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Defoaming: Antifoams and mechanical methods

Peter R. Garrett

School of Chemical Engineering and Analytical Science, University of Manchester, Oxford Road, Manchester M13 9PL, UK

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ABSTRACT

Recent progress in both the mode of action of antifoams and mechanical defoaming is reviewed. New insights concern the simulation of the orientation of particles in interfaces and films, the role of dynamic surface effects in antifoam action, antifoam action under micro-gravity, deactivation of oil/particle antifoams and antifoam action in hydrocarbon media. Progress in mechanical defoaming is mainly confined to new insights concerning the use of ultrasound.

1. Introduction

Defoaming is a surprisingly ubiquitous requirement. In the oil industry, for example, processes such as gas–crude oil separation and desulphurization of natural gas by bubbling through alkanolamine solutions usually require defoaming, which often involves the use of chemical antifoams. Other industrial processes such as the jet dying of textiles, radioactive waste treatment, the kraft pulp process and fermentation using oxygen bubble columns are also beset by unwanted foam. Again treatment with antifoams is often used but mechanical means are sometimes employed in the case of bubble columns. The control of flotation froth in mineral processing can be adversely affected if hydrophobed mineral particles too readily destabilize the froth. Formation of undesirable foam can also be an aspect of the use of certain formulated products such as waterborne latex paints, and detergents for use with machine washing of textiles and dishes. This problem usually necessitates the addition of antifoams to the relevant formulations. However some products, such as shampoos and hand dishwashing liquids, are designed to produce copious amounts of foam during use. These products must be formulated to minimize the antifoam effects of the triglyceride soils which are intrinsic to their application. There are even medical applications of defoaming. These include the use of antifoams to treat gastrointestinal gas, to eliminate any foam obscuring the view of colonoscopy cameras and in filters for removal of foam bubbles from the aspirated blood derived from surgery in order to permit recirculation. Defoaming is therefore clearly widely relevant in many contexts and does in fact present many interesting challenges to fundamental scientific understanding. This is however not always recognized in academic circles. A recent foam conference for example, included only one paper explicitly concerning defoaming [1] out of a total of over 100 oral and poster presentations.

Despite this seeming lack of recent interest much progress has been made in understanding the mode of action of antifoams over the past thirty years. A detailed account of that progress can be found in a recent monograph [2**] which is concerned with defoaming by both antifoams and mechanical means. Briefer accounts of defoaming by antifoams have also been published recently by Denkov et al. [3*] and Karakashev and Grozdanova [4]. Another recent review by Owen [5] is distinct in that it ignores much of the progress made over the past twenty years. Earlier noteworthy reviews include those by Miller [6] and Denkov [7**].

Use of antifoams always implies contamination of the system to be defoamed. Such contamination is, however, sometimes unacceptable. Examples include preparation of pharmaceuticals by fermentation and downstream processing in petrochemical plants where catalysts may be poisoned by antifoam residues. In these situations recourse is sometimes made to defoaming by mechanical means, utilizing for example either ultrasonic or various rotational devices. Progress in understanding the mode of action of such devices has however been rather limited. A complete review is to be found in the recent monograph [2**].

Developments in the understanding of the mode of action of antifoams, which have been published over the past 5 years or so, are the main concern of this review. Earlier work, however, is also cited in order to provide relevant context. Antifoams are defined here as particles, oils or mixtures of oils and particles which reduce either the foamability or foam stability of the liquid in which they are dispersed. Some account of defoaming by mechanical means is also included where however a dearth of recent relevant publications means a review largely confined to ultrasonic defoaming.

E-mail addresses: p.garrett@manchester.ac.uk, pgarcgar@btinternet.com.

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2. Defoaming by particles

2.1. Hydrophobic particles; theory

It is now well known that finely divided particles, which are sufficiently hydrophobic, can produce antifoam effects when dispersed in aqueous surfactant solution [2**,3*,8]. Whether these effects are apparent is dependent upon the contact angle and the shape of the particles. In the case of spherical particles antifoam effects are only present if the contact angle (measured through the aqueous phase), θ_{AW}> ~90° [2**, 3*,8]. As the film drains the particles bridge the film, and dewet (now often called the "bridging–dewetting mechanism" after Denkov [7**]) leaving a hole in the foam film which subsequently expands to cause film rupture. The essentials of this mechanism have been verified experimentally in model experiments for spheres using high-speed cinematography [8].

Joshi et al. [9*] present interesting observations concerning the antifoam mechanism of hydrophobic fatty alcohol particles in aqueous surfactant solution. The fatty alcohols consist of a blend of $C_{14}-C_{30}$ chain lengths. The particles appear to have a spherical or ellipsoidal geometry and should therefore require contact angles > 90° in any given aqueous medium for antifoam effect. However in the absence of surfactant the particles possessed advancing and receding contact angles of 93° and 95° respectively and in the relevant aqueous surfactant solution 85° and 71° respectively. The effect of these particles on the stability of the film formed between two colliding bubbles was observed by video-microscopy. In these experiments the fatty alcohol particles were dispersed in an aqueous concentrated ethoxylated alcohol solution containing a thickener and preservative — the resultant concoction often being described commercially as an aqueous or surfactant antifoam. This concoction was then added to an aqueous solution of a second surfactant in order to achieve an antifoam effect for the latter. In this arrangement one bubble was allowed to equilibrate with the antifoam dispersion so that the fatty alcohol particles could attach to the relevant air–water surface. The second bubble was then grown towards the first to form a film between the two bubbles. The subsequent flow of liquid from the film produced a surface tension gradient and effectively removed the particles. However when that flow ceased, as the second bubble closely approached the first, a reverse flow occurred because the surface tension of the air–water surfaces in the film was now higher than that on the remaining surface of the first bubble. The resulting Marangoni effect dragged the antifoam particles back into the film which then rapidly ruptured by a bridging mechanism. Joshi et al. [9*] attribute the origin of the reverse flow to desorption of surfactant from the fatty alcohol particles. However spreading from the shorter chain length fatty acids in the blend used here could also contribute (the equilibrium spreading pressure of, for example octadecanol – a component of the blend used – will lower the surface tension of water at the relevant temperature to some 20 mN m^{-1} below that of the solutions of the second surfactant considered here [10]). Clearly a dynamic process is occurring which probably means that dynamic contact angles are relevant which could explain the apparent discrepancy between the measured receding angles and the requirement that θ_{AW}> ~ 90°.

There are in fact two main difficulties with generalizing the condition θ_{AW}> ~ 90° to all foamability measurements. The first concerns measurement of the contact angle under conditions directly relevant for those actually existing during foam generation. As the work of Joshi et al. [9*] suggests contact angle hysteresis and dynamic effects due to the rate of surfactant transport relative to the rate of air–water surface generation can conspire to produce antifoam effects even though the receding contact angle <90° [2**]. However arguably a more significant factor concerns particle geometry. The presence of sharp edges and rugosities appears to confer antifoam effects at contact angles significantly <90° [2**].

Orthorhombic particles have received particular recent interest in this context following the work of Dippenaar [8] more than thirty years ago. Dippenaar [8] investigated the rupture of single aqueous films by orthorhombic hydrophobed galena particles using high-speed cinematography. He attributed his finding that aqueous film rupture by such particles occurs with contact angles of only (80 ± 8)° to the particle shape. He concluded that such particles could adopt two orientations at the air–water surface as that surface is pinned to edges as shown in Fig. 1a and b. According to Dippenaar [8] only the diagonal orientation can give rise to foam film rupture by a mechanism analogous to that for a sphere but in this case, for a particle of a square cross-section, contact angles must lie in the range $45° < \theta_{AW} < 135°$.

A problem with this argument concerns the assumption that only two orientations of an orthorhombic particle at a planar air–water surface are possible. That is strictly only true if the aspect ratio ≫ 1. In the case of the diagonal orientation the air–water surface must satisfy the contact angle against the two particle end surfaces perpendicular to the plane of the paper as shown in Fig. 1c and d. If for example the air–water surface remote from the particle is planar then the capillary pressure across that surface must be zero. For equilibrium the capillary pressure in the segment of air–water surface against the particle ends must also be zero. That is only possible if it forms a catenoid element, which must also contact everywhere the perpendicular surface of the particle at the relevant contact angle. In the case of a particle with an aspect ratio close to unity the contribution of the surface energy of the two particle end surfaces, including the catenoid elements, to the total work of adhesion of the particle to the air–water surface must be significant. This factor therefore greatly complicates calculation of the relative work of adhesion and probabilities of the two orientations depicted in Fig. 1a and b in the case of aspect ratios close to unity. It also suggests the possibility that yet other orientations are possible.

Calculating the relative work of adhesion for orthorhombic particles as a function of contact angles has been made tractable by use of an iterative surface energy minimization technique described by Morris et al. [11–13,14**]. The technique makes use of the Surface Evolver software developed by Brakke [15]. A more detailed description of the use of this technique is given in the accompanying review by Morris et al. [16]. It permits calculation of the (surface) energy profile of a particle in an air–water surface or foam film as a function of the orientation, contact angle and shape. The profile reveals the presence of energy minima, consistent with stable orientations, where the depth of the minima gives an indication of their relative probabilities. This analysis reveals, for example, four possible orientations for an orthorhombic particle bridging a foam film [14**]. These are designated vertical, horizontal, rotated and diagonal and are shown in Fig. 2. The relative stabilities of these orientations are determined by both the contact angle and the aspect ratio of the particle. This is exemplified in Table 1 for the aspect ratios corresponding to the only direct experimental observations of the rupture of aqueous films by orthorhombic particles.

Careful examination of the cinematographic film frames of Dippenaar [8] reveals that the aspect ratio of the orthorhombic hydrophobed galena particle is about 1.4. With a contact angle in the range of 72–88° (i.e. 80 ± 8°) the results of Table 1 would suggest that either both horizontal and diagonal orientations are likely to co-exist or that the diagonal orientation alone is to be present. Dippenaar [8] suggests that his observations are in fact consistent with the former possibility. However the relevant cinematographic frames do suggest a reconfiguration to a rotated orientation immediately prior to rupture of the aqueous film. Morris and Cilliers [13] have recently repeated these observations of Dippenaar [8] with a similar hydrophobed galena particle of contact angle in the range of 70–90° (i.e. 80 ± 10°) but of aspect ratio unity. As expected from the calculations summarized in Table 1 this particle adopted a rotated orientation although with no apparent observations of either horizontal or vertical orientations.

Morris et al. [11–13,14**] have extended these surface energy minimization calculations to estimate the critical capillary pressure required to rupture an aqueous film containing a bridging orthorhombic particle. In particular Morris and Cilliers [13] have compared such calculations