



## The effect of calcium on the foam behaviour of aqueous sodium alkyl benzene sulphonate solutions. 4. The role of particles in triglyceride-based antifoam mixtures



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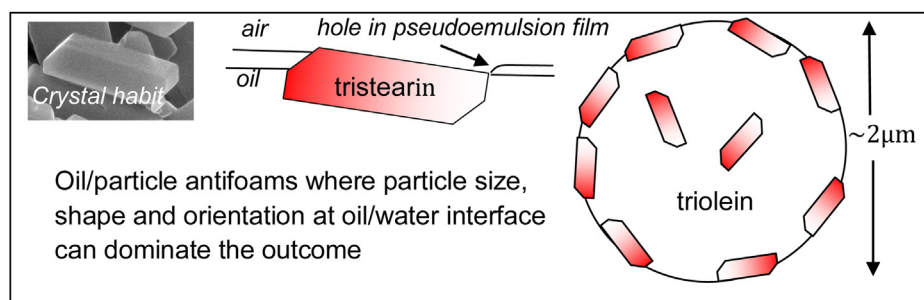
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### HIGHLIGHTS

- Tristearin is more efficient than stearic acid in promoting antifoam action by triolein.
- Contact angles of stearic acid and tristearin at surfaces relevant for antifoam action are similar.
- Surface energy minimization has been used to calculate orientations from morphology and contact angle.
- Calculations show orientations cannot explain differences in effectiveness.
- By contrast earlier findings concerning particle size and aggregation are consistent with differences.

### GRAPHICAL ABSTRACT



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### ABSTRACT

Mixtures of triolein with stearic acid were significantly less effective as antifoams than mixtures with tristearin. Measurements of contact angles at oil-water and air-water surfaces combined with consideration of crystal morphology have permitted exploration of the possibility that these differences concern the relative effectiveness of particles in rupturing triolein-water-air pseudoemulsion films. No significant difference in the theoretical effectiveness of tristearin and stearic acid in their potential to rupture pseudoemulsion films is however apparent. This suggests that the earlier finding that relative antifoam effectiveness rather concerned particle size and aggregation where stearic acid particles were, for example, more than an order of magnitude larger than the tristearin particles, implying lower probabilities of presence in drops and films.

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## 1. Introduction

It has been shown in Part 2 [1] of this series of papers that triolein mixtures with either a saturated fatty acid, stearic acid, or a saturated triglyceride, tristearin, are effective antifoams in reducing the foamability of saline solutions of typical sodium alkyl benzene sulphonates. Such mixtures replicate to some extent the antifoam behaviour of model sebum, which in turn replicates the adverse

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effect of oily soil on foam generation during the hand washing of textiles – a habit still practised by millions of consumers.

Both the stearic acid and tristearin are only sparingly soluble in triolein at ambient temperatures so these materials presumably then function by destabilisation of oil-water-air pseudoemulsion films in the general manner of oil-particle antifoam mixtures [2–4]. However we have shown in Part 3 [5] that under the near equilibrium conditions prevailing after foam generation has ceased the bridging coefficient of triolein with the selected surfactant solution becomes negative. The oil cannot therefore then function as an antifoam ingredient. In this case the oil/particle mixture becomes ineffective regardless of the properties of the particles.

As described in Part 2 [1] oil-particle mixtures were prepared by rapid cooling in an ultrasonic bath of a melt of either the saturated fatty acid or the triglyceride in triolein. However the resulting dispersions of crystalline particles were radically different, presumably reflecting differences in nucleation arising from differences in solubility in triolein. The dispersions of stearic acid revealed particles sizes at least an order of magnitude greater than those present in dispersions of tristearin. Much aggregation to form large oily-agglomerates was also apparent when the former was dispersed in aqueous solution. It was concluded in Part 2 [1] that these properties of the triolein-stearic acid mixture contributed significantly to the observed inferior antifoam effectiveness of that mixture. However it is known that the relative effectiveness of particles in this respect can also be influenced by both the contact angles at the relevant fluid-fluid surfaces and the geometry of the particles.

Here we consider the possibility that these two factors also contribute significantly to the differences in antifoam effectiveness of triolein-stearic acid and triolein/tristearin mixtures. The potential role of both tristearin and stearic acid particles in rupturing pseudoemulsion films has therefore been explored by measurement of the relevant contact angles and consideration of particle morphology. The relatively simple morphology adopted by stearic acid particles crystallised from triolein meant that interpretation was facilitated by calculation of the probable orientations of the particles at oil-water surfaces as a function of contact angle and geometry using the surface energy minimization technique of Morris et al [6–9] which makes use of the Surface Evolver software developed by Brakke [10]. However the complex morphology of tristearin particles, crystallised from triolein, meant that only a two-dimensional interpretation was possible – an approach essentially similar to that adopted by Dippenaar when considering the rupture of foam films by orthorhombic particles [11].

## 2. Materials and methods

### 2.1. Materials

All materials used are described in Papers 1 and 2 [12,1], together with the relevant procedures for the preparation and dispersal of antifoams. Here we note that sodium *p*-dodecyl 4-phenyl sulphonate (C12 4-phenyl SO<sub>3</sub>Na) was nominally pure and NaLAS was a commercial linear alkyl benzene sulphonate.

### 2.2. Contact angles

Air/surfactant solution and triolein/surfactant solution advancing and receding contact angles on compressed discs of tristearin and stearic acid were measured using the sessile drop technique (Camtel Ltd., UK). Discs of tristearin and stearic acid were prepared by compressing the crystals using evacuable pellet dies (Specac Ltd.) at 20 Pa. Triolein/surfactant solution contact angles were measured by first immersing the discs in triolein and subsequently applying a drop of the solution. Solutions of triolein contained suf-

ficient tristearin or stearic acid to ensure saturation and prevent dissolution of the surfaces of the discs.

### 2.3. Scanning electron microscopy

The crystal morphology and structure of tristearin and stearic acid crystallized from triolein were observed using a scanning electron microscope (SEM, Quanta 200 ESEN, FEI Ltd.). Samples were spread on a stage and sputter coated with a gold/platinum alloy in a vacuum to render them electrically conductive.

## 3. Results and discussion

### 3.1. Contact angles

It is generally accepted that the role of the particles in oil/particle antifoams concerns rupture of the oil-water-air pseudoemulsion film (see various reviews [2–4]). Essentially the particle adheres to the oil-water surface so that it protrudes into the pseudoemulsion film. As that film thins the particle emerges into the air-water surface to form a bridging configuration where it adheres to both oil-water and air-water surfaces. Depending upon the magnitudes of the oil-water and air-water contact angles this bridging configuration produces an unbalanced capillary force in the vicinity of the particle leading to enhanced film drainage. Eventually the oil-water and air-water surfaces become coincident upon the particle so that a hole forms in the pseudoemulsion film which leads to film rupture. The theoretical conditions, which must be satisfied for this process, are dependent upon the geometry of the particle [2,3,13]. In the case of a spherical particle they are for example;

$$90^\circ < \theta_{OW}^T < 180^\circ \quad (1)$$

where  $\theta_{OW}^T$  is the oil-water contact angle at the particle, measured through the aqueous phase. It indicates that the particle should sit mainly in the oil phase. In addition it is necessary that

$$\theta_{AW} > 180^\circ - \theta_{OW} \quad (2)$$

where  $\theta_{AW}$  is the air-water contact angle at the particle and again measured through the aqueous phase.

As we will see the particles of tristearin and stearic acid are not spherical and therefore different conditions will prevail if they are to rupture pseudoemulsion films. Moreover the pseudoemulsion films are thermodynamically stable under equilibrium conditions in the case of the solutions containing Ca<sup>2+</sup> as shown in Part 3 [5]. Neither emergence into the air-water surface nor, therefore, film rupture is possible under those equilibrium conditions, irrespective of the effect of the particles. Indeed if a surfactant solution has a sufficiently low air-water surface tension to perfectly wet the oil as a duplex film it is likely that it will also perfectly wet a solid which is less hydrophobic than the oil (which is a necessary condition if the solid is to adhere to the oil-water interface). Not surprisingly then attempts to measure the equilibrium air-water contact angles of such solutions against compressed discs of both tristearin and stearic acid revealed low values – zero or close to zero. By contrast the oil-water contact angles,  $\theta_{OW}^T$ , measured on such discs, through the aqueous phase, were both finite and »90°. Therefore the particles are preferentially wetted by the oil. Results are presented in Table 1 and S1 (in Supplementary material) for solutions of sodium dodecyl 4-phenyl sulphonate and NaLAS respectively. Both advancing and receding contact angles are presented where hysteresis is seen to be either absent or small in the case of stearic acid, which implies that the surfaces are relatively smooth. Tristearin and stearic acid clearly both, at least, satisfy Eq. (1) under all solution conditions considered. The presence of calcium is seen to generally decrease the contact angles, which must presumably be

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