# The effect of calcium on the foam behaviour of aqueous sodium alkyl benzene sulphonate solutions. 3. The role of the oil in triglyceride-based antifoams
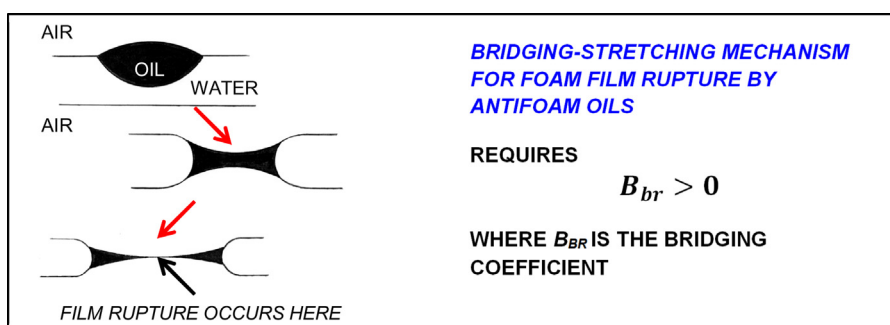
Peter R. Garrett *, Li Ran [1]

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

### HIGHLIGHTS

- With the selected solutions triolein-based antifoams are only effective during the non-equilibrium conditions of foam generation but not after foam generation ceases and near-equilibrium conditions prevail.
- The antifoam action of oils is caused by the formation of unstable bridging configurations where the bridging coefficient $B_{br} > 0$.
- Measurements of near-equilibrium bridging coefficients however indicate $B_{br} < 0$ which indicates the absence of antifoam action under those conditions.
- It can be shown that the bridging coefficient could change sign under non-equilibrium conditions leading to antifoam action.

### GRAPHICAL ABSTRACT



BRIDGING-STRETCHING MECHANISM FOR FOAM FILM RUPTURE BY ANTIFOAM OILS

REQUIRES

$$B_{br} > 0$$

WHERE $B_{BR}$ IS THE BRIDGING COEFFICIENT

### ARTICLE INFO

### ABSTRACT

A feature of mixtures of triolein with either stearic acid or tristearin particles as antifoams for certain micellar solutions of sodium dodecyl benzene sulphonate is that they are effective only during foam generation but no longer function after foam generation has ceased. Antifoam action by the antifoam oil is determined by positive values of the bridging coefficient. Bridging coefficients were found to be negative under the near equilibrium conditions prevailing after foam generation ceased. However measurements of dynamic surface tensions indicated that if surface ages >0.1 s prevailed under the dynamic conditions of foam generation then that would alter the sign of the bridging coefficients. Such dynamic conditions were replicated by drawing single foam films at different rates from solutions containing triolein-based antifoam. Antifoam effectiveness was significantly reduced in the case of foam films drawn at extremely slow rates so that near equilibrium conditions prevailed.

© 2016 Elsevier B.V. All rights reserved.

* Corresponding author at: School of Chemical Engineering and Analytical Science, The Mill, University of Manchester, Oxford Road, Manchester M13 9PL, United Kingdom.
E-mail address: p.garrett@manchester.ac.uk (P.R. Garrett).
[1] Present address: TrendPac, 1 Corella Close, Berkeley Vale, NSW 2261, Australia.
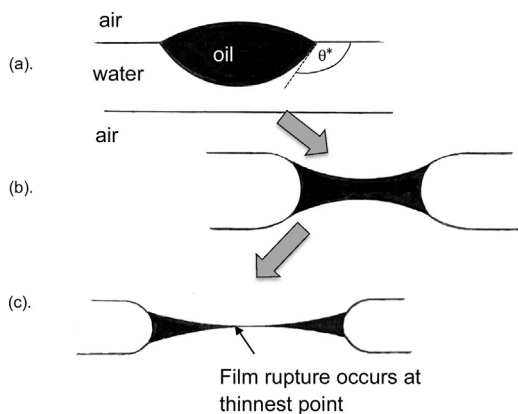
**Fig. 1.** Schematic illustration of the Bridging-Stretching mechanism of foam film rupture by an oil lens. (a,b) Bridging of foam film surfaces by an antifoam lens leads to formation of an oil bridge with unbalanced capillary pressures at oil-water and air-water surfaces. (c) Bridge stretches until rupture occurs as the two concave air-oil surfaces approach one another. Rupture of the bridge in this manner leads to rupture of whole foam film [2–7].

## 1. Introduction

We have shown in Part 2 [1] that the antifoam behaviour of a typical model sebum can be replicated in most respects by mixtures of triolein with particles of either a fatty acid or a triglyceride. It seems probable that these antifoams are examples of the typical oil-based antifoams used in aqueous solutions where the function of the particles concerns the rupture of the, otherwise metastable, oil-water-air pseudoemulsion films [2]. The metastability of such films derives from positive contributions to the disjoining pressure isotherm often principally of an electrostatic nature. The role of the oil has been shown to concern bridging configurations formed by oil drops in aqueous foam films [2–4] which can give rise to foam collapse as capillary forces and film drainage lead to stretching of the bridging drops until the two air-oil surfaces of the drop become coincident to form a hole which expands catastrophically [4–7]. A schematic illustrating this "bridging-stretching" process is shown in Fig. 1.

For this bridging-stretching process to occur, however, the oil drops must first emerge into both sides of a foam film despite the metastability of the oil-water-air pseudoemulsion films. Rupture of these pseudoemulsion films must therefore occur if drops are to assume this bridging configuration. It has been shown that presence of hydrophobic particles adhering to the oil-water surfaces of oil drops can facilitate pseudoemulsion rupture of those films provided they satisfy certain criteria. The latter concern particle geometry and the contact angles at both the oil-water and air-water surfaces [2,6,7]. A detailed review of these mechanistic considerations is to be found elsewhere [2].

The formation of unstable bridging configurations by oil drops in foam films is determined by the so-called bridging coefficient, which should be positive for antifoam oils in a given foaming solution [2–4,6,7]. Pseudoemulsion films can be stable, metastable or unstable. If they are stable then the oil cannot emerge into the air-water surface regardless of the presence of particles. Such films are characterised by negative values of the so-called entry coefficient. If they are unstable then there is no necessity for the presence of particles to rupture pseudoemulsion films. The role of the particles is therefore confined to situations where those films are metastable in a given solution. Since the pseudoemulsion films formed in aqueous surfactant solutions are usually metastable the ubiquitous presence of particles in antifoam oils is easily understood. Unstable and metastable pseudoemulsion films are both characterised by positive values of the entry coefficients.

We have therefore made measurements of both bridging and entry coefficients for triolein with the aqueous salt solutions of sodium alkyl benzene sulphonates described in Parts 1 [8] and 2 [1] where the pH and $Ca^{2+}$ concentration was varied. Antifoam effects were observed only under the conditions prevailing during foam generation, but not after generation ceased. Establishment of the cause of this behaviour was a particular concern. Measurements of entry and bridging coefficients suggest that it derives from the higher dynamic surface tensions prevailing during foam generation relative to the near-equilibrium values prevailing as foam generation ceases.

We have also measured the effect of triolein-based antifoams on the stability of foam films drawn at various rates using a vertically mounted film frame. This technique affords some indication of the relative significance of the rate of film formation (and therefore the rate of foam formation), film thickness and drop size in determining film rupture in the presence of antifoam.

## 2. Materials and methods

### 2.1. Materials

All materials used are described in Papers 1 [8] and 2 [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 $SO_3Na$) was nominally pure and NaLAS was a commercial linear alkyl benzene sulphonate.

### 2.2. Surface and interfacial tensions

Air-water surface tensions and spreading effects at the air-water surface were all measured using the Wilhelmy plate technique (CDCA-100 Surface tensiometer, Camtel Ltd., UK) using a roughened platinum plate. Interfacial tensions were measured by the pendant drop method (Camtel UK). In both cases equilibration for one hour provided near-equilibrium measurements.

Dynamic surface tensions were measured using a maximum bubble pressure tensiometer (BPA-1S; SINTERFACE technologies, De).

All surface and interfacial measurements were made at 25 °C.

### 2.3. Drawing of vertical foam films using a film frame

Foam films were drawn at different velocities using a glass film frame placed in a thermostatically controlled glass vessel at 25 °C using apparatus similar to that described elsewhere [9,10]. The frame could be drawn at velocities between 0.015 cm s$^{-1}$ and 45 cm s$^{-1}$ to predetermined heights using a computer controlled stepper motor. Foam film instability due to evaporation was avoided by pre-equilibration of this closed vessel with respect to water vapour pressure for 3 h before drawing films. Red monochromatic light (using an LED source of wavelength 619–629 nm) illuminated the films which could be imaged using an SLR camera (Canon EOS).

## 3. Theory

If the oil is to function as an antifoam it must first emerge into the air-water surface of foam films. Subsequently it must form an unstable bridging configuration where the oil drop is drawn apart to initiate film rupture—the so-called bridging-stretching mechanism illustrated in Fig. 1 [2–5].

Emergence into the air-water surface is determined by the so-called entry coefficient E, which is defined

$$E = \sigma_{AW} + \sigma_{OW} - \sigma_{OA} \tag{1}$$