Aqueous Foams

Aqueous Foams Stabilized Solely by Silica Nanoparticles**

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Foams occur as end products or during the processing of products in a wide range of areas including the detergent, food, and cosmetic industries. They are mixtures of immiscible fluids in which a vapor phase is dispersed as millimeter-sized bubbles in the continuous phase of a liquid.[1] To prevent collapse of the foam, surfactants or proteins are usually added whose molecules cover the liquid/vapor interfaces. Small solid particles exhibit some similarities with such molecules by adsorbing at interfaces and acting as excellent emulsifiers of oil and water.[2] However, the use of small solid particles in stabilizing aqueous foams in air–water–particle systems in the absence of any other surface-active substance has not been demonstrated previously. Here we describe the preparation and stability of aqueous foams stabilized solely by nanoparticles of silica that exhibit different extents of hydrophobicity. By using a novel dispersion method, suitably hydrophobic particles can be dispersed in water and very stable foams can be formed in which aggregates of particles adsorb at the surfaces of micrometer-sized bubbles.

Certain small solid particles have been used in conjunction with surfactant molecules, which they adsorb at fluid/fluid interfaces, to either stabilize or destabilize drops in emulsions and bubbles in foams.[2] It is only recently, however, that their precise role is being elucidated in surfactant-free systems. Unlike surfactant molecules, most colloidal particles, although surface-active, are not amphiphilic. The exceptions

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[**] We thank Wacker-Chemie, Burghausen, for donating the silica particles.

DOI: 10.1002/ange.200462470

are so-called Janus particles, in which two separated regions of different wettability exist on the surface of a given particle. Such particles are both surface-active and amphiphilic.[2] The particles used in this work are not amphiphilic, but are homogeneously coated. In contrast to surfactant molecules, adsorption of solid particles to fluid/liquid interfaces does not change the interfacial tension.[3] A key parameter that affects adsorption appears to be the contact angle, θ (measured through water), that particles exhibit at the interface. The angle θ increases with the hydrophobicity of the particle. If θ is large enough, particles prefer to stay in air (or oil) rather than in water. However, if adsorbed, they are strongly held at the fluid interface. The energy ΔG required to remove a small spherical particle of radius r from an air/water surface is at a maximum at $\theta = 90^\circ$.[2] It can be shown that for the particles used here for which $r \approx 10^{-7}$ m and $\theta = 90^\circ$, ΔG is several orders of magnitude greater than the thermal energy. Hence, the particles are practically irreversibly adsorbed, in marked contrast to surfactant molecules that adsorb and desorb reversibly.

The well-documented flotation method relies on the attachment of mineral particles to air bubbles by adding to the slurry surface-active molecules as frothing agents and collectors.[4] Only two examples have been reported in which particles are employed as foam stabilizers in water-containing systems. Wilson[5] utilized relatively large, charged polystyrene latex particles (several µm) and varied the pH and the concentrations of salt and added surfactant to optimize foaming. These results indicate that θ approaches 90° for systems that display high foamability and stability. Sun and Gao[6] used particles (diameter $d \geq 1$ µm) of either teflon, polyethylene, or polyvinylchloride, but needed to add 20–40 wt % of ethanol to the aqueous dispersions to obtain a foam in sufficient quantity and of reasonable stability. Similarly, air-in-liquid metal (e.g. Al) foams are thought to be stabilized by ceramic particles such as SiC, but the underlying physics is not understood and surface-active impurities are commonly present.[7]

We show here the effect of the inherent hydrophobicity of silica nanoparticles on their ability to stabilize aqueous foams. Particles of intermediate hydrophobicity act as emulsifiers of oil and water by the formation of close-packed adsorbed layers at interfaces, which prevents coalescence of droplets.[8] They also adsorb around air bubbles and drastically slow down or halt completely the transfer of gas between them.[9] Hydrophilic silica particles contain surface silanol groups that react with silanizing agents to impart hydrophobicity. The latter is quantified in terms of the residual content of SiOH, which varies here from 100 to 14 %. On the basis of a simple theory for predicting the contact angle that a particle exhibits at an air/water surface when the surface-energy components of the solid are known,[10] we calculate that $\theta = 13^\circ$ for the most hydrophilic silica particles and $\theta = 84^\circ$ for the most hydrophobic ones used here (see inset in Figure 1). In acknowledgement of the fact that more hydrophobic particles are required to adsorb for foam stabilization, we prepare foams either with particles initially in air or by dispersing them in water with the aid of ethanol, which is deliberately removed *before* the foaming tests.

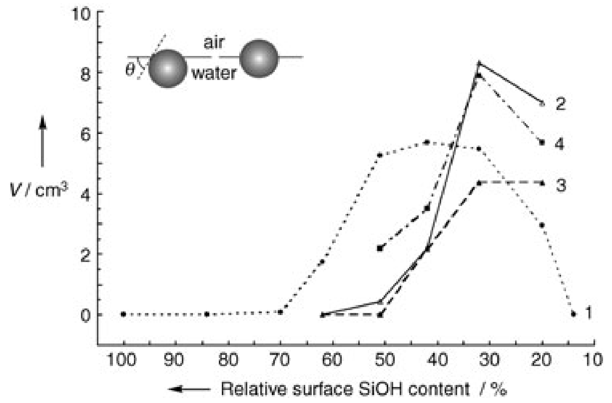

Figure 1. Volume of foam (*V*) produced at room temperature from 7 cm^3 of water in the presence of fumed silica nanoparticles of different hydrophobicity (given as the percentage of SiOH on their surfaces) at 3 wt/v% (hand-shaken, 1) and 0.86 wt/v% (homogenized, 2–4). The conditions and time delays after the formation of the foam are 1) no salt, 0 and 1 h (-----), 2) no salt, 10 s (——), 3) no salt, 27 h (– – –), and 4) 8.5 mM NaCl, 13.5 h (–•–•). The inset shows schematically the position of a particle at an air–water surface if hydrophilic (high % SiOH, left) or more hydrophobic (low % SiOH, right).

Figure 1 shows the volume of foam produced as a function of the hydrophobicity of the nanoparticles under different conditions. In the absence of salt and for hand-shaken systems (3 wt/v % particles initially in air, curve 1) no foam is formed for hydrophilic ($\geq$ 70 % SiOH) or very hydrophobic particles (14 % SiOH, dry powder remained on water surface), but the foamability increases progressively for particles of intermediate hydrophobicity. These foams contain approximately 30 % water when formed and are subsequently very stable to collapse. An alternative method is to disperse the particles in a solution of water/ethanol, which allows the more hydrophobic particles to become wetted, then to remove the ethanol by repeated sedimentation–redispersion cycles in pure water, and aerate the dispersion by using an Ultra Turrax homogenizer. The initial volume of foam in this case (0.86 wt/v % particles, curve 2) shows a more pronounced maximum with respect to the hydrophobicity of the particles, with the most effective being those that contain 32 % SiOH.

The foams obtained with 32 and 20 % SiOH are wet and even after a long time contain around 60 % water. They are very stable to collapse. The decrease in their volume is a result of water drainage and bubble compaction, but not to loss of air (Figure 1, curve 3, 27 h). This is also evident in Figure 2 in which photographs of the vessels for particles of different hydrophobicities (% SiOH, given) are shown at 10 minutes (upper) and 13.5 hours (lower) after homogenization. For particles with a surface content of SiOH of greater than 42 %, it can be seen that they reside mainly in the water phase (cloudy) with little foam, whereas for particles with 32 and 20 % SiOH they are located entirely within the white, creamy foam that envelopes the air bubbles. The size of the bubbles decreases progressively with an increase in hydrophobicity of the particles.

The stability of the foam prepared with particles that contain 32 % SiOH was measured by using the Dispersion Stability Analyzer 24 (DiStA 24)[11] and compared to that of

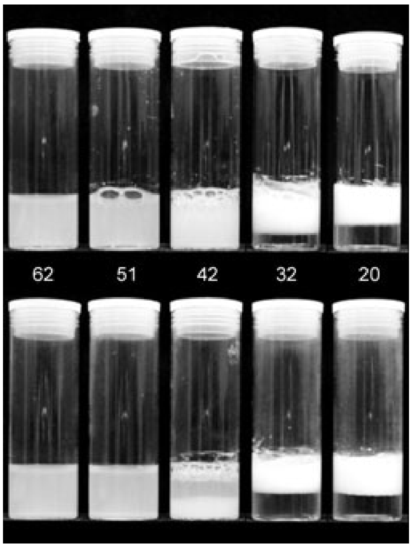

Figure 2. Appearance of vessels at room temperature at 10 minutes (upper) and 13.5 h (lower) after homogenization of aqueous dispersions containing 0.86 wt/v% silica particles (of different hydrophobicities, given as the percentage of SiOH (62, 51, 42, 32, and 20%) on their surfaces) in pure water.

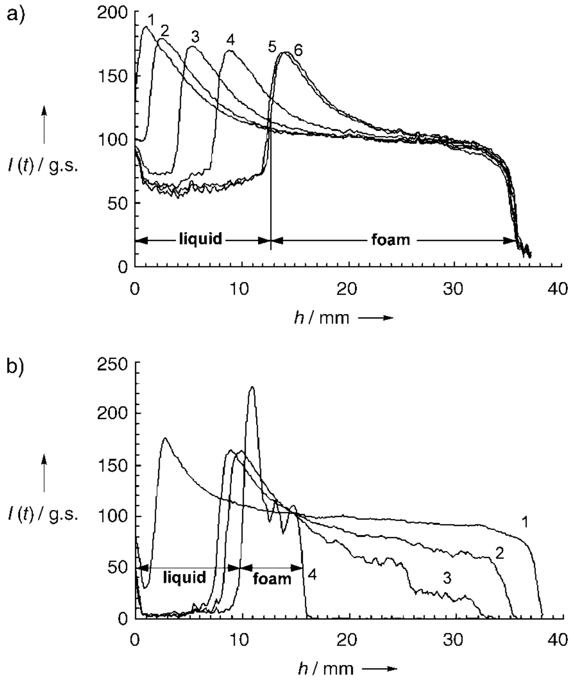

Figure 3. Vertical profiles (versus height, *h*) of scattered light in grayscale (g.s.) units measured using DiStA 24 at 25 °C at different times after generation of the foam by homogenization: a) with 1 wt/v% silica particles in pure water containing 32% SiOH on their surfaces: 1) 30 s, 2) 10.5 min, 3) 31 min, 4) 1 h, 5) 24 h, and 6) 62 h; b) with 5.8 wt% aqueous SDS: 1) 36 s, 2) 10.6 min, 3) 31 min, and 4) 18 h.

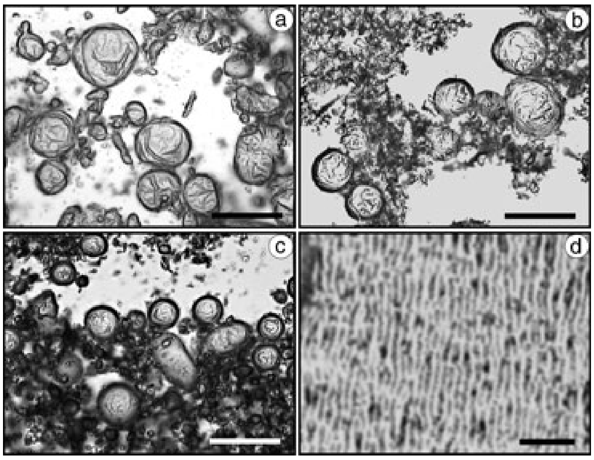

Figure 4. Optical microscopy images of aqueous foams stabilized by silica nanoparticles that contain 32% SiOH on their surfaces. Conditions and time after formation by homogenization: a) no salt, 3 wt/v% particles, 40 h, b) 8.5 mM NaCl, 0.86 wt/v% particles, 5 min, and c) 1 M NaCl, 0.37 wt/v% particles, 5 min. Also shown in d) is the image of a planar monolayer of silica nanoparticles (with 50% SiOH) at the air–water surface after compression to a surface pressure of 70 mN m^{-1}. The corrugations are parallel to the trough barriers. All scale bars:50 μm.

foams made with the popular surfactant sodium dodecyl sulphate (SDS). This analyzer uses a scanner to take side images of the foam at preset time intervals. The images are automatically analyzed, and the vertical profile of light scattered from the sample is obtained. The destructive processes that occur in the foam can be detected and monitored well before it is possible to observe them with the naked eye.

The vertical profiles of the scattered light intensity are shown in Figure 3 for the silica-stabilized foam (part a) and that stabilized by the surfactant (part b) at different times after formation of the foam. In both cases the intensity of the light close to the bottom of the sample decreases with time, while the maximum light intensity shifts upwards. These changes are a result of the drainage of water from between the bubbles in the foam, with a clear serum appearing at the bottom in contact with a concentrated foam at the top (see Figure 2). In the case of the particle-stabilized foam, this drainage takes place relatively slowly and is over after several hours. By contrast, the fast drainage of water out of the foam in the surfactant-stabilized case (few minutes) leads to a significant shift upwards of the intensity maximum and a drastic decrease in the intensity in the upper part of the profile. The collapse of the foam is accompanied by the appearance of local maxima and minima. Such changes in the light intensity are a direct consequence of coarsening of the foam as a result of both bubble coalescence and disproportionation. Adsorbed particles clearly prevent the occurrence of both of these phenomena.

Optical microscope images of bubbles in foams stabilized by particles with 32% SiOH, in the presence and absence of salt, are given in Figure 4a–c. Distinct nonspherical bubbles, with diameters of 5–50 μm, are a feature of these systems. Their surfaces are rough as a result of ripples. Similar ripples have been observed in the case of a planar air/water monolayer of silica nanoparticles after compression (Figure 4d) which suggests that the bubbles are covered with dense particle layers compressed to a high surface pressure that is close to the surface tension of water (71.9 mN m^{-1}).[12]

Stable bubbles are probably formed by coalescence between smaller bubbles that are covered with dilute particle layers during homogenization.[13] As the bubble area decreases, excess particles cannot be released as they are irreversibly adsorbed and so the surface corrugates to increase in area. As silica particles in water and bare air–water surfaces are negatively charged, it is anticipated that addition of salt to water should enhance the transfer of particles to the surface by reducing the energy barrier to adsorption.[14] It may also increase their contact angle as hydrophobicity increases, with both of these factors leading to improved stabilization of the foam. Indeed, this is the case as seen in Figure 1 (curve 4) and in Figure 5, in which even a small amount of electrolyte (8.5 mM) improves both the foamability and foam stability. Particles that are initially relatively hydrophilic (42 and 51 % SiOH) can now stabilize foams to a higher extent than in the absence of salt (compare with Figure 2).

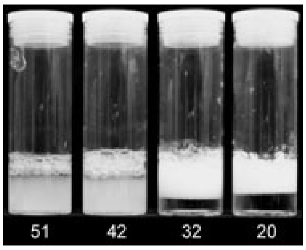

Figure 5. Appearance of vessels at room temperature in systems containing 0.86 wt/v% silica nanoparticles of different hydrophobicity (given as the percentage SiOH) in 8.5 mM NaCl at $t = 13.5$ h after formation of the foam by homogenization. Note that particles reside mainly in water for SiOH contents of 51 and 42%, but are entirely within the foam for SiOH contents of 32 and 20%.

Nanoparticles are effective foaming agents of air and water, and by controlling their hydrophobicity, foams that are completely stable to collapse, coalescence, and disproportionation can be prepared. We plan to investigate further the influence of pH and the concentration of salt in these systems. Manipulation of the behavior of particles adsorbed at fluid interfaces in this way enables the development of a novel range of foams for use in food, detergent, and cosmetic formulations.[15]

Experimental Section

Methods: Fumed silica particles of primary diameter 20–50 nm and surface area 200 $m^2 g^{-1}$ were supplied by Wacker-Chemie. During preparation, some particles fuse irreversibly to form aggregates (few hundred nm) of particles. The different hydrophobic grades were obtained after silanization of hydrophilic silica with dichlorodimethylsilane.[8] Their surface content of silanol varied from 100 to 14%. Water was passed through a reverse osmosis unit and then a Milli-Q reagent system—its pH value was 5.6 owing to dissolved CO_2. The salt used was NaCl (99.9% pure) from Prolabo. Foams were prepared in sample tubes (inner diameter:2.5 cm, height:7.5 cm) either by shaking by hand the system of powdered particles resting on 7 cm^3 of water (20 s, frequency:5 Hz) or by aerating the same volume of an aqueous dispersion of particles by using an Ultra Turrax homogeniser (Janke & Kunkel) with a 1.8-cm-diameter head operating at 11000 rpm for 3 minutes (6×30 s with 30 s rest periods). In the latter, the powders were wet with ethanol, then mixed with water to give a suspension that contained < 2 wt% ethanol. The ethanol was removed by repeated sedimentation–redispersion cycles in pure water to attain less than 10^{-4} wt% residual ethanol. Photographs of the vessels were taken with a Kodak DX4330 digital camera. The surfactant-stabilized foam was formed by homogenizing 5 cm^3 of an aqueous solution of SDS (Lancaster, 99%) at 8000 rpm for 1 minute. The stability of the foams was measured with the automated Dispersion Stability Analyser 24 developed recently.[11] An optical microscope (Nikon Optiphot-2) was used to observe the structure around and between the bubbles in the foams. A planar monolayer at the air–water surface was formed by the spreading of a dispersion of silica particles in chloroform and compressing in a Langmuir trough. The images were captured by the same microscope in reflected light.

Received: October 29, 2004
Revised: March 22, 2005

Keywords: foams · interfaces · nanostructures · silica · surface chemistry

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[13] We anticipate that the fumed silica particles will aggregate in bulk and that the extent of aggregation may depend on the hydrophobicity of the particle and the concentration of the electrolyte. Whether discrete primary particles or aggregates of particles, or both, adsorb around air bubbles is not known, but work to determine this is in progress. One consequence of particle aggregation is the increased viscosity of the aqueous phase (gelling) which results in slower drainage of foam films and increased stability of the foam.

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[15] Note added in proof: Since the submission of this article, a paper by Alargova et al. appeared which describes the stabilization of aqueous foams by micron-long polymer rod particles: R. G. Alargova, D. S. Warhadpande, V. N. Paunov, O. D. Velev, *Langmuir* **2004**, *20*, 10371–10374.