Current Opinion in Colloid & Interface Science 13 (2008) 134–140

Current Opinion in
COLLOID and
INTERFACE SCIENCE

www.elsevier.com/locate/cocis

Foams and foam films stabilised by solid particles

Tommy S. Horozov *

Surfactant & Colloid Group, Department of Chemistry, University of Hull, Hull, HU6 7RX, UK

Received 8 August 2007; accepted 31 October 2007
Available online 13 November 2007

Abstract

Recent developments in the field of particle-stabilised aqueous foams and foam films are reviewed. Reports on ultrastable foams stabilised by solid particles are highlighted and factors responsible for the extraordinary foam stability are discussed in view of the recent experimental and theoretical results. Mechanisms of foam film stabilisation by solid particles and the role of different factors in the film stability are considered. Link between the film stability and that of particle-stabilised foams is discussed.

Keywords: Foams; Foam films; Bubbles; Stabilization; Solid particles

1. Introduction

Small solid particles can attach to planar or curved liquid interfaces and are a subject of considerable attention recently [1••,2•,3•,4]. Their ability to stabilise bubbles and emulsion droplets was recognised a long time ago, but the potential of solid particles alone for stabilising emulsions and foams was fully demonstrated during the last decade [1••,2•,3•]. Different aspects of foam stabilisation by solid particles have been partially covered in previous reviews [1••,2•,3•]. However, remarkable progress in this field was achieved within the last couple of years and several reports dealing with important aspects of solid-stabilised foams appeared very recently. An update of the current knowledge for the role of solid particles in stabilisation of bubbles, aqueous films and foams is given here. The emphasis is on the literature from the last 3 years, though some previous key articles are also referenced for consistency.

2. Ultrastable aqueous foams

Stabilising effect of solid particles in aqueous foams under dynamic conditions at continuous bubble generation is well known, and its role in froth flotation of minerals [5,6] or boiling suspensions [7–9] has been extensively investigated. The dynamic foams, however, are very unstable and rapidly collapse once the bubbling is terminated. Only very recently it has been demonstrated that solid particles alone [10••,11••,12] or with appropriate surfactant [13•] are able to stabilise aqueous foams to an extent they can survive for weeks or more even under extremely harsh conditions (e.g. drying or vacuum treatment). Some of these works reporting ultrastable foams are worth to be considered in more detail.

Recently, Alargova et al. [10••] have demonstrated that particles with non-spherical shape can act as an effective foam stabiliser in the absence of any additives. They used polymer rodlike particles with an average length of 23.5 μm and an average diameter of 0.6 μm. Their contact angle at the air–water surface measured through the water was $\theta \approx 80°$. It was found that fairly dilute microrod suspensions (0.2–2.2 wt.%) in pure water readily produce foams upon shaking. The foams have been stable for more than 3 weeks even under drying in an open vessel. It has been extremely difficult to destroy the foam even at more harsh conditions of fast drying and expansion in a vacuum. Microscopic examination revealed that the microrod foams were made of small (10–100 μm) approximately spherical air bubbles. They shape did not change for the whole period of observation. The bubbles were covered with dense hairy shells of entangled microrods. Similar arrangement of intertwined rods was observed at the surface of single foam films. The films were rather thick (~ 1–2 μm) and very stable which was attributed to the mechanical rigidity of the continuous net of overlapping and entangled microrods at the

---

* Tel.: +44 1482 465220; fax: +44 1482 466410.
E-mail address: t.s.horozov@hull.ac.uk.

doi:10.1016/j.cocis.2007.11.009

film surface. The authors concluded that the strong particle attachment to the bubbles, microrod entanglement, formation of rigid hairy shells, and sustaining of thick films between the bubbles were the main factors for the extraordinary stability of the microrod-stabilised foams. This was also supported by the unexpected destabilising effect of a popular foam-forming surfactant (sodium dodecylsulfate) on the particle-stabilised foams. Soon after the surfactant had been introduced, the microrod particles began to transfer from the foam into the liquid and to sediment at the bottom. As a result more than 70% of the foam had been destroyed within 30 min. The destabilising action of the surfactant was attributed to its adsorption on the fairly hydrophobic particle surface, thus making the microrods more hydrophilic and less strongly attached to the air–water surface. These findings suggest that flexible rodlike particles with high aspect ratio and appropriate hydrophobicity can be very effective foam stabilisers. Interestingly, hydrophobic filamentous bacteria, identified in the stable biological foams in waste water treatment plants, have filament dimensions of ~0.5–2 μm diameter and ~50–200 μm length [14–16], therefore very similar to those of microrods used in [10••]. It is believed that the filamentous species attach to and stabilize air bubbles to form thick, stable, persistent and scum-like foam on the surface of aeration basins and settling tanks, thus causing a serious problem [14–16].

Very stable aqueous foams have also been obtained by means of spherical micro- or nanoparticles. Binks and Horozov [11••] used near spherical fumed silica nanoparticles (primary diameter ≈30 nm) hydrophobised to different extents, to investigate the effect of particle hydrophobicity on foam stability in the absence of any surfactant. Foams were prepared either by shaking by hand the system of powdered particles resting on water (3 w/v%) or by aerating an aqueous dispersion of particles (0.86 w/v%) by using an Ultra Turrax homogeniser. In the latter, the powders had been dispersed in water with the aid of ethanol, which was deliberately removed by several sedimentation-redispersion cycles in pure water before the foaming tests. Stable foams were obtained by both methods (either without or with 8.5 mM NaCl in the water) when particles with intermediate hydrophobicity were used. The foams produced by homogenisation of the aqueous dispersions were with larger initial volumes than the hand-shaken ones. They also showed a more pronounced maximum with respect to the hydrophobicity of the particles, with the most effective being those containing at their surface 32% SiOH (about one third of that at the surface of unmodified hydrophilic particles, 100% SiOH). The foams were wet and even after several days contained about 60% water. They were very stable to collapse. Similar to the stable micro-rod foams [10••], a slow decrease in their volume was detected during the first 24 h as a result of water drainage and bubble compaction, but not of gas loss. Almost all particles were retained in the white, creamy foam on the top of a clear liquid below. Optical microscope images revealed that the foam contained micron-sized non-spherical bubbles (5–50 μm) surrounded by branched particle aggregates. It was suggested that particle aggregation increased the viscosity of the aqueous phase (gelling) which resulted in slower drainage of the foam films and increased foam stability. The bubble surfaces were rough as a result of ripples similar to those observed in the case of a planar air–water monolayer of silica nanoparticles after compression. It was inferred that the bubbles were covered with dense particle layers compressed to a high surface pressure that is close to the surface tension of water.

Preparation of stable foams from latex suspensions in the absence of any additives has been reported recently by Fujii et al. [12,17]. In contrast to previous studies [18] they used sterically stabilised latex particles, therefore additional additives (electrolyte or surfactant) were not needed to induce foaming. A series of near-monodisperse sterically stabilised and charge-stabilised polystyrene latexes with diameters in the range 0.2–1.6 μm were synthesised by dispersion or emulsion polymerisation. Foams were prepared from thoroughly purified aqueous suspensions (1–10 wt.%) either by shaking by hand or by bubbling nitrogen through the suspensions. The most stable foams were those obtained at the largest concentration of particles with biggest size. They were stable to drying with little or no change in volume. Highly ordered particulate bilayers have been identified in the dry foam by means of SEM and optical microscopy, thus supporting the previous finding [18] that the films between the bubbles in the wet foam are composed of a bilayer of particles separated by water.

Above findings demonstrate that aqueous suspensions of certain solid particles with inherent hydrophobicity are able to make extremely stable foams in the absence of any surfactant. Particle shape, size, concentration and hydrophobicity have been identified as the main factors for the foam stabilisation. The optimum particle hydrophobicity has been achieved ether in advance, by appropriate chemical synthesis [10••,12,17] or surface modification [11••], or after dispersing the particles in the aqueous phase by adjusting the pH and electrolyte concentration [18]. Alternatively, an in-situ hydrophobisation of initially hydrophilic particles can be accomplished through the adsorption of appropriate amphiphiles on the particle surface. This approach is widely used in froth flotation [5,6] but its potential and versatility for preparation of ultrastable aqueous foams stabilised by inorganic nanoparticles was demonstrated only recently.

Gonzenbach et al. [13•,19,20] applied short-chain amphiphiles (carboxylic acids, alkyl gallates and alkylamines) to concentrated suspensions (15–45 vol.%) of different oxide and nonoxide particles (e.g. silica, alumina, calcium phosphate etc.) and produced high-volume foams by mechanical frothing of the suspensions. The foams with air contents between 45 and 90% and average bubble sizes between 20 and 80 μm were completely stable against drainage, coalescence and disproportionation for days. This remarkable foam stability was attributed to the strong attachment of particles at the air–water interface and the formation of an attractive particle network at the interface and throughout the foam lamella. It has also been demonstrated that the microstructure of these foams can be tailored in a wide range by adjusting the composition of the initial colloidal suspension [20] that could be useful for various applications including the fabrication of macroporous ceramics [21].