This configuration can occur only if:

\[ \theta_{AW} < 90^\circ \]  

(7.4)

![Diagram of air-water-air film stabilisation](image)

**Fig. 7.32.** Stabilisation of air-water-air film by a hypothetical tristearin particle with \( \theta_{AW} < 90^\circ \), where is \( \theta_{AW} \) measured through the aqueous phase.

If this tristearin particle is sitting in an oil phase, it would also adopt the same configuration as that adopted at the air-water surface. An analogous configuration could form at the oil-water interface as shown in Fig. 7.33 (a) if condition (7.5) is satisfied:

\[ 90^\circ < \theta_{OW} < 180^\circ \]  

(7.5)

The air-water-oil pseudoemulsion film will be ruptured by the tristearin particle as shown
in Fig. 7.33 (b) only if:

$$\theta^o < \theta_{AW}$$  \hspace{2cm} (7.6)

Fig. 7.33. Rupture of air-water-oil pseudoemulsion film by a hypothetical tristearin particle if $90^0 < \theta_{OW} < 180^0$ and $\theta_{AW} > 0$, where $\theta_{OW}$ and $\theta_{AW}$ are measured through the aqueous phase. Rupture of oil-water-oil but not water-oil-water emulsion films if $\theta_{OW} > 90^0$.

Compared with stearic acid, the tristearin crystalline particles have more edges as shown in Fig. 7.16 (b). Most of these tristearin particles are more likely to form aggregates during crystallization. These characteristics of tristearin particles present series problems with respect to the likely configuration adopted at fluid/fluid surfaces and therefore the true nature of their role in antifoam mechanism. Other theoretical techniques such as use of the Surface Evolver [17] may be necessary to elucidate that behaviour rigorously.

We therefore find that, in principle, a crystalline particle with sharp edges, such as stearic acid or tristearin, can exhibit no antifoam effects by itself, but still invert oil-in-water emulsions and rupture oil-water-air pseudoemulsion films provided the particle satisfies
certain conditions (conditions (7.1) - (7.3) for stearic acid and (7.4) - (7.6) for tristearin). This is clearly consistent with the findings of experiments involving mixtures of triolein/stearic acid and triolein/tristearin. Triolein/tristearin antifoam is generally more effective than triolein/stearic acid antifoam. This is probably due to deactivation of the latter during antifoam dispersion as a result of formation of large inactive agglomerates as we will discuss in Chapter 8 [11, 12].

7.6 Summary

A detailed study has been made of the spreading behaviour at the air-water surface of the antifoam considered here – sebum soil, triolein/stearic acid and triolein/tristearin. No evidence of spreading was found under equilibrium or dynamic conditions. The “spreading-fluid entrainment” antifoam mechanism shown in Fig.2.19 would therefore appear to have no role in the mode of action of these antifoams.

The most likely antifoam mechanism for oil-based antifoams is the so-called bridging-stretching mechanism which requires that the bridging coefficient defined by equation (2.22) be positive. However, under near-equilibrium conditions, the bridging coefficient for triolein was found everywhere to be negative. This is consistent with minimum antifoam action for triolein-based antifoams during the near-equilibrium conditions prevailing after foam generation has ceased. These antifoams were however effective under the non-equilibrium conditions prevailing during foam generation. It seems likely that the high dynamic air-water surface tensions (see Chapter 4) relevant under such conditions mean a reversal of the sign of the bridging coefficients, so that the antifoam action then occurs.

Stearic acid and tristearin are crystallized from triolein to form particles with distinct geometries. The roles of stearic acid and tristearin particles as antifoam promoters for triolein are similar. Neither of them exhibits any antifoam effect when used alone. The
experimental evidence suggests that these particles adhere to triolein/water surfaces to rupture both air-water-oil pseudoemulsion films and oil-water-oil emulsion films. Measured contact angles are $\theta_{ow} > 90^\circ$ consistent with such behaviour.

7.7 Acknowledgement

We are particularly grateful to Slavka Tcholakova and Radka Petkova in Sofia University for making the FTT measurements.

7.8 References

13. Ramsden, W., Separation of Solids in the Surface-Layers of Solutions and


Chapter 8 Antifoam Deactivation

8.1 Introduction

Oil/particle synergistic antifoams appear to lose their activity during continuous foam generation. Studies of silicone/silica antifoam mixtures by Denkov et al. [1] suggest that this antifoam deactivation behaviour is accompanied by formation of both particle-free droplets, which are unable to emerge into the air-water surfaces and act as antifoams; and by formation of particle-rich droplets, which may aggregate to form large inactive agglomerates.

A spread layer is usually present at the air-water surface during silicone antifoam function. This layer assists emergence of oil droplets into the air-water surface [1]. It is removed during deactivation. This phenomenon is therefore of some significance in that process. Here we are dealing with a non-spreading oil (see section 7.2.2) and it is of some interest to establish whether deactivation still occurs. We note however that evidence that non-spreading oil/particle antifoam mixtures such as hydrophobic oil / hydrophobed silica mixtures do deactivate has in fact already been found [2].

As we have seen, both triolein/stearic acid and triolein/tristearin are effective antifoams in NaLAS solutions at pH 3, 7, 10.5 and in both the absence and presence of calcium. These antifoams do not spread at air-water surfaces as discussed in Chapter 7. In order to establish whether deactivation of these antifoams occurs, we have measured the foamability of NaLAS solutions by continuous generation in the presence of various antifoams - sebum soil, triolein/stearic acid and triolein/tristearin.

Antifoam dispersed in commercial NaLAS has been used in tumbling tube rotation experiments (250 ml solutions for 2 hours and one week’s continuous rotation respectively) under two conditions - pH 3, in the absence of Ca^{2+} and pH 10.5, in the presence of
5.25×10^{-4} \text{ M Ca}^{2+}. The latter condition involves sodium and calcium soap formation from fatty acids, causing a potential change of particle properties. We also examined the antifoam droplet size distribution before and after two hours’ foam generation, in order to establish the role, if any, of reduction in droplet size in antifoam deactivation [3]. The rheology of these antifoams was also studied in order to give some indication of the rate of antifoam disproportionation (or in another words the rate of formation of particle-rich and particle-free droplets).

**8.2 Effect of Changes in Antifoam Concentration**

For triolein/stearic acid and triolein/tristearin antifoams, the loss of their activity means a decrease of the effective mixed oil/particle antifoam concentration in surfactant solution. In interpreting antifoam deactivation, it is necessary therefore to understand the relationship between antifoam concentration and effectiveness. A statistical theory described by Garrett [4] demonstrates that for a given surfactant solution and foaming method, the plots of initial foam volumes (or foamability) against logarithm of antifoam concentration should be isomorphous, independent of the nature of antifoam.

If the number of antifoam entities attached to a given bubble is $N$, and the probability of antifoam not working is $q$, then the probability of that bubble surviving should be $q^N$. If we define $F$ as the volume of air in foam with antifoam / volume of air in foam in the absence of antifoam and if the bubbles are assumed to be spherical, we can write:

$$ F = \frac{\int_0^r P(r)q^{N(r)}dr}{\int_0^r P(r)dr} $$  \hspace{1cm} (8.1) $$

where $P(r)$ is the normalized bubble size distribution. Suppose two different antifoams of species $i$ and $j$ are dispersed by a high speed emulsifier, for example, in the same surfactant solution respectively. $c_i^0$ and $c_j^0$ are the antifoam concentrations for the same $F$. We can
therefore write:

\[
\int_0^\infty P(r)q_i^{N_i(r)} dr = \int_0^\infty P(r)q_j^{N_j(r)} dr \tag{8.2}
\]

where \( N_i(r) \) is linearly dependent on antifoam concentration \( c_i \), and \( N_j(r) \) is linearly dependent on antifoam concentration \( c_j \) [4]. We may deduce from equation (8.1) and (8.2)

\[
\left[ \frac{dF}{d \lg c_i} \right]^0 = \left[ \frac{dF}{d \lg c_j} \right]^0 \tag{8.3}
\]

This means the same slope would be adopted by different antifoam dispersions at the same value of \( F \).

This behaviour has been shown in both tumbling tube and cylinder shaking foaming tests by using different antifoams - sebum soil, triolein/stearic acid and triolein/tristearin (for triolein/tristearin only cylinder shaking results are available) in the same surfactant solutions. Plots of \( F \) vs. \( \log [c/c^0] \) for \( 2.0 \times 10^{-3} \) M NaLAS at pH 3, in the absence of \( \text{Ca}^{2+} \) and pH 10.5, in the presence of \( \text{Ca}^{2+} \) by both methods, where \( c^0 \) is the antifoam concentration when \( F = 0.5 \) are shown in Fig.8.1 (a) and (b) and Fig.8.2 (a) and (b) respectively. As suggested by the theory, these \( F \) vs. \( \log [c/c^0] \) plots by sebum soil, triolein/stearic acid and triolein/tristearin antifoams almost lie on the same curve, independent of those antifoam properties. Changing the solution condition from pH 3 in the absence of \( \text{Ca}^{2+} \) to pH 10.5 in the presence of \( \text{Ca}^{2+} \) means a violation of the basic assumption of the above theory that the surfactant solutions should be identical. However, the effect of the change in solution conditions is small so that it is still possible to make a reasonable representation of all the data by one single plot as shown in Fig. 8.1 (c) and Fig. 8.2 (c).
Fig. 8.1. Plots of $F$ against log $[c/c^0]$ for solutions of $2.0 \times 10^{-3}$ M NaLAS in $1.7 \times 10^{-2}$ M NaCl by Tumbling Tube method after 10 rotations at (a) pH 3, in the absence of Ca$^{2+}$; (b) pH 10.5, $5.25 \times 10^{-4}$ M Ca$^{2+}$; (c) both conditions of pH 3, in the absence of Ca$^{2+}$ and pH 10.5, $5.25 \times 10^{-4}$ M Ca$^{2+}$. Antifoams were dispersed by Ultra–Turrax at the Temperature of $25 \pm 1 ^\circ$C; ◇ Sebum soil antifoam, □ Triolein/stearic acid antifoam; $c^0$ is the antifoam concentration when $F = 0.5$. 
Fig. 8.2. Plots of $F$ against log $[c/c^0]$ for solutions of $2.0 \times 10^{-3}$ M NaLAS in $1.7 \times 10^{-2}$ M NaCl by Cylinder Shaking after 10 s at (a) pH 3, in the absence of Ca$^{2+}$; (b) pH 10.5, $5.25 \times 10^{-4}$ M Ca$^{2+}$; (c) both conditions of pH 3, in the absence of Ca$^{2+}$ and pH 10.5, $5.25 \times 10^{-4}$ M Ca$^{2+}$. Antifoams were dispersed by Ultra–Turrax at the Temperature of 25±1 °C; ♦ Sebum soil antifoam, □ Triolein/stearic acid antifoam, ▲ Triolein/tristearin antifoam; $c^0$ is the antifoam concentration when $F = 0.5$. 
8.3 Deactivation of Triolein/Stearic acid Antifoam

The tumbling tube methodology has been used to study the antifoam deactivation behaviour of sebum soil, triolein/stearic acid and triolein/tristearin antifoams, which were dispersed in surfactant solutions by Ultra-Turrax, as described in section 3.3.2. The effect on foamability after deactivation of 2 hours continuous rotation is shown in Fig.8.3 at pH 3 in the absence of Ca\(^{2+}\) and pH 10.5 in the presence of 5.25\times10^{-4} \text{ M Ca}^{2+}. Triolein/stearic acid antifoam is seen to completely deactivate after rotation of the tubes for 1 hour. By contrast, sebum soil and triolein/tristearin antifoams retain their activity for at least 2 hours.
Fig. 8.3. Deactivation of sebum soil, triolein/stearic acid and triolein/tristearin antifoams at 1.0 g l\(^{-1}\) by tumbling tube methodology in 2.0\(\times\)10\(^{-3}\) M NaLAS with 1.7\(\times\)10\(^{-2}\) M NaCl and Temperature of 25±1 °C; (a) at pH 3, in the absence of Ca\(^{2+}\); (b) at pH 10.5, 5.25\(\times\)10\(^{-4}\) M Ca\(^{2+}\); (c) triolein/stearic acid antifoam at both pH 3 without Ca\(^{2+}\) and pH 10.5 with Ca\(^{2+}\) conditions. ▲ In the absence of antifoam, ■ In the presence of sebum soil antifoam, ◇ In the presence of triolein/stearic acid antifoam at pH 3, without Ca\(^{2+}\), ◆ In the presence of triolein/stearic acid antifoam at pH 10.5, with Ca\(^{2+}\), □ In the presence of triolein/tristearin antifoam.

Some authors [5, 6] have attributed antifoam exhaustion to a significant reduction of antifoam droplet sizes. However, the droplet size of triolein/stearic acid antifoam measured by optical microscopy did not change even after two hours rotation as shown in Fig. 8.4 and Fig. 8.5. Reduction of droplet size does not therefore explain why triolein/stearic acid deactivates.

Denkov et al. [1] have shown that dispersed silicone oil/hydrophobic silica antifoam, subject to continuous shaking, maintains a constant droplet size despite deactivation. This implies that disproportionation must therefore involves both splitting and coalescence of droplets to produce a steady state. However, this observation of Denkov et al. appears to neglect the presence, after deactivation, of a small number of very large silica-rich agglomerates.
Fig. 8.4. Optical micrographs of triolein/stearic acid antifoam droplets at 1.0 g l⁻¹ dispersed in 2.0×10⁻³ M NaLAS at 1.7×10⁻² M NaCl pH 3 and Temperature of 25±1 °C by Ultra–Turrax; (a) before deactivation experiment; (b) after deactivation experiment.

Large particle-rich agglomerates were in fact detected after deactivation experiments with triolein/stearic acid antifoam. They were attached to the inner wall of the tumbling tubes. It is not therefore surprising that they were not detected by light scattering. Images of these large agglomerates are shown in Fig 8.6 and 8.7. They have been found in both NaLAS solutions at pH 3, in the absence of Ca²⁺ and pH 10.5, in the presence of Ca²⁺. Such agglomerates must form by continuous coalescence of particle-rich droplets where the agglomerates have extremely high viscosities so that splitting cannot occur. They are clearly too large (> 100.0μm) to be trapped in foam films and are not in any case sufficiently numerous to contribute significantly to the overall antifoam behaviour irrespective of that effect.
Agglomerates formed at pH 3, in the absence of Ca$^{2+}$ are probably relatively concentrated mixtures of stearic acid crystalline particles with triolein. These agglomerates are significantly smaller than those formed at pH 10.5 and in the presence of Ca$^{2+}$, where stearic acid is expected to be converted to sodium and calcium soaps. Those latter agglomerates found at high pH appear to contain lamellar liquid crystalline material as revealed by optical microscopy as shown in Fig.8.7. Such liquid crystalline particles could be a mixture of fatty acid-soaps-water or even NaLAS-fatty acid-water [7]. Establishment of their nature will require application of other techniques, such as X-Ray analysis. It is probable that they are more hydrophilic than the crystals of stearic acid. Moreover they

Fig.8.5. Triolein/stearic acid antifoam droplet size distribution in 2.0×10$^{-3}$ M NaLAS at 1.7×10$^{-2}$ M NaCl, pH 3 and at Temperature of 25±1 °C; (a) before deactivation experiment; (b) after deactivation experiment.
will lack the fixed geometry of crystalline particle which we have seen can play an important role in antifoam effectiveness, see section 7.5. This may imply that the conversion of crystalline stearic acid into these liquid crystalline particles plays an additional role in determining the rate of antifoam deactivation, and is at least part of the explanation of the enhanced rate of deactivation at pH 10.5 in the presence of Ca$^{2+}$ relative to that at pH 3.

**Fig. 8.6.** Optical micrographs crossing the polarizer of stearic acid agglomerates formed after a 2 hours continuous rotation by tumbling tube rotation in $2.0 \times 10^{-3}$ M NaLAS, in the presence of $1.7 \times 10^{-2}$ M NaCl at pH 3, in the absence of $5.25 \times 10^{-4}$ M Ca$^{2+}$, at Temperature of $25 \pm 1$ $^0$C. The scale bar represents 100.0μm.
Fig. 8.7. Optical micrographs crossing the polarizer of stearic acid and stearate soaps (sodium and calcium) agglomerate formed after a 2 hours continuous rotation by tumbling tube in $2.0 \times 10^{-3}$ M NaLAS, in the presence of $1.7 \times 10^{-2}$ M NaCl, $5.25 \times 10^{-4}$ M $\text{Ca}^{2+}$, at pH 10.5 and Temperature of $25 \pm 1 \, ^{\circ}\text{C}$. The scale bar represents $100.0 \mu\text{m}$.

The change in solution condition from pH 3 in the absence of $\text{Ca}^{2+}$ to pH 10.5 in the presence of $5.25 \times 10^{-4}$ M $\text{Ca}^{2+}$ clearly has a marked effect on the rate of deactivation as
shown in Fig.8.3 (c). We may model this effect by supposing that we have two different antifoams (corresponding to triolein/stearic acid and triolein/stearate soaps, which deactivate at different rates [8]). For representation of the antifoam effect, we can use \( F = \frac{V_{af}(t)}{V_0(t)} \) = Volume of air in foam in the presence of antifoam / Volume of air in the absence of antifoam. Obviously, both \( V_{af}(t) \) and \( V_0(t) \) will increase with time \( t \) in a typical antifoam deactivation experiment, such as in the tumbling tube rotation, where foam is continuously generated. However, if there is no deactivation of the antifoam, then \( F \) will remain constant even though both \( V_{af}(t) \) and \( V_0(t) \) increase with time. Thus in a process of continuous generation of foam, for example, if 50% of the foam that would have been generated after 10 minutes is destroyed, then the same proportion will be destroyed after 30 minutes. \( F \) should then be time independent if there is no deactivation of the antifoam. Any increase in \( F \) with time will therefore be caused by deactivation.

Plots of \( F \) vs. \( \log [c/c^0] \) for triolein/stearic acid at pH 3 in the absence of Ca\(^{2+}\) and at pH 10.5 in the presence of Ca\(^{2+}\) are shown in Fig.8.8.

![Fig.8.8. Plots of \( F \) against \( \log [c/c^0] \) for solutions of 2.0×10\(^{-3}\) M NaLAS in 1.7×10\(^{-2}\) M NaCl in the presence of triolein/stearic acid by Tumbling Tube method after 10 rotations; □ pH 3, in the absence of Ca\(^{2+}\); ◆ pH 10.5, in the presence of 5.25×10\(^{-4}\) M Ca\(^{2+}\).](image-url)
It is seen that we can represent all the data with a single linear plot with reasonable accuracy (although as we have stated the surfactant solution conditions are not constant as strictly required for equation (8.3) to be valid). Therefore, using the results in Fig.8.9 for the tumbling tube we can approximate by

\[ F_1 = K \log c_1 + B_1 \]  \hspace{1cm} (8.4)

for triolein/stearic acid antifoam at pH 10.5 and Ca\(^{2+}\): 5.25×10\(^{-4}\) M, where some liquid crystalline particles of unknown composition appear to form, and

\[ F_2 = K \log c_2 + B_2 \]  \hspace{1cm} (8.5)

for the antifoam at pH 3 and nil Ca\(^{2+}\), where only triolein/stearic acid particle will be present. Here \( K \) is a constant assumed to be independent of antifoam, so that \( dF / d\log[c] = K \) \([4]\). \( B_1 \) and \( B_2 \) are constants dependent on antifoam function; and \( c_1 \) and \( c_2 \) are effective antifoam concentrations in g l\(^{-1}\). Therefore, \( B_1 \) and \( B_2 \) are equal to the respective \( F \) values at \( c_1 = 1 \) g l\(^{-1}\) and \( c_2 = 1 \) g l\(^{-1}\) before any deactivation has occurred (when \( t \sim 0 \)).

Subtracting equation (8.5) from (8.4) gives

\[ F_1 - F_2 = K \log(c_1 / c_2) + B_1 - B_2 \]  \hspace{1cm} (8.6)

or

\[ \Delta F = K \log(c_1 / c_2) + \Delta B \]  \hspace{1cm} (8.7)

This equation is of course valid only if the \( c_1 \) and \( c_2 \) are both > 0.

If equation (8.7) is differentiated with respect to time, then the rate of increase of \( \Delta F \) as the antifoams deactivate can be written as:
\[
\frac{d\Delta F}{dt} = K \frac{d \log(c_1 / c_2)}{dt}
\]  
(8.8)

since $\Delta B$ concerns the difference in $F$ under initial conditions and is therefore independent of time.

If both antifoams are supposed to deactivate by a first order reaction, the time dependence of the concentrations is then given by

\[-\frac{dc_1}{dt} = A_1 c_1\]  
(8.9)

and

\[-\frac{dc_2}{dt} = A_2 c_2\]  
(8.10)

where $A_1$ and $A_2$ are rate constants characteristic of each antifoam.

In the case where the rate of deactivation is the same for the two antifoams at the same concentration (so $A_1 = A_2$), then we have

\[
\frac{d \log c_1}{dt} - \frac{d \log c_2}{dt} = 0
\]  
(8.11)

or

\[
\frac{d \log(c_1 / c_2)}{dt} = 0
\]  
(8.12)

Substituting equation (8.12) in equation (8.8) yields

\[
\frac{d\Delta F}{dt} = 0
\]  
(8.13)
which means that the difference in $F$ values between the two antifoam dispersions should remain constant as they deactivate with time.

However, the deactivation results shown in Fig. 8.3 (c) indicate that $\Delta F$ increases with time, which must mean that either $A_1 \neq A_2$ or that first order deactivation kinetics are not relevant. Supposing then that deactivation is first order (i.e. equations (8.9) and (8.10) remain applicable) and that $A_1 \neq A_2$, we must have

$$
\frac{d \log c_1}{dt} - \frac{d \log c_2}{dt} = \frac{d \log (c_1 / c_2)}{dt} = A_1 - A_2
$$

(8.14)

So substituting equation (8.14) in equation (8.8) then gives

$$
\frac{d \Delta F}{dt} = K (A_1 - A_2)
$$

(8.15)

which can be integrated to

$$
\Delta F = K (A_1 - A_2) t + \Delta F_{t=0}
$$

(8.16)

meaning that plots of $\Delta F$ found with the two antifoams, against time $t$ should be linear and intercept the foam height axis at $\Delta F_{t=0}$. In fact, as seen in Fig. 8.9, an approximately linear time dependence of $\Delta F$ is found. Results where the most rapidly deactivating antifoam is giving a foam height corresponding to a full vessel are off-scale and will not be considered (the results after 20 minutes agitation) because then $c_1 = 0$ and the results lie outside the range of applicability of the theory.
Fig. 8.9. Plot of $\Delta F$ against Time for $2.0 \times 10^{-3}$ M NaLAS, in $1.7 \times 10^{-2}$ M NaCl, in the presence of 1.0 g l$^{-1}$ antifoams dispersed at the Temperature of 25±1 °C after 20 minutes’ rotation in the tumbling tubes.

A better fit could possibly be obtained if rate expressions for antifoam deactivation accounted for both droplet splitting (first order) and coalescence (second order). Equations (8.9) would then have the form

$$-\frac{dc_1}{dt} = A_1c_1 + D_1c_1^2$$

where $D_1$ is a second order rate constant. Another problem concerns the limits the linear relationship between $\log_{10}$ [antifoam concentration] and $F$ in equations (8.4) and (8.5) – that will break down as $F \rightarrow 1$.

8.4 Deactivation of Sebum Soil and Triolein/Tristearin Antifoams

Sebum soil and triolein/tristearin retain their antifoam activity after only 2 hours rotation of tumbling tube, but slowly deactivate after one week’s continuous foam generation. The complexity of sebum soil precludes ready explanation for the slow rate of deactivation except by analogy with respect to triolein/tristearin.
One of the most obvious differences between triolein/stearic acid and triolein/tristearin mixtures concerns the sizes of the particulate components. Small particle sizes in the case of triolein/tristearin mean enormously higher number concentrations of particles in dispersed oil droplets. Indeed as we have seen a significant proportion of large stearic acid particles are even removed as large oil/particle agglomerates just after dispersal in surfactant solution.

Let us suppose then that one of the processes of deactivation concerns formation of inactive particle-free droplets. Randomization of the distribution of particles across droplets after coalescence and splitting must mean that the probability \( Q \) of formation of inactive particle-free droplets is given [9]

\[
Q = \exp(-N/M)
\]

(8.18)

where \( N \) is the number of particles and \( M \) is number of oil droplets. As the antifoam is dispersed, we must find that \( N/M \) declines. However, provided we have \( N/M \geq 5 \), then \( Q \rightarrow 0 \).

Similar droplet size distributions shown in Fig.7.19 means that the number of droplets of triolein/stearic acid \( M_1 \) is nearly equal to the number of droplets of triolein/tristearin \( M_2 \). However, comparison of the particle size distribution given in Fig.7.12 and Fig.7.15 suggests that there are more large particles of stearic acid than for tristearin in a given weight of the material. Therefore we must have \( N_1 << N_2 \), where \( N_i \) is the average number stearic acid particles in each triolein droplet, and \( N_2 \) is the average number of tristearin particles in each triolein droplet. We must therefore have, \( Q_1 >> Q_2 \), which may partially explain the significant difference in the deactivation rate between these two antifoams. This explanation cannot however be complete – removal of antifoam material in the form of large agglomerates also must make a contribution. This will involve a non-random process which lies outside the relevance of equation (8.18).
In an attempt to understand the relative propensity to form large inactive agglomerates, we considered the rheological behaviour of these antifoams. Viscosities as a function of shear rate for sebum soil, triolein/stearic acid and triolein/tristearin at 25 °C are presented in Fig.8.10. Triolein oil at this temperature is Newtonian with a constant viscosity of around 0.7 Pas over a shear rate of from 0.1 to 100 s⁻¹. Addition of particles to triolein causes an obvious enhancement of the viscosity of the relevant antifoams, especially at a low shear rates from 0.1 to 1 s⁻¹. The greater the number of small particles present in the oil, the higher the viscosity.

![Viscosities of sebum soil, triolein/stearic acid, triolein/tristearin and triolein measured at a temperature of 25±1 °C in a shear rate range from 0.1 to 100 s⁻¹.](image)

**Fig.8.10.** Viscosities of sebum soil, triolein/stearic acid, triolein/tristearin and triolein measured at a temperature of 25±1 °C in a shear rate range from 0.1 to 100 s⁻¹.

It is known that increases in the viscosity of silicone/silica antifoams reduce the rate of deactivation [3]. It seems similar behaviour may be apparent with the antifoams considered here where the relatively low viscosity of the triolein/stearic acid antifoam appears to correlate with relatively rapid deactivation. Obviously, the higher the viscosity, the less readily antifoam droplets will split. However, droplet size measurements shown in Fig.7.18 and 7.19 are all similar. Perhaps the formation of large inactive particle-rich agglomerates (such as these shown in Fig.8.6 and 8.7) is inhibited by high viscosities because their formation requires both splitting and coalescence. This follows because coalescence without splitting cannot result in increases in the particle concentration in the coalesced
droplets. Formation of particle-free droplets is also inhibited if particle splitting cannot readily occur. It is easy to see why all this could be realized. Consider for example a distribution of droplets, each of which contains 5 particles. If splitting to form debris droplets of equal volume is allowed, then there is a possibility of such droplets being formed with from 0 particles up to 5 particles. Coalescence of two of the latter could produce a droplet of the original size containing 10 particles at the expense of forming another droplet with a diminished number of particles to the original concentration [8].

8.5 Summary

Immediately after the dispersion of triolein/stearic acid antifoam, oil droplets containing stearic acid particles are present in surfactant solutions. There is however a significant loss of stearic acid particles because of formation of large agglomerates (see in Fig. 7.21), some of which were found floating at the air-water surface. These large fatty acid/oil agglomerates were in fact removed before commencing the deactivation experiment. When the tumbling tubes start rotating, formation of additional large agglomerates occurs probably through a process of splitting and coalescence. This results in a gradual deactivation of antifoam activity with an increase in the proportion of large (probably particle-rich inactive) agglomerates. Total deactivation of oil/particle antifoams can occur by this process.

More rapid deactivation for triolein/stearic acid antifoam has been observed at pH 10.5, in the presence of Ca$^{2+}$, the condition where a conversion of stearic acids to stearate soaps is expected to occur. This apparently results in the gradual formation of lamellar phase of unknown composition, which may be more readily wetted by the aqueous phase.

A simple model for the relative deactivation of triolein/stearic acid antifoam at pH 3 in the absence of Ca$^{2+}$ and pH 10.5 in the presence of Ca$^{2+}$ appears to suggest that the process is first order. This would imply that droplet splitting is the rate determining process in
deactivation despite the obvious role of droplet coalescence to form large agglomerates.

Triolein/tristearin and sebum soil deactivate extremely slowly, being completely deactivated only after one week of continuous foam generation by rotating tubes. Slower deactivation in the case of triolein/tristearin may be caused by the presence of a larger number of tristearin crystalline particles initially present in each oil droplet. The greater the concentration of particles, the less readily particle-free droplet formation can occur. These tristearin particles also cause an increase of viscosity of triolein. This may inhibit the splitting process and therefore the formation of both particle-free droplets and droplets with increasing particle concentration which ultimately leads to formation of large inactive particle-rich agglomerates.

8.6 References

8. Garrett, P.R., Personal communication.
Chapter 9 Effect of SDS (co-surfactant) on Foam Behaviour of C$_{12}$ 4-phenyl SO$_3$Na Solutions

9.1 Introduction

High foam powder detergent formulations usually contain two or three other surfactants (so-called co-surfactants) besides NaLAS. These co-surfactants are usually formulated into detergents to improve the cleaning and the foaming performance of NaLAS [1]. There are three types of co-surfactants used in detergent products currently, including: Sodium Primary Alkyl Sulfate (NaPAS), Sodium Alkyl Ether Sulfate (NaAES) and ethoxylated fatty alcohol, as described in Chapter 1. Arguably the most commonly considered co-surfactant in this context is NaPAS. The effect of NaPAS on foam behaviour of NaLAS in the absence and presence of antifoam was therefore studied. A pure C$_{12}$ 4-phenyl SO$_3$Na was mixed with Sodium Dodecyl Sulfate (SDS) at a molar ratio of 4:1 to form binary surfactant system. Use of C$_{12}$ 4-phenyl SO$_3$Na avoids the presence of surface active impurities. This will mean more precise measurements of equilibrium and dynamic surface tensions, and Ca$^{2+}$-surfactant precipitation boundaries in the relevant phase diagram, providing a more accurate indication of the impact of SDS on the overall foam behaviour.

This chapter describes the relationship between the Ca$^{2+}$ - C$_{12}$ 4-phenyl SO$_3^-$/SDS precipitation phase diagram and foam behaviour in both the absence and presence of triolein-based antifoam (with stearic acid and tristearin as particles). As with the NaLAS and pure C$_{12}$ 4-phenyl SO$_3$Na solutions described in Chapters 4 and 5, again we used a scan at different Ca$^{2+}$ levels at a surfactant concentration above the CMC (equivalent to the scan ABC in Fig.4.2).
9.2 Ca\(^{2+}\)-C\(_{12}\) 4-phenyl SO\(_3^-\)/SDS Phase Diagram and Surface Tension Behaviour

We prepared a precipitation phase diagram of Ca\(^{2+}\)-C\(_{12}\) 4-phenyl SO\(_3^-\)/SDS, similar to that of Ca\(^{2+}\)-C\(_{12}\) 4-phenyl SO\(_3^-\) shown in Fig.4.6. For this we determined a relevant monomer-micellar boundary, a monomer-precipitate boundary and a micellar-precipitate boundary. The monomer-micellar boundary is determined by three CMC values calculated based on the equilibrium surface tension measurement of 2.0×10\(^{-3}\) M C\(_{12}\) 4-phenyl SO\(_3^-\)Na/SDS solutions at pH 10.5 and in the absence of Ca\(^{2+}\); in the presence of 1.0×10\(^{-4}\) M and 2.0×10\(^{-4}\) M Ca\(^{2+}\) respectively. Gibbs plots of Surface Tension vs. log\(_{10}\) (C\(_{12}\) 4-phenyl SO\(_3^-\)Na/SDS concentration) are presented in Fig. 9.1, where the equilibrium surface tensions are measured by the Wilhelmy plate method after 1 hour as a compromise.

The Ca\(^{2+}\)-C\(_{12}\) 4-phenyl SO\(_3^-\)/SDS precipitation boundaries were again determined by observation of the onset of turbidity in a C\(_{12}\) 4-phenyl SO\(_3^-\)Na/SDS solution with increasing Ca\(^{2+}\) concentration, as described in section 3.3.3. A comparison of Ca\(^{2+}\)-C\(_{12}\) 4-phenyl SO\(_3^-\)/SDS precipitation phase diagram and Ca\(^{2+}\)-C\(_{12}\) 4-phenyl SO\(_3^-\) precipitation phase diagram is made and shown in Fig. 9.2.
Fig. 9.1. Equilibrium surface tension of $2.0 \times 10^{-3}$ M C$_{12}$ 4-phenyl SO$_3$Na/SDS (4/1) in $1.7 \times 10^{-2}$ M NaCl, at pH 10.5 and Temperature of 25±1°C. (a) in the absence of Ca$^{2+}$; (b) in the presence of $1.0 \times 10^{-4}$ M Ca$^{2+}$; (c) in the presence of $2.0 \times 10^{-4}$ M Ca$^{2+}$. 
Fig. 9.2. Ca\(^{2+}\)-C\(_{12}\) 4-phenyl SO\(_3\)\(^-\) and Ca\(^{2+}\)-C\(_{12}\) 4-phenyl SO\(_3\)\(^-\)/SDS (4/1) precipitation phase diagrams measured in 1.7×10\(^{-2}\) M NaCl, at pH 10.5 and Temperature of 25±1 °C; □ C\(_{12}\) 4-phenyl SO\(_3\)Na/SDS; ■ C\(_{12}\) 4-phenyl SO\(_3\)Na.

The effect of SDS on the position and slope of the monomer-precipitate boundary can be used to establish whether the precipitate is pure Ca(C\(_{12}\) 4-phenyl SO\(_3\))\(_2\) or a mixed Ca(C\(_{12}\) 4-phenyl SO\(_3\)/SDS)\(_2\) precipitate. Solubility products, K\(_{sp}\), for Ca(C\(_{12}\) 4-phenyl SO\(_3\))\(_2\), calculated for precipitation from pure C\(_{12}\) 4-phenyl SO\(_3\)Na are compared with those calculated for precipitation from C\(_{12}\) 4-phenyl SO\(_3\)Na/SDS mixed solutions in Table 9.1 (correcting for ionic activities using equation (4.5)). They are seen to be essentially similar which implies neither Ca(SDS)\(_2\) or mixed Ca(C\(_{12}\) 4-phenyl SO\(_3\)/SDS)\(_2\) precipitation is occurring. The SDS then has the effect of being simply a diluent so that the monomer-micellar precipitation boundary is displaced to higher overall surfactant concentration in order to ensure a high enough concentration of C\(_{12}\) 4-phenyl SO\(_3\)\(^-\) to satisfy the solubility product. In this context, we should remember that the solubility product of Ca(SDS)\(_2\) (see Table 1.3) is more than an order of magnitude greater than that of Ca(C\(_{12}\) 4-phenyl SO\(_3\))\(_2\).
Table 9.1 Solubility products for Ca(C_{12} 4-phenyl SO_3)_{2} calculated in pure C_{12} 4-phenyl SO_3Na and C_{12} 4-phenyl SO_3Na/SDS mixed solution at 1.7\times10^{-2} M NaCl, pH 10.5 and Temperature of 25\pm1^\circ C.

<table>
<thead>
<tr>
<th>Surfactant concentration / 10^{-4} M</th>
<th>C_{12} 4-phenyl SO_3Na/SDS solution</th>
<th>C_{12} 4-phenyl SO_3Na solution</th>
</tr>
</thead>
<tbody>
<tr>
<td>Ca^{2+} concentration / 10^{-4} M</td>
<td>1.6   2.0  2.5  3  3.5</td>
<td>1.6   2.5  3  3.5</td>
</tr>
<tr>
<td>Solubility Product (K_{sp}) / 10^{-11}</td>
<td>2.535  2.495  2.642  2.399  2.415</td>
<td>2.938  2.938  2.825  2.455</td>
</tr>
</tbody>
</table>

In the region above the monomer-micellar boundary, surfactant micelles and monomers coexist in bulk solution. In C_{12} 4-phenyl SO_3Na/SDS solution, mixed C_{12} 4-phenyl SO_3Na and SDS micelles will form, while in C_{12} 4-phenyl-SO_3Na solution, only single surfactant micelles will be present. The presence of these mixed micelles in the former solution will result in a diminished precipitation of Ca(C_{12} 4-phenyl SO_3)_{2} liquid crystalline particles in the micellar-precipitate region. In this region, if Ca(C_{12} 4-phenyl SO_3)_{2} tends to precipitate out from the mixed micelles, this will result in an increase of the proportion of SDS in the remaining micelles. This will decrease the proportion and therefore activity of C_{12} 4-phenyl-SO_3Na in the mixed micelles, inhibiting further precipitation. Higher micelle surfactant concentrations would therefore be present in the C_{12} 4-phenyl SO_3Na/SDS solution in the micellar-precipitate region. A faster transport of surfactant to the air-water interface will inevitably result from this higher surfactant level, which correlates with lower dynamic surface tension of C_{12} 4-phenyl SO_3Na/SDS solution measured at low surface age of 0.1s and 1.0s when Ca^{2+} \geq 10\times10^{-4} M, as shown in Fig.9.3.
**Fig.9.3.** Dynamic surface tensions solutions of C_{12} 4-phenyl SO_3Na and C_{12} 4-phenyl SO_3Na/SDS (4/1) at 2.0×10^{-3} M in the presence of 1.7×10^{-2} M NaCl, at pH 10.5 and Temperature of 25±1 °C; ◻ C_{12} 4-phenyl SO_3Na/SDS at 0.1 s; ▲ C_{12} 4-phenyl SO_3Na at 0.1 s; □ C_{12} 4-phenyl SO_3Na/SDS at 1 s; ■ C_{12} 4-phenyl SO_3Na at 1 s.

**9.3 Effect of SDS on Foamability and Foam Stability in the Absence of Antifoam**

Results of foamability and foam stability of C_{12} 4-phenyl SO_3Na and C_{12} 4-phenyl SO_3Na/SDS solutions at pH 3 and 10.5, and in the presence of Ca^{2+} from 0 to 40×10^{-4} M are presented in Fig. 9.4. Ca^{2+}-C_{12} 4 phenyl-SO_3 precipitation determines the foamability of both surfactant solutions in the absence of builder and antifoams. After the micellar-precipitate boundaries (in the case of C_{12} 4-phenyl SO_3Na, Ca^{2+} ≥ 5.25×10^{-4} M; and in the case of C_{12} 4 phenyl-SO_3Na/SDS, Ca^{2+} ≥ 6.75×10^{-4} M), the foamabilities of both systems decrease with an increase of Ca^{2+} concentration. This correlates with a decrease in the rates of surfactant adsorption to the air-water surfaces under dynamic conditions.
However, higher foamabilities for the C\textsubscript{12} 4-phenyl SO\textsubscript{3}Na/SDS system in this micellar precipitation region are found than for the pure C\textsubscript{12} 4-phenyl SO\textsubscript{3}Na system. This effect is presumably largely due to more rapid surfactant transport to the air-water surfaces in the former system, as revealed by dynamic surface tension measurements at low surface age, shown in Fig. 9.3.

![Graph](image1)

(a) Foamability and foam stability in cylinder shaking of 2.0×10\textsuperscript{-3} M C\textsubscript{12} 4-phenyl SO\textsubscript{3}Na (and C\textsubscript{12} 4-phenyl SO\textsubscript{3}Na/SDS: 4/1), in 1.7×10\textsuperscript{-2} M NaCl and at Temperature of 25±1 °C. (a) immediately after shaking for 10 s; (b) after standing for 10 min; ◇ C\textsubscript{12} 4-phenyl SO\textsubscript{3}Na/SDS at pH 3; ◆ C\textsubscript{12} 4-phenyl SO\textsubscript{3}Na/SDS at pH 10.5; □ C\textsubscript{12} 4-phenyl SO\textsubscript{3}Na at pH 3; ■ C\textsubscript{12} 4-phenyl SO\textsubscript{3}Na at pH 10.5.
Volumes of foam generated by cylinder shaking of both C_{12} 4-phenyl SO_{3}Na and C_{12} 4-phenyl SO_{3}Na/SDS are constant after 10 minutes. There is no effect of the pH on either foamability or foam stability. This is analogous to the behaviour of pure C_{12} 4-phenyl SO_{3}Na as shown in Fig. 4.13.

9.4 Effect of SDS on Foamability and Foam Stability in the Presence of Antifoams

Triolein/stearic acid (90/5) and triolein/tristearin (90/5) were dispersed at 1.0 g l^{-1} in both C_{12} 4-phenyl SO_{3}Na/SDS and C_{12} 4-phenyl SO_{3}Na solutions as described in section 3.3.2.2. A significant decrease of the foamabilities by both surfactant solutions is seen under all pH and Ca^{2+} concentration conditions after the addition of these two antifoams. Results of the foamabilities are presented in Fig. 9.5 (in the presence of triolein/stearic acid antifoam) and Fig. 9.7 (in the presence of triolein/tristearin antifoam).

In the presence of triolein/stearic acid antifoam, the foamability of the C_{12} 4-phenyl SO_{3}Na/SDS surfactant system is higher than that of the C_{12} 4-phenyl SO_{3}Na system at Ca^{2+} concentration greater than those at the micellar-precipitate boundary (where Ca^{2+} \geq 6.75 \times 10^{-4} M). This effect is more marked at pH 3 (see in Fig. 9.5 (a)), where no formation of sodium and calcium soaps occurs, so the antifoam is relatively less effective. This behaviour may again be attributed to faster surfactant transport to the air-water surface in the case of C_{12} 4-phenyl SO_{3}Na/SDS micellar mixture. However, the enhancement in foamability due to the presence of SDS is less pronounced than in the absence of antifoam, becoming negligible at pH 10.5 where soap formation occurs.

Foam generated by both surfactant systems is stable after 10 minutes, as shown in Fig. 9.6. This means the antifoam effect of triolein/stearic acid is diminished under equilibrium conditions (where the bridging coefficient B^e < 0, for triolein, at least in the case of the pure C_{12} 4-phenyl SO_{3}Na as shown in Table 7.2).
Fig. 9.5. Foamability in cylinder shaking of $2.0 \times 10^{-3}$ M $\text{C}_{12}$ 4-phenyl $\text{SO}_3\text{Na}$ (and $\text{C}_{12}$ 4-phenyl $\text{SO}_3\text{Na}$/SDS: 4/1) in $1.7 \times 10^{-2}$ M NaCl, in the presence of 1.0 g l$^{-1}$ Triolein/stearic acid antifoam and at Temperature of $25 \pm 1 \degree$C; (a) at pH 3; (b) at pH 10.5; □ $\text{C}_{12}$ 4-phenyl $\text{SO}_3\text{Na}$; ◇ $\text{C}_{12}$ 4-phenyl $\text{SO}_3\text{Na}$/SDS.
Fig. 9.6. Foam stability in cylinder shaking after 10 min of $2.0 \times 10^{-3}$ M C$_{12}$-phenyl SO$_3$Na (and C$_{12}$-phenyl SO$_3$Na/SDS: 4/1) in $1.7 \times 10^{-2}$ M NaCl, in the presence of 1.0 g l$^{-1}$ Trilein/stearic acid antifoam and at Temperature of $25 \pm 1$ °C; (a) at pH 3; (b) at pH 10.5; □ C$_{12}$-phenyl SO$_3$Na; ◇ C$_{12}$-phenyl SO$_3$Na/SDS.
With the triolein/tristearin antifoam, presence of SDS also enhances the foamability of $\text{C}_{12}\text{4-phenyl SO}_3\text{Na}$ as shown in Fig. 9.7. No difference in the foamability and foam stability is produced by varying the pH. This is presumably because there is no change in the properties of tristearin particles under these different conditions.

**Fig. 9.7.** Foamability in cylinder shaking after of $2.0 \times 10^{-3}$ M $\text{C}_{12}$ 4-phenyl $\text{SO}_3\text{Na}$ (and $\text{C}_{12}$ 4-phenyl $\text{SO}_3\text{Na}$/SDS: 4/1) in $1.7 \times 10^{-2}$ M NaCl, in the presence of $1.0 \text{ g l}^{-1}$ Triolein/tristearin antifoam and at Temperature of $25 \pm 1^\circ \text{C}$; (a) at pH 3; (b) at pH 10.5; □ $\text{C}_{12}$ 4-phenyl $\text{SO}_3\text{Na}$; Δ $\text{C}_{12}$ 4-phenyl $\text{SO}_3\text{Na}$/SDS.
Comparison of Fig. 9.7 with Fig. 9.8 reveals little change in foam volume which implies that the antifoam effect of triolein/tristearin is negligible under the near-equilibrium conditions prevailing in foam stability measurements after 10 minutes. Again at least in the case of C$_{12}$ 4-phenyl SO$_3$Na, this would be expected, because $B^c < 0$, for triolein, as shown in Table 7.2.

Fig.9.8. Foam stability in cylinder shaking after 10min of 2.0×10$^{-3}$ M C$_{12}$ 4-phenyl SO$_3$Na (and C$_{12}$ 4-phenyl SO$_3$Na/SDS: 4/1) in 1.7×10$^{-2}$ M NaCl, in the presence of 1.0 g l$^{-1}$ Triolein/tristearin and at Temperature of 25±1 °C; (a) at pH 3; (b) at pH 10.5; □ C$_{12}$ 4-phenyl SO$_3$Na; ◇ C$_{12}$ 4-phenyl SO$_3$Na/SDS.
In the presence of sebum soil antifoam, the effect of SDS on the foamability of C_{12} 4-phenyl SO_3 Na is negligible. A summary of the $F$ values for C_{12} 4-phenyl-SO_3 Na and C_{12} 4-phenyl SO_3 Na/SDS (4/1) surfactant systems, showing generally the same foam behaviour at pH 3 and 10.5 in the presence and absence of Ca^{2+} is presented in Table 9.1.

**Table 9.1.** $F$ profile in cylinder shaking under the condition of 2.0×10^{-3} M C_{12} 4-phenyl SO_3 Na (and C_{12} 4-phenyl SO_3 Na/SDS: 4/1) in 1.7×10^{-2} M NaCl, 5.25×10^{-4} M Ca^{2+}, in the presence of 1.0 g l^{-1} sebum soil antifoam and at Temperature of 25±1 °C.

<table>
<thead>
<tr>
<th>Surfactant system</th>
<th>$F$ after 10s</th>
<th>$F$ after 10 min</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>pH = 3</td>
<td>pH = 10.5</td>
</tr>
<tr>
<td></td>
<td>nil Ca^{2+}</td>
<td>With Ca^{2+}</td>
</tr>
<tr>
<td>C_{12} 4-phenyl SO_3 Na</td>
<td>0.3</td>
<td>0.2</td>
</tr>
<tr>
<td>C_{12} 4-phenyl SO_3 Na/SDS (4/1)</td>
<td>0.3</td>
<td>0.2</td>
</tr>
</tbody>
</table>

**9.5 Summary**

The effect of SDS in enhancing foamability and foam stability is only significant in the absence of antifoam in the micellar-precipitate region, which correlates with enhanced rates of surfactant transport to air-water surfaces (which in turn correlates with a higher concentration of micellar surfactant at high calcium levels).

In the presence of antifoam, especially sebum soil and triolein/tristearin antifoams, the effect of antifoam dominates the overall foaming profile. In the micellar region up to the micellar-precipitate boundary, SDS does not reduce the dynamic air-water surface tension as measured at surface ages of 0.1 s and 1.0 s (see in Fig.9.3). It therefore does not reduce the entry coefficient of antifoam droplets. In the micellar-precipitate region where Ca^{2+} ≥
10×10⁻⁴ M, SDS causes decreases in air-water surface tensions at a surface age of 0.1 s, of ≈5 mN m⁻¹ relative to that of a pure C₁₂ 4-phenyl SO₃Na system. This reduction however is not enough to switch off the antifoam effect. The slight enhancement in foamability in the micellar-precipitate region can again be attributed to faster surfactant transport due to the presence of C₁₂ 4-phenyl SO₃Na/SDS mixed micelles.

9.6 References

Chapter 10 Summary and Conclusions

10.1 Summary

This project has included an experimental study of the physical chemistry of foam generation under conditions relevant for the hand wash – by air entrainment of a typical micellar anionic surfactant solution in the presence of polyvalent metal ions and oily soil. Understanding of the process of foam generation in the context of the washing of clothes by hand is surprisingly limited in view of the ubiquitous nature of a habit employed by hundreds of millions of consumers across the globe. Consideration of the key features of the process reveals an extraordinary degree of complexity which perhaps provides some explanation for that lack of understanding. It is characterised by three key interrelated factors – methodology, surfactant solution properties and the antifoam action of deterged soil. Here we have sought to further understanding of these factors by following an essentially experimental study.

The methodology of consumers in this context simply involves rapid air entrainment into a surfactant solution containing emulsified antifoam materials derived from soil - so-called sebum soil which, as we have seen, is an effective antifoam. The resulting foam is necessarily polydisperse. Obviously the volume of entrained air, and therefore foam, formed at this stage represents the key point of satisfaction or otherwise of consumers. The stability over prolonged times of the resulting foam is of less significance. Foam tests intended to simulate this aeration process use shaking, tumbling or impinging jets rather than pneumatic methods. We have shown that the foamabilities measured by two such tests – cylinder shaking and tumbling tube rotation correlate with a coefficient of $\geq 0.95$ for many systems both in the presence and absence of antifoam (see in Fig. 6.3 (a)). These two methodologies differ significantly in dimensionality, including foam heights for a given system, but are both characterised by high Reynolds numbers ($> 10^5$). The stability of the relevant foam films during air-entrainment using these methodologies cannot therefore be
related to the hydrostatic head.

This correlation deteriorates with foam stability measurement using these two methodologies as indicated by a correlation coefficient of only ~0.82 (see in Fig. 6.3 (b)). The deterioration in the correlation derives from differences in foam stability in the presence of sebum soil antifoam with these two methodologies. Foam is less stable if generated by the tumbling tube method. This is surprising because foam heights, measured from the top of the liquid phase, are higher with cylinder shaking. Therefore both hydrostatic head and equilibrium Plateau border capillary pressures are higher with the latter. Tentatively we have attributed the effect to the difference in bubble size distribution between the two methodologies. Larger bubbles generated by the tumbling tube method mean larger foam films and higher probabilities of the presence of antifoam entities as the films drain. That larger bubbles may in fact be preferentially ruptured by antifoam entities has been shown by comparing the bubble size distribution of foam generated in the presence of sebum soil antifoam with that in the absence of such an antifoam.

Efficient entrainment of air in the absence of antifoam is easily ensured if a sufficient concentration of a suitable micellar anionic surfactant is used and both antifoam and polyvalent ions are absent. Here we have used the usual optimum chain length sodium linear alkyl benzene sulphonate as either a pure surfactant (named as C\textsubscript{12} 4-phenyl SO\textsubscript{3}Na) or as an equivalent commercial blend of chain lengths and isomers (named as NaLAS). With anionic surfactants the main constraint on effectiveness, in the absence of antifoam, derives from the presence of calcium and other polyvalent ions in hard water which result in the formation of insoluble precipitates. In practice this problem is usually avoided by the addition of a suitable complexing agent (a “builder”). Here we seek understanding of surfactant foam behaviour in the absence of such agents, an interest which reflects the potential cost and environmental disadvantages which can be involved in their use. We have measured the so-called precipitation phase diagram for both NaLAS (see in Fig. 4.4) and C\textsubscript{12} 4-phenyl SO\textsubscript{3}Na (see in Fig. 4.6) where increasing concentrations of Ca\textsuperscript{2+} in the absence of micelles reveals an apparent solubility product suggestive of 1:2 stoichiometry – the relevant precipitates
Ca(LAS)$_2$ and Ca(C$_{12}$ 4-phenyl SO$_3$)$_2$ however appear to be lamellar phase liquid crystalline particles. Addition of increasing concentrations of Ca$^{2+}$ to micellar surfactant solutions crosses the so-called micellar-precipitate boundary into a phase region where Ca(LAS)$_2$ or Ca(C$_{12}$ 4-phenyl SO$_3$)$_2$ precipitate coexists with micelles and monomeric surfactant. This region is essentially invariant according to the phase rule so that the equilibrium air-water surface tension remains constant with increasing concentrations of calcium and therefore of precipitate of Ca(LAS)$_2$ or Ca(C$_{12}$ 4-phenyl SO$_3$)$_2$. By contrast the dynamic surface tension increases dramatically in this region reflecting the slow transport of the Ca(LAS)$_2$ or Ca(C$_{12}$ 4-phenyl SO$_3$)$_2$ precipitates (see in Fig. 4.11 and Fig. 4.16 respectively). In consequence foam generation rapidly declines at the micellar-precipitate boundary – reflecting low surfactant adsorptions, low disjoining pressures and high capillary pressures all conspiring to diminish foam film stability. Such foam behaviour cannot be reversed by filtration of the precipitate from the solution. The precipitate particles therefore have no antifoam effect. This is hardly surprising because if they are indeed mesophase entities then we would be expect them to be hydrophilic and therefore without effect.

We have also studied the effect of a co-surfactant (Sodium Dodecyl Sulphate, SDS) on this behaviour of C$_{12}$ 4-phenyl SO$_3$Na. Up to a molar ratio of SDS/C$_{12}$ 4-phenyl SO$_3$Na (1/4) produces a small expected movement of the micellar-precipitate boundary and enhancement of foam in the presence of calcium in the micellar-precipitation region (see in Fig.9.4). This correlates with enhanced rates of surfactant transport to air-water surfaces (which in turn correlates with a higher concentration of micellar surfactant at high calcium levels, see in Fig. 9.3).

Foam behaviour in this context, and in the absence of precipitation of anionic surfactant by polyvalent metal ions, is often totally dominated by the effect of sebum soil. This sebum soil is usually simulated in practical tests with a synthetic mixture of various saturated and unsaturated triglycerides (using for example olive oil and sunflower oil), saturated and unsaturated fatty acids and hydrocarbons (see in Appendix 3.1 and 3.2). Such a mixture may be realistic but complexity implies a probable lack of clarity in establishing its mode of
action. Such clarity is of course not without significance in establishing the limits of possible formulation in eliminating or minimising antifoam action. Here we therefore sought first to find a simpler combination of materials which had essentially the same antifoam behaviour as the oily soil. Then we sought to establish the mode of action of that material.

Few studies have been made of triglyceride/fatty acid combinations as antifoams. The most recent [1, 2] concerned mixtures of triolein and oleic acid. This mixture is a single phase oil. It is without effect unless calcium is present in the aqueous phase and unless the pH is high so that insoluble calcium oleate particles can be formed at the oil-water interface. The mixture can then function as a typical oil/particle antifoam. Here the function of the particles concerns rupture of the oil-water-air pseudoemulsion film which would otherwise prevent emergence of the oil droplet into the air-water surfaces of foam films. Presence of oil droplets in those surfaces can mean formation of unstable bridging configurations leading to foam film collapse [3, 4].

We have found that triolein/oleic acid mixtures do not reproduce the antifoam behaviour of a typical simulated sebum soil (see in Table 5.6). Unlike the triolein/oleic acid mixture the selected simulated sebum soil is intrinsically a mixture of oil and particles. It appears to function almost equally well as an antifoam whether or not calcium is present and even at pHs so low that calcium soaps cannot form (see in Fig. 5.3, 5.6 and 5.8). This behaviour could however be reproduced with mixtures of triolein/stearic acid (see Fig. 5.13 and 5.14) and triolein/tristearin (see Fig. 5.15 and 5.16). In the case of the former stearic acid crystals function as the antifoam particle at low pH, sodium stearate particles form at high pH and the absence of calcium, and calcium stearate particles form at high pH and in the presence of calcium. By contrast tristearin is a saturated triglyceride which lacks this chemistry and therefore the complexity.

We further studied the antifoam mechanism of both triolein/stearic acid and triolein/tristearin mixtures. The spreading behaviour of sebum soil, triolein/stearic acid and triolein/tristearin at the air-water surface of the antifoam was first considered here – no
evidence of spreading was found under equilibrium or dynamic conditions. The "spreading-fluid entrainment" antifoam mechanism shown in Fig.2.19 would therefore appear to have no role in the mode of action of these antifoams.

Another mode of antifoam action which is adopted by oil-based antifoams concerns formation of unstable oil bridges in foam films [5]. These effects occur only when the so-called bridging coefficient is positive, as shown in Fig.2.19. However, under near-equilibrium conditions, the bridging coefficient for triolein was found to be negative at all the pH conditions and in the presence and absence of Ca\(^{2+}\) (see Tables 7.1 and 7.2). This explains the minimal antifoam action of triolein-based antifoams when measuring foam stability where near-equilibrium conditions are expected to prevail. These antifoams were however effective when measuring foamability where non-equilibrium dynamic conditions prevail. It seems likely that the high dynamic air-water surface tensions (see in Fig. 4.11 and Fig. 9.3 for NaLAS and C\(_{12}\) 4-phenyl SO\(_3\)Na respectively) in the rapidly expanded foam films tend to cause a reversal of the sign of bridging coefficients from negative to positive. Antifoam action by triolein/stearic acid and triolein/tristearin mixtures may therefore occur.

Triolein droplets alone in NaLAS solutions however do not exhibit any antifoam effect even in the dynamic conditions as shown in Table 5.5. This indicates the presence of a stable air-water-oil pseudoemulsion film. The role of stearic acid and tristearin particle in rupturing this air-water-triolein pseudoemulsion film therefore became important for us to study.

Both stearic acid and triolein have a small but significant solubility in triolein even at ambient temperature. In preparation of the antifoams it is necessary therefore to avoid the effects of Ostwald ripening on crystal size which would carry the risk of irreproducible antifoam behaviour. We therefore adopted a procedure (see in section 3.3.2.1) where the triolein/stearic acid was heated to 70 °C and the triolein/tristearin was heated to 55 °C to form clear melts. These were then cooled rapidly and remixed in an iced ultrasonic water
bath (before immediate dispersal in surfactant solution). Using this procedure tristearin formed particles of suboptical size \( \leq 0.5\mu m \). By contrast stearic acid formed lozenge shaped platelets with a wide range of dimensions, distributing from \(~1\) to \(~200\ \mu m\).

Stearic acid and tristearin crystallized from triolein to formed particles with distinct geometries. Their detailed crystal structures were imaged using optical microscopy and electron scanning microscopy as shown in Fig. 7.13 and Fig. 7.14 (for stearic acid) and Fig. 7.16 and Fig. 7.17 (for tristearin). We find that both stearic acid and tristearin particles exhibit no antifoam effect by themselves, but they can invert oil-in-water emulsions to water-in-oil emulsions by rupturing the oil-water-oil emulsion films. Measured oil-water contact angles \( \theta_{OW} > 90^\circ \) (measured through the aqueous phase) of both particles are consistent with such behaviour. The oil-water-air pseudoemulsion films will also be ruptured if the particles satisfy certain conditions (for example conditions (7.1) - (7.3) for stearic acid and conditions (7.4) - (7.6) for tristearin). Use of the Film Trapping Technique (FTT) [6] shows the presence of tristearin particles causes a significant decrease of the critical capillary pressure required for triolein droplets to emerge into the air-water surfaces. This reveals that crystalline particles at oil-water interface will destabilise the air-water-triolein pseudoemulsion film, promoting the emergence of oil droplets to form unstable bridging configurations, as indicated by \( B^d > 0 \) under dynamic conditions.

Although exhibiting the same qualitative behaviour as synthetic sebum soil antifoam, the triolein/stearic acid mixtures were significantly less effective. This is probably due to antifoam deactivation of triolein/stearic acid by formation of inactive large agglomerates after antifoam dispersion. Those agglomerates were in fact removed before each foaming experiment. Moreover the antifoam effect with the triolein/stearic acid mixture deactivated rapidly, as shown in Fig 8.3, unlike that of sebum soil antifoam which showed no deterioration after continuous aeration for more than an hour. Triolein/tristearin mixtures were at least as effective as sebum soil antifoam and, as shown in Fig. 8.3, did not exhibit significant deactivation after similar periods. It seems likely that the rate of antifoam deactivation is determined, at least in part, by the rate of splitting and coalescence to form
inactive particle-rich and particle-free droplets as described by Denkov and coworkers [7, 8] for poly-dimathlsiloxane oil / hydrophobed silica particle antifoam. The lower stearic acid particle concentration in oil droplets means a higher probability of formation of particle-free droplets. It seems likely that the differences between triolein/stearic acid and triolein/tristearin at least in part also concern the formation of additional large inactive agglomerates in the case of the former antifoam, after a process of continuous splitting and coalescence between antifoam droplets. Here the conversion of stearic acids to stearate soaps at pH 10.5 and in the presence of Ca\(^{2+}\) results in a more rapid antifoam deactivation when compared with that at pH 3 and in the absence of Ca\(^{2+}\). This may be caused by a gradual formation of lamellar phase of unknown composition, which may be more hydrophilic, and therefore more easily separated from the oil phase.

10.2 Conclusions

The most significant findings of this project are:

- Foamability of NaLAS and C\(_{12}\) 4-phenyl SO\(_3\)Na solutions in the absence of antifoam is essentially independent of pH and declines markedly after the micellar-precipitate boundary of the Ca\(^{2+}\)-LAS\(^{-}\) (or C\(_{12}\) 4-phenyl SO\(_3\)\(^{-}\)) precipitation phase diagram, due to diminished rates of transport of surfactant to the rapidly generated air-water surfaces formed during foam generation.

- Sebum soil shows a significant antifoam effect under all pH and Ca\(^{2+}\) concentration conditions tested. That it did not apparently require formation of soaps suggests that the essential physical nature of the sebum soil is determined by the presence of particulate components dispersed in liquid oils. This antifoam behaviour of sebum soil can be modeled by two well-characterized (pure) oil/particle mixtures - triolein/stearic acid and triolein/tristearin.

- Comparison of foamability measurements by cylinder shaking and tumbling tube revealed a good correlation, both in the presence and absence of sebum soil antifoam. Comparison of foam stability measurements in the presence of sebum soil antifoam by
the two chosen methods revealed a marked deterioration in the correlation. This is attributed to the fact that larger bubbles in the case of the tumbling tube methodology could result in a higher concentration of antifoam droplets trapped in film during drainage and therefore rendering foam films more vulnerable to rupture.

- Triolein droplets alone do not have any antifoam effect. The air-water-triolein pseudoemulsion films are required to be ruptured by stearic acid and tristearin particles for triolein droplets to emerge into the air-water surfaces to form unstable bridging configuration (so-called the “bridging-stretching” mechanism). This effect is only expected to occur in foamability measurement where dynamic conditions prevail, as bridging coefficients of triolein measured in near-equilibrium conditions are less than zero. This explains the less significant antifoam effect of sebum soil, triolein/stearic acid and triolein/tristearin in foam stability measurement where the near-equilibrium conditions prevail.

- Triolein/stearic acid deactivates more rapidly than sebum soil and triolein/tristearin in a continuous foam generation process. The antifoam deactivation appears to be first order and the rate of deactivation seems to be determined by the rate of splitting and coalescence to form particle-rich and particle-free droplets. Total deactivation of oil/particle antifoams is accompanied by the formation of large inactive agglomerates.

- The effect of SDS in foam enhancement is only significant in the absence of antifoam at Ca\(^{2+}\) concentration greater than that at the micellar-precipitate boundary in the Ca\(^{2+}\)-C\(_{12}\)4-phenyl SO\(_3\)^— precipitation phase diagram. The reason can be attributed to the enhanced rates of transport to air-water surfaces. In the presence of antifoam, the overall foam profile is only slightly enhanced by the presence of SDS.

### 10.3 Future Work

More studies related to this project could be followed, which may include:

- The effects of slow transport of surfactant to air-water surfaces during the foam generation on foamability should be further investigated. Here we have, for example,
no basis upon which to compare the time scales of the dynamic surface tensions shown with a given method of foam generation. What are the relevant time scales for adsorption when the foams are generated by different methodologies?

- The accurate air-water, oil-water and oil-air surface tension values in dynamic conditions should also be measured. These values would in principle affect the stability of the air-water-oil pseudoemulsion films and bridging coefficients, so the antifoam effect in foamability measurement.

- It has not been possible to image the stearic acid and tristearin particles at the surfaces of oil droplets after antifoam dispersion. Particularly in the case of stearic acid and tristearin crystalline particles, the exact role of particle geometry, in rupturing the oil-water-oil emulsion and air-water-oil pseudoemulsion films has not been fully established. Other techniques, such as the Surface Evolver program may be used to study the probable configurations of particles of various geometries adopted at the relevant oil-water and air-water surfaces.

- We have not confirmed the formation of particle-free droplets after a continuous foam generation process; and we do not know the exact compositions of the large agglomerates formed in the case of triolein/stearic acid antifoam. We also have no adequate theory or simulation of the process of deactivation of oil/particle antifoams.

We believe these issues should be addressed in future work.

10.4 References


