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Research paper

The effect of calcium on the foam behaviour of aqueous sodium alkyl benzene sulphonate solutions. 2. In the Presence of triglyceride-based antifoam mixtures revised version

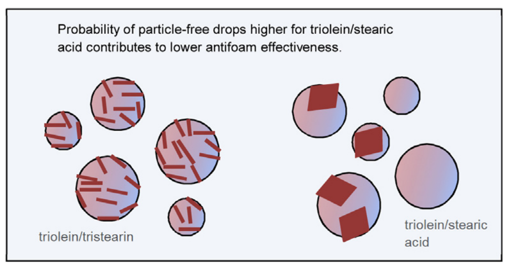
Peter R. Garrett*, Li Ran[1]

School of Chemical Engineering and Analytical Science, The Mill, University of Manchester, Oxford Road, Manchester M13 9PL, United Kingdom

HIGHLIGHTS

- The particles intrinsic to sebum can promote antifoam action.
- Mixtures of triolein with stearic acid or tristearin replicate sebum antifoam action closely.
- None of these antifoams show deactivation during prolonged foam generation.
- Differences in effectiveness between stearic acid and tristearin crystallised from triolein mainly concern crystal size.

GRAPHICAL ABSTRACT



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ABSTRACT

Here we have sought to establish the likely key ingredients which determine the antifoam behaviour of model sebum together with key specific aspects of their mode of action. Since the overall composition of sebum is dominated by unsaturated triglycerides we selected triolein as the oil. Tristearin and stearic acid were selected as particulate components since both are only sparingly soluble in triolein and are likely to replicate the absence of strong dependence upon changes in pH or [Ca^{2+}] found with sebum. Triolein/tristearin mixtures were, under most circumstances, at least as effective as the model sebum but totally unaffected by changes in [Ca^{2+}] and pH. However triolein/stearic acid mixtuures replicated the weak dependence upon [Ca^{2+}] of model sebum and pH but were less effective. The ineffectiveness of the former appeared to concern the relatively large size of stearic acid particles crystalizing from a melt in triolein – at least an order of magnitude larger than the particle sizes of tristearin prepared in a similar manner, showing a tendency to aggregate and form large, ineffective, triolein/stearic acid agglomerates. The large particle size of stearic acid particles also leads to a high probability of formation of ineffective particle-free drops upon dispersal in solution.

1. Introduction

In Part 1 [1] we have considered the effect of Ca^{2+} and pH on the foam and dynamic surface behaviour of solutions of sodium alkyl benzene sulphonates at ionic strengths typical of those used in the hand washing of clothes. We have shown that precipitation of a non-labile lamellar phase at relatively high Ca^{2+} concentrations leads to diminished rates of transport of surfactant to air-water surfaces. In turn this leads to a decline in foamability with no obvious decrease in the stability of any foam formed. Such adverse effects on foamability can usually be mitigated by use of either complexing agents (so called "builders") or co-surfactants or both.

* Corresponding author.
E-mail address: p.garrett@manchester.ac.uk (P.R. Garrett).
[1] Present address: TrendPac, 1 Corella Close, Berkeley Vale NSW 2261, Australia.

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Practical applications of these surfactants include both the hand washing of clothes and dishes where ready generation of copious amounts of foam is a requirement. Similar considerations are relevant for shampooing although sodium alkyl benzene sulphonates are not usually employed in that context. However all these processes invariably produce finely dispersed triglyceride-based oily soils, which can act as effective antifoams. For both the hand washing of clothes and shampooing, human sebum represents the most relevant oily soil whereas triglyceride-based food residues represent the relevant oily soils in hand dish washing. Here we are concerned to establish the role of Ca^{2+}, pH and composition in determining the antifoam effectiveness of such oily soils both in the presence and absence of the lamellar phase precipitation found with the sodium alkyl benzene sulphonates described in Part 1 [1].

Human sebum is mainly a complex and variable mixture of triglycerides (~23–41 wt%), wax monoesters (~20–25 wt%), free fatty acids (~16–27 wt%), squalene (~9–12 wt%) and minor components (~6–16 wt%) such as cholesterol [2–5]. This variation appears to derive mainly from the body location of the samples [2]. The oily soil component of food residues is likely to contain similar compounds but be even more variable in composition, involving a combination of dairy fat, meat fat (see for example Wood et al. [6]) and vegetable fats, often after subjection to processes such as partial hydrolysis of fats, hydrogenation of unsaturated compounds and various cooking methods. By contrast the variability of the composition of human sebum is limited only by body location and specific genetic factors [7,8]. There is however a distinction to be made between the condition of fresh sebum on hair during shampooing and that on clothes where periods of ageing are often involved before washing. Such ageing can mean significant chemical composition changes after just a few days as a result of oxidation of unsaturated hydrocarbon chains and enzymatic hydrolysis of triglycerides [9].

The variability of sebum between individuals and the difficulty of acquisition has meant that it is often modelled for research purposes by blending various combinations of triglycerides, wax monoesters, fatty acids, squalene and minor components such as cholesterol [10–15]. There is however no general agreement about the composition of such models – Stefaniak and Harvey [1] for example list 18 different combinations of ingredients utilised by various authors for use in various contexts!

Here we have explored the antifoam behaviour of a model sebum as representative of many triglyceride-based oily soils. That behaviour was explored after dispersal in solutions of both a sodium dodecyl 4-phenyl sulphonate and a commercial blend of sodium alkyl benzene sulphonate. These sodium alkyl benzene sulphonates find particular application in hand washing of textiles at ambient temperatures in emerging markets. The study has also included the antifoam behaviour of various combinations of compounds which are present in that model sebum in order to better understand antifoam effects which are specific to this type of triglyceride-based oily material. This approach is of obvious direct relevance for shampoo and clothes washing. The similar but rather more varied chemistry of oily soils found in food residues suggests that any distinctive antifoam phenomena found with any combinations of the constituent components of model sebum will also probably be found with such residues.

An aspect of oily soil antifoam behaviour has been reported by Zhang et al. [17] who published a study of the effect of triolein/oleic acid mixtures on the foam stability of aqueous solutions of both a sodium alkyl ether sulphate and an alcohol ethoxylate. They established that effective antifoam action by such mixtures requires that the oleic acid react with any calcium ions present in the aqueous phase to precipitate calcium oleate particles at the oil-water surface. Presence of the particles concerns the rupture of oil-water-air pseudoemulsion films which is typical of the behaviour found with oil/hydrophobic particle mixed antifoams dispersed in aqueous solutions (see for example Garrett [18] and Denkov [19]). Since triglycerides and fatty acids are present in both sebum and model sebum it is reasonable to suppose that similar effects, due to precipitation of calcium soaps at the oil-water surface, also represent a feature of the antifoam behaviour of these materials. However formation of calcium soap precipitates requires not only that calcium ions be present in the aqueous phase but that the pH be sufficiently high to ensure ionisation of the fatty acid in order to facilitate reaction with divalent calcium ions [17].

Human sebum is known to be a solid/liquid mixture at the human skin surface temperature of ~32° [16,20–22]. Moreover Motwani et al. [23] have formulated various models of sebum based upon known ingredients and variability and have demonstrated, using DSC, that those models also consist of solid/liquid mixtures at that temperature. It is therefore possible that the particulate component in such mixtures could be effective in rupturing the relevant pseudoemulsion films so that formation of calcium soaps would not then be a necessary aspect of the antifoam behaviour of sebum. Here we therefore seek to distinguish between these possibilities by examining the relative effectiveness of a model sebum as a function of pH and calcium content of the aqueous phase. We also compare the antifoam effectiveness of model sebum with simple mixtures of typical components present in the model selected so that they can unambiguously only function by one or the other of these two mechanisms.

It is well-known that the antifoam effectiveness of certain oil/particle antifoam mixtures deteriorates with the repeated agitation accompanying emulsification and foam generation [24] We have therefore sought to establish whether such effects are apparent with the triglyceride-based antifoams considered here. Therefore the effect of continuous foam generation on the antifoam effectiveness of a model sebum dispersion has been compared with that of simple triolein/particle mixtures.

2. Materials and methods

2.1. Materials

A model sebum soil (prepared to a composition and methodology of Procter and Gamble UK and supplied by Warwick Equest, UK from ingredients in turn supplied by VWR International, LLC) was used as received [15]. This material is an opaque paste at ambient temperature, prepared by blending the following ingredients as a melt; coconut oil (15 wt%), olive oil (15 wt%), cottonseed oil (15 wt%), oleic acid (15 wt%), myristic acid (5 wt%), palmitic acid (5 wt%), stearic acid (5 wt%), cholesterol (5 wt%), paraffin oil (15 wt%), squalene (5 wt%). It was stored at ~ 5 °C in a closed vessel before use.

Triolein (≥99.0%), tristearin (≥99.0%), oleic acid (≥99.0%) and stearic acid (≥99.0%) were obtained from Sigma-Aldrich (UK) and used as received. All other materials are as described in Part 1 [1].

2.2. Foam measurements

Both the Bartsch [25] and tumbling cylinder methodologies were used as described previously in Part 1 [1]. With the tumbling cylinder methodology volumes of foam depend on the liquid volume present in the cylinders. Cylinders with this methodology contained either 500 cm^3 or 250 cm^3 liquid as indicated in the relevant figures.

2.3. Preparation and dispersal of antifoams

Model sebum and mixtures of triolein with tristearin and triolein with stearic acid were used as antifoams. In general the

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