Stabilization of Foams with Inorganic Colloidal Particles

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Wet foams are used in many important technologies either as end or intermediate products. However, the thermodynamic instability of wet foams leads to undesired bubble coarsening over time. Foam stability can be drastically improved by using particles instead of surfactants as foam stabilizers, since particles tend to adsorb irreversibly at the air−water interface. Recently, we presented a novel method for the preparation of high-volume particle-stabilized foams which show neither bubble growth nor drainage over more than 4 days. The method is based on the in-situ hydrophobization of initially hydrophilic particles to enable their adsorption on the surface of air bubbles. In-situ hydrophobization is accomplished through the adsorption of short-chain amphiphiles on the particle surface. In this work, we illustrate how this novel method can be applied to particles with various surface chemistries. For that purpose, the functional group of the amphiphilic molecule was tailored according to the surface chemistry of the particles to be used as foam stabilizers. Short-chain carboxylic acids, alkyl gallates, and alkylamines were shown to be appropriate amphiphiles to in-situ hydrophobize the surface of different inorganic particles. Ultrastable wet foams of various chemical compositions were prepared using these amphiphiles. The simplicity and versatility of this approach is expected to aid the formulation of stable wet foams for a variety of applications in materials manufacturing, food, cosmetics, and oil recovery, among others.

1. Introduction

Wet foams are routinely used as end or intermediate products in many different areas ranging from cosmetics and food to oil recovery and materials manufacture.[1] However, wet foams are thermodynamically unstable because of their large air−water interfacial area and thus high overall free energy. Surfactants or proteins[2−4] are often used to reduce the free energy of wet foams by lowering the air−water interface tension. Nevertheless, surfactants can be easily desorbed from the interface because their energy of attachment to the interface is comparable to thermal energy (few kTs, k being Boltzmann's constant and T the temperature). As a result, destabilization mechanisms such as bubble coalescence and disproportionation (Ostwald ripening) cannot be completely prevented in surfactant-stabilized foams. This leads to bubble coarsening over time.[2−4]

To improve the stability of wet foams, particles have been used to adsorb at the air−water interface.[5−11] The adsorption of particles reduces the highly energetic interfacial area and lowers, therefore, the free energy of the system. Because of their energy of attachment of about $10^3−10^5$ kTs, particles tend to adsorb irreversibly at the interface.[5] Attempts to deliberately adsorb particles at an air−water interface resulted in foams remarkably more resistant against coalescence and disproportionation than foams stabilized by surfactants and proteins.[6−10] However, in these studies, stable foams were only achieved after extensive drainage and creaming of the initially aerated suspension.

Recently, we reported a simple method for the preparation of high-volume particle-stabilized foams which show neither bubble growth nor drainage over several days.[11,12] The method is based on the in-situ hydrophobization of initially hydrophilic particles through the adsorption of short-chain amphiphiles on the particle surface. The short amphiphiles exhibit high solubility and high critical micelle concentrations in water and can therefore modify high concentrations of particles in the initial suspension (typically between 5 and 45 vol %). This allows for the stabilization of a large air−water interfacial area, leading to high-volume particle-stabilized foams. This novel foaming method has been extensively described using alumina as model colloidal particles for foam stabilization.[11] In fact, the approach used for the surface hydrophobization of alumina particles can be easily extended to colloidal particles of different chemical compositions.[11] This imparts versatility to the method and allows one to add specific functionalities to the wet or dried foams, widening the number of applications where particle-stabilized foams can be used.

The aim of this work is to investigate the use of this novel approach for the modification of colloid particles with different surface chemistries to prepare high-volume stable foams of various chemical compositions. The approach used for the modification of oxide particles of various surface chemistries is described below and is subsequently exemplified using three different types of amphiphilic molecules.

2. Surface Chemistry and Modification of Oxide Particles in Water

The formation of high-volume particle-stabilized foams is based on the adsorption of partially hydrophobized particles to the air−water interface. It has been recently shown that alumina particles can be in-situ hydrophobized upon surface adsorption

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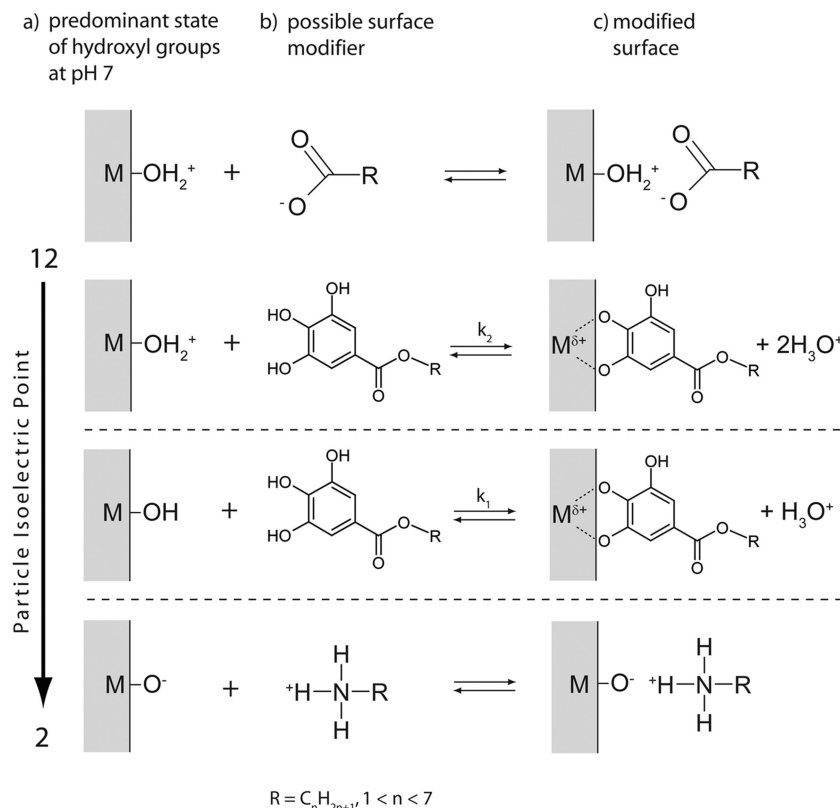
Figure 1. (a) Predominant state of the surface hydroxyl groups at pH 7 for particles with different isoelectric points. (b) Possible surface modifiers for predominantly positive, neutral, or negative surfaces: carboxylic acids or alkyl gallates, alkyl gallates, and alkylamines, respectively. (c) Modified surfaces highlighting the electrostatic-driven adsorption of carboxylic acids and alkylamines, as well as the ligand-exchange reaction of alkyl gallates on the oxide surface. The adsorption of alkyl gallates onto positively charged surfaces is favored over the adsorption onto neutral surfaces ($k_1 < k_2$).

of short-chain carboxylic acids at acidic pH conditions.[11,12] These molecules adsorb electrostatically with their hydrophilic head-group onto the particle surface,[13] leaving the hydrophobic tail in contact with the aqueous medium. The degree of particle hydrophobization depends on the amount of adsorbed carboxylic acid and the length of the hydrophobic tail.[12]

To extend this approach to different types of inorganic particles, one has to deliberately select amphiphilic molecules exhibiting a short hydrophobic tail (two to seven carbons) combined with a headgroup that is able to adsorb on each specific particle surface. Therefore, the choice of the amphiphile headgroup highly depends on the surface chemistry of the particle involved.

The surface chemistry of oxide particles in water is determined by the protonation and deprotonation reactions of surface hydroxyl groups ($-$OH) with H_3O^+ and OH^- ions from the aqueous medium (Figure 1). The reactivity of the hydroxyl groups is strongly influenced by the charge-to-size ratio of the underlying metal ion of the solid oxide.[14] Oxides of metals with high charge-to-size ratio (e.g., Si^{4+}) tend to have predominantly deprotonated hydroxyl groups on the surface ($-O^-$), whereas oxides consisting of metals with low charge-to-size ratio (e.g., Mg^{2+}) display mainly protonated hydroxyl groups on the surface ($-OH_2^+$). Such trends are valid in aqueous media containing equal concentrations of H_3O^+ and OH^- ions (pH = 7).[14] By changing the pH and thus the concentration of H_3O^+ and OH^- ions in the aqueous phase, one can affect the relative density of surface protonated ($-OH_2^+$) and deprotonated ($-O^-$) groups. The pH at which the relative density of surface protonated and surface deprotonated groups is equal is called isoelectric point (IEP).

The adsorption of molecules from the aqueous medium onto the surface of oxide particles can be driven by (1) electrostatic interactions between the particle surface charge and ionized molecules or (2) specific chemical reactions between the molecule and the surface hydroxyl groups. In case of oxides exhibiting predominantly positive or negative charges on the surface (high and low IEPs, respectively), the electrostatic adsorption of amphiphilic molecules is a convenient approach for surface hydrophobization. Therefore, protonated amines and deprotonated carboxylic acid groups can be used for the surface modification of oxides exhibiting low and high IEPs, respectively (Figure 1).

For oxides with intermediate IEPs and zero net charge, surface hydrophobization can be accomplished by choosing amphiphiles with functional groups that react with the surface hydroxyl groups. Pyrogallol groups are known to efficiently adsorb on oxide surfaces via ligand-exchange reactions[13] and thus can be used in combination with a short hydrocarbon tail as surface modifiers of particles with intermediate IEP (Figure 1). In this case, the adsorption on positively charged surfaces is favored over the adsorption on neutral surfaces ($k_1 < k_2$) since the protonated hydroxyl group ($-OH_2^+$) is a better leaving group compared to the neutral hydroxyl group ($-$OH).[13]

With this simple and versatile approach based on the selection of amphiphiles with suitable headgroups and tail lengths, one should be able to impart surface hydrophobicity on particles of various chemical compositions. In the following sections, we illustrate the versatility of this approach using the three selected amphiphiles outlined in Figure 1.

3. Materials and Methods

3.1. Materials. The colloidal particles used in this study were acquired from the following suppliers: γ-Al$_2$O$_3$, $d_{50} \sim 30$ nm,

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Nanotechnologies Inc. (Austin, TX); δ-Al$_2$O$_3$, d_{50} ∼ 70 nm, Nanophase Technologies Co. (Romeoville, IL); α-Al$_2$O$_3$, d_{50} ∼ 200 nm (grade Ceralox HPA-0.5), Sasol North America Inc. (Tucson, AZ); α-Al$_2$O$_3$, d_{50} ∼ 1800 nm (grade CL 2500 SG), Alcoa Co. (Ludwigshafen, Germany); ZrO$_2$, d_{50} ∼ 50 nm (grade TZ-3Y−E), Tosoh Corporation (Tokyo, Japan); β-Ca$_3$(PO$_4$)$_2$, d_{50} ∼ 50 nm, Flame Powders AG (Schlieren, Switzerland); SiO$_2$, d_{50} ∼ 80 nm (grade Snowtex ZL), Nissan Chemical (Houston, TX); Portland cement (grade CEM I 32,5R, Lugato Chemie, Hamburg, Germany); Ti, d_{50} ∼ 600 nm (Melorium Technologies, Inc., Rochester, NY).

The short-chain amphiphilic molecules investigated were butyric acid, valeric acid, propyl gallate, butyl gallate, butylamine, and hexylamine (Fluka AG, Buchs, Switzerland). Other chemicals used in the experiments were deionized water, hydrochloric acid (2 N, Titrisol, Merck, Germany), Triton X-45 (Fluka AG, Buchs, Switzerland), and sodium hydroxide (1 N, Titrisol, Merck, Germany).

3.2. Suspension Preparation. Suspensions were prepared by stepwise adding the dry powder to deioinized water upon continuous stirring with a standard laboratory mixer. The pH of all suspensions was either adjusted or monitored to electrostatically stabilize the particles. In case of alumina suspensions containing carboxylic acids, the pH was set to values below 5 by adding small aliquots of a 2 N HCl aqueous solution. For the alumina suspensions with propyl gallate, the powder was added into an aqueous solution already containing 506 mmol/L NaOH and 29 mmol/L propyl gallate resulting in a suspension with pH ∼ 9.8. In case of silica suspensions, the powder was added to pure water, and no further pH adjustment was needed. The solids loading of the alumina and silica suspensions was set to 50 and 45 vol %, respectively. In a typical formulation for alumina suspensions using carboxylic acids as surface modifiers, 270 g α-Al$_2$O$_3$ (Ceralox) was added to 65.94 g of water containing 1.898 mL 2 N HCl.

Homogenization and powder deagglomeration was carried out on a ballmill for at least 18 h using polyethylene milling pots and alumina balls in case of alumina particles or zirconia balls in case of silica particles (ball diameter: 10 mm). A mass ratio balls:powder of approximately 2:1 was used in both cases. After the ball-milling procedure, the pH of the suspensions was ∼5.5, ∼9.5, and ∼8.5 in case of alumina to be coated with carboxylic acids, alumina with propyl gallate, and silica, respectively. A diluted aqueous solution containing the amphiphile and pH-adjusting agents was then slowly and dropwise added to the ballmilled suspension under gentle magnetic stirring to avoid local particle coagulation. Afterwards, the pH was set to its desired value and the amount of water needed to achieve a certain solids content was added.
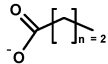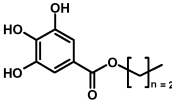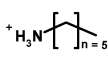
3.3. Zeta-Potential Measurements. Zeta-potential measurements (DT1200, Dispersion Technologies Inc., Mount Cisco, NY) were conducted in 2 vol % suspensions to determine the surface charge and the isoelectric point of the particles. Prior to each experiment, the suspensions were ultrasonicated for 5 min to obtain a homogeneous suspension. The pH of the suspension was initially set to values above 10 using a 1 N NaOH solution and was afterwards gradually decreased using a 1 N HNO$_3$ solution while acquiring the zeta potential data.

3.4. Surface Tension Measurements. The surface tension of the suspensions was assessed using the pendant drop method (PAT1, Sinterface Technologies, Berlin, Germany).[15] Suspensions were prepared using the ball-milling procedure mentioned above. The amphiphile was added dropwise upon magnetic stirring and the solids loading was set to 35 vol %. The drop volume was fixed at a constant value within the range 12−35 mm^3, depending on the surface tension of the suspension.

3.5. Foaming and Foam Characterization. Foaming of 150 mL suspension was carried out using a household mixer (Kenwood, Major Classic) at full power (800 W) for 3 min.

The foam density was measured with a custom-built tool which consisted of a cylindrical plastic cup with small holes on the bottom and a massive sliding stamp on top. The foam was carefully filled

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Table 1. Amphiphiles Used to Surface Modify Particles with Different Surface Chemistries and the Conditions under Which the Experiments Were Carried Out

Predominant state of surface hydroxyl groups	Amphiphile	Particles / IEP	Solvent / pH	Solids content (vol%)
M−OH$_2^+$ M−OH$_2^+$	Butyric acid	Al$_2$O$_3$ / 9.4	Water / pH 4.75	35
M−OH M−OH	Propyl gallate	Al$_2$O$_3$ / 9.4	Water / pH 9.9	35
M−O$^-$ M−O$^-$	Hexyl amine	SiO$_2$ / 1.5	Water / pH 10.6	35

into the cup and then slightly compressed with the stamp to remove possible air pockets introduced during filling. During this procedure, a fraction of the foam is expelled through the small holes on the bottom of the cup, avoiding an excessive compression of the foam inside the cylinder. The volume between the bottom of the stamp and the bottom of the cylinder was kept constant. Dividing the mass of the foam by its volume resulted in the foam density.

The bubble size distribution of the wet foam was evaluated using an optical microscope in transmission mode (Polyvar MET, Reichert-Jung, Austria) connected to a digital camera. For each sample, five pictures were taken and a minimum of 150 bubbles were evaluated. The bubble sizes were measured with the linear intercept method using the software Linear Intercept (TU Darmstadt, Germany).

4. Results and Discussion

4.1. In-Situ Hydrophobization. The in-situ hydrophobization of particles with different surface chemistries was accomplished using butyric acid, propyl gallate, and hexylamine as amphiphiles (Table 1).

Colloidal particles containing predominantly −OH$_2^+$, −OH, and −O$^-$ groups on the surface were selected to represent the possible surface chemistries typically encountered in oxide surfaces.

Surfaces with predominantly −OH$_2^+$ and −OH groups were provided using alumina particles at acidic (pH 4.75) and slightly alkaline conditions (pH 9.9), respectively (Table 1). The zeta potential data shown in Figure 2 for bare alumina particles confirm that the surface exhibits mainly −OH$_2^+$ (positive net charge) and −OH (neutral net charge) groups at these pH conditions. Surfaces displaying mostly −O$^-$ groups, on the other hand, were obtained using silica particles in alkaline solutions (pH 10.6), as indicated in Table 1. The negative zeta potential obtained for bare silica at alkaline pHs (Figure 2) confirms the predominance of −O$^-$ groups on the silica surface at this condition.

The amphiphiles butyric acid and hexylamine are expected to adsorb onto the alumina and silica particles, respectively, through electrostatic interactions between the charged surfaces and the oppositely ionized amphiphilic molecules (Figure 1). Ionization of the amphiphiles occurs via deprotonation and protonation reactions of the carboxylate and amine groups, respectively, in aqueous solution. The deprotonation of the carboxylate group
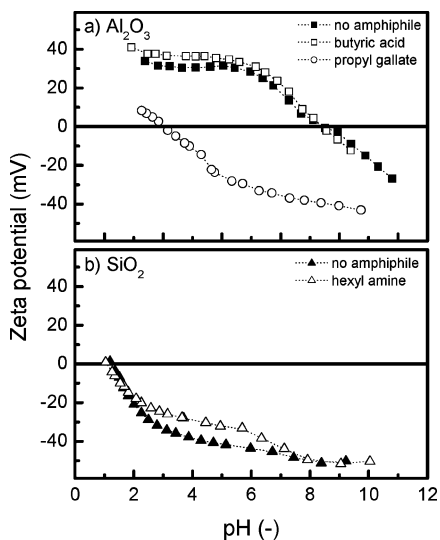
Figure 2. Zeta potentials of (a) alumina in the absence of amphiphiles (■), with butyric acid (2 mmol/L, □) and with propyl gallate (4 mmol/L, ○); and (b) silica in the absence of amphiphiles (▲) and modified with hexylamine (2.5 mmol/L, △). All suspensions contained 2 vol % of particles.

takes place at pH values in the vicinity of or higher than the pK_a value of this functional group which is equal to 4.63.[16] On the other hand, the protonation of the amine group occurs at pH values close to or lower than the pK_a value of this functional group which is equal to 10.66.[17] Surface modification of particles using these amphiphiles was carried out at pHs close to the molecules' pK_a values (Table 1). Under this condition, approximately half of the amphiphilic molecules present in the aqueous medium are ionized and capable of adsorbing on the oppositely charged particle surface.

The adsorption of propyl gallate on oxide surfaces, on the other hand, occurs via a ligand-exchange reaction[13] where the surface hydroxyl groups ($-OH$ or $-OH_2^+$) are replaced by one or more of the molecule's hydroxyl groups ($-OH$ or $-O^-$). Therefore, the adsorption of gallate molecules does not necessarily require oppositely charged surfaces and amphiphiles and can even occur at pH values where the groups on the surface and on the molecules exhibit the same charge sign.

Figure 2 shows that the electrostatic adsorption of butyric acid on alumina and hexylamine on silica does not change the IEP of the particles, suggesting a nonspecific adsorption of these amphiphiles on the particle surface. Conversely, the adsorption of propyl gallate shifts the IEP of alumina to more acidic values, indicating that additional negative charges are incorporated on the surface upon adsorption. These additional negative charges might result from (1) the coordination of two of the molecule's $-OH$ groups to a surface metal ion that was originally bond to only one $-OH$ group (Figure 1) or (2) the exchange of a positively charged $-OH_2^+$ group on the surface by at least one of the molecule's $-OH$ groups.[13]

4.2. Suspension Surface Tension. The degree of particle hydrophobization achieved through the surface adsorption of amphiphiles was investigated with the help of surface tension measurements. The surface tension of suspensions containing 35 vol % particles and different initial concentrations of amphiphiles is shown in Figure 3.
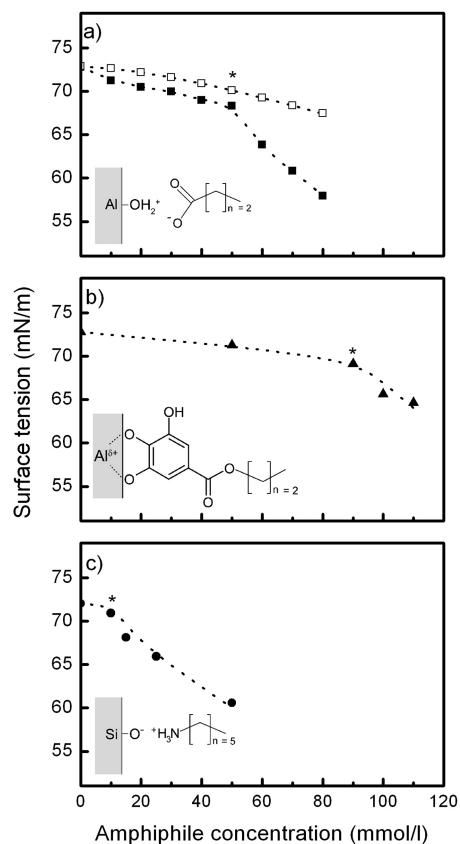
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Figure 3. Surface tension of (a) alumina suspensions at pH 4.75 containing different initial amounts of butyric acid (■) and the estimated contribution of the free amphiphiles alone (□), (b) alumina suspensions at pH 9.9 containing different initial amounts of propyl gallate (▲), and (c) silica suspensions at pH 10.6 containing different initial amounts of hexylamine (●). All suspensions contained 35 vol % of particles.

A decrease in surface tension upon increasing the initial amphiphile concentration in solution is observed for all the evaluated suspensions. For alumina hydrophobized with carboxylic acids, it has been shown[11,12] that part of the total reduction in surface tension results from the adsorption of free amphiphilic molecules to the air−water interface (Figure 3a, open symbols). However, above a critical amphiphile concentration (marked by * in the graph), a relatively strong decrease in surface tension is observed. Above this critical amphiphile concentration, the particles are sufficiently hydrophobic to attach to the air−water interface, leading to a decrease in surface tension more pronounced than that expected from the free amphiphiles alone (Figure 3a). This significant reduction in surface tension upon particle adsorption is caused by a decrease of the total area of the highly energetic air−water interface. Particle adsorption to the air−water interface for amphiphile additions higher than the critical concentration (*) was directly confirmed by confocal laser scanning microscopy images of air bubbles covered with fluorescent partially hydrophobized silica particles.[11]

The surface tension exhibits a similar behavior in the case of suspensions containing alumina particles coated with propyl gallate (Figure 3b) and silica particles modified with hexylamine (Figure 3c).

The critical amphiphile concentration is markedly different for the different amphiphilic molecules investigated here. In general, it has been observed that the critical amphiphile concentration is lower for amphiphiles with longer hydrophobic tails.[11] This observation results from the fact that for amphiphiles with a longer hydrocarbon tail, a lower concentration in solution
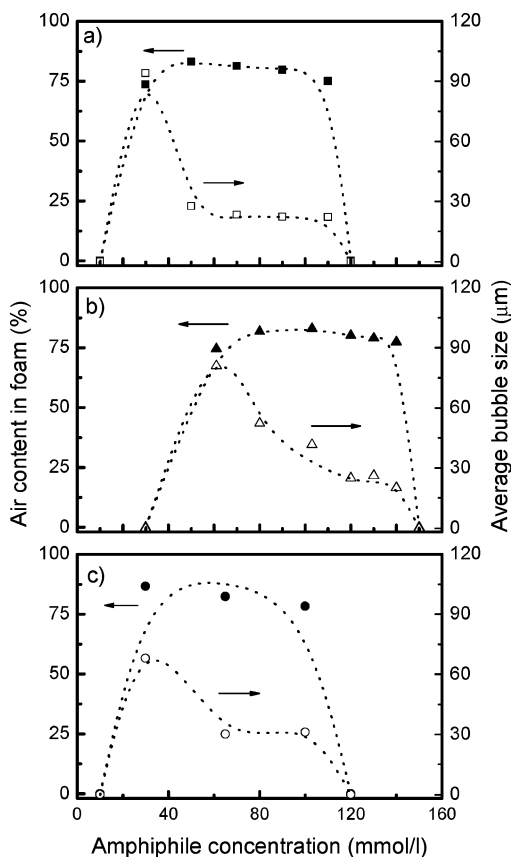
Figure 4. Air content (full symbols) and average bubble size (open symbols) of (a) alumina suspensions at pH 4.75 containing different initial amounts of butyric acid (■), (b) alumina suspensions at pH 9.9 containing different initial amounts of propyl gallate (▲), and (c) silica suspensions at pH 10.6 containing different initial amounts of hexylamine (●). All suspensions contained 35 vol % of particles.

Figure 5. Stability of a shaving foam (Gillette, □), an alumina foam containing 50 mM butyric acid at pH 4.75 (■), an alumina foam containing 100 mM propyl gallate at pH 9.9 (▲), and a silica foam containing 65 mM hexylamine at pH 10.6 (●). All suspensions contained 35 vol % of particles.

is required to impart sufficient hydrophobicity on the particle surface. This trend explains the lower critical concentration observed for silica particles coated with the relatively long amphiphile hexylamine, as compared to the alumina particles modified with the shorter butyric acid and propyl gallate molecules (Figure 3).

Surprisingly, the critical amphiphile concentrations in the case of butyric acid and propyl gallate adsorbed on alumina are quite different (Figure 3), despite the similar length of their hydrophobic tails. This might be attributed to the fact that alkyl gallates can be oxidized and form trimers at alkaline pHs.[18] These trimers are insoluble in water and precipitate out of the liquid phase. This has also been observed by aging a solution of propyl gallate in water at pH > 10. Because of this precipitation, the concentration of dissolved propyl gallate in suspension decreases. Therefore, a higher concentration of propyl gallate is needed to achieve the same particle hydrophobicity as with butyric acid.

4.3. Foaming. The attachment of particles to the air−water interface enables the stabilization of air bubbles and consequently the formation of high-volume foams upon mechanical frothing. The air content and the average bubble size of the resulting foams strongly depend on the degree of particle hydrophobization and therefore on the initial concentration of amphiphile in the suspension, as shown in Figure 4.

For all investigated suspensions, the amount of incorporated air increases strongly above a certain amphiphile concentration in the suspension. Below this concentration, the particles are not
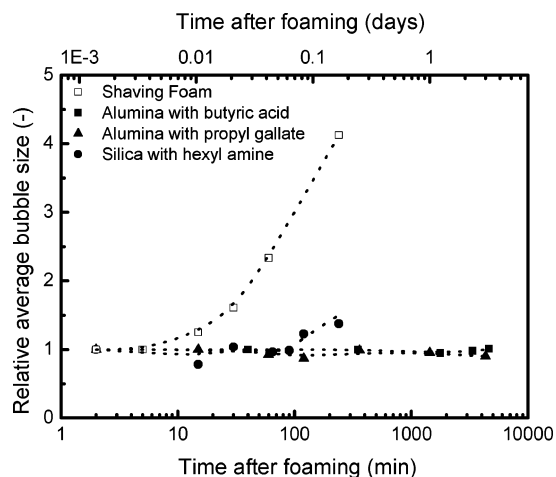
sufficiently hydrophobic to adsorb to the air−water interface and are therefore not able to stabilize air bubbles. With increasing amphiphile concentration, particles become sufficiently hydrophobic to adsorb at the surface of freshly incorporated air bubbles, resulting in foams with up to 85% air content. On the other hand, the average bubble size decreases with increasing amphiphile concentration and particle hydrophobicity. This is probably related to the decrease in surface tension and increase in foam viscosity obtained for higher amphiphile concentrations. These conditions decrease the resistance of air bubbles against rupture and enhance the shear stresses around the bubbles during the mechanical mixing of the suspension.[19−21] As a result, the mechanical rupture of freshly incorporated bubbles is facilitated, leading to foams with smaller average bubble sizes.

The decrease in the foam air content at high amphiphile concentrations can be attributed to an increase in the suspension viscosity that ultimately hinders air incorporation by mechanical frothing. In case of electrostatically adsorbed amphiphiles (e.g., carboxylic acids, alkylamines), the observed increase in viscosity arises from the screening of the particle surface charges by the oppositely charged amphiphiles in solution. Such screening effect leads to particle coagulation by van der Waals and hydrophobic attractive forces.[12] On the other hand, alkyl gallates adsorbed by ligand-exchange reactions on the surface do not act as oppositely charged counterions in solution. Therefore, the viscosity increase in this case is caused by the screening effect of the other counterions used to adjust the suspension pH. The amount of NaOH required to control the suspension pH was observed to increase linearly with the increase in amphiphile concentration. Therefore, a pronounced screening effect and a significant increase in the suspension viscosity was observed at high alkyl gallate concentrations.

4.4. Foam Stability. The stability of the particle-stabilized foams prepared with different amphiphilic molecules is compared in Figure 5 to that of a standard shaving foam stabilized by surfactants. The particle-stabilized foams show no significant bubble growth for more than 4 days, as opposed to the remarkable

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Table 2. Particle-Stabilized Foams Produced from a Variety of Oxide and Nonoxide Particles Using the Approach Shown in Figure 1

	particle			amphiphile				
type	size, d$_{50}$ (nm)	IEP	type	concentrated (mmol/L)	solvent	solids content (vol %)	air content (%)	average bubble size (μm)
				Particles with Basic IEP				
Portland cement	na[a]	na[b]	propyl gallate	112	water, pH >10	45	>80	na
γ-Al$_2$O$_3$	30	9	valeric acid	60	water, pH 4.75	15	90	56
δ-Al$_2$O$_3$	70	9	valeric acid	50	water, pH 4.75	20	90	47
α-Al$_2$O$_3$	200	9.4	valeric acid	30	water, pH 4.75	35	80	26
α-Al$_2$O$_3$	1800	9	valeric acid	20	water, pH 4.75	25	66	40
α-Al$_2$O$_3$	200	9.4	propyl gallate	100	water pH 9.9	35	83	30
				Particles with Intermediate IEP				
ZrO$_2$	50	~7	propyl gallate	80	water pH 9.9	22	79	70
Ca$_3$(PO$_4$)$_2$	50	~7	butyl gallate	40	water pH 9.9	17	86	45
Ti	~600	4.5	propyl gallate	316	water pH 9.9	19	91	na
				Particles with Acidic IEP				
SiO$_2$	80	~1	hexylamine	65	water, pH 10.6	35	82	30

[a] na: not available. [b] In the case of cement, the IEP is poorly defined because of the continuous reaction between the particle surface and the aqueous phase. Under alkaline pHs, Portland cement particles are positively charged because of the specific adsorption of Ca^{2+} ions on the surface.[25]

coarsening observed in the surfactant-stabilized foams within the first 4 h after foaming (Figure 5). In contrast to other particle-stabilized foams,[6,7,9,10] our foams percolate throughout the whole liquid phase and exhibit no drainage over days. This results from the high concentration of modified particles in the initial suspension, which allows for the stabilization of an enormous total air−water interfacial area.

The remarkable resistance of the particle-stabilized foams against coarsening has been attributed to the irreversible adsorption of the partially hydrophobic particles at the air−water interface.[5−8,10] Apparently, the adsorbed particles form a percolating armor along the air−water interface which mechanically withstands the lower pressures caused by gas diffusion out of the small bubbles during Ostwald ripening.[11,12,22]

The formation of a particle network between the air bubbles is also expected to hinder foam coarsening.[5,8,11] This might explain the fact that foams stabilized with partially hydrophobized silica were more prone to coarsening than those stabilized with alumina particles. Because of their lower Hamaker constant (0.83×10^{-20} J as compared to 5.3×10^{-20} J for alumina[23,24]), silica particles are expected to form a weaker colloidal network within the foam lamella decreasing the long-term stability of the foam (Figure 5).

The adsorption of particles at the interface plays a crucial role in the high foam stability reported here. Foams prepared from suspensions containing the amphiphile butylamine and 35 vol % of nonadsorbed alumina particles in the liquid phase collapsed within a few seconds after mechanical frothing. The addition of 1 M NaCl to the suspension to coagulate the nonadsorbed particles in the liquid phase also led to very unstable foams. Using a standard long-chain surfactant (Triton X-45) in combination with a suspension containing 35 vol % of non-modified alumina particles lead to foams which were stable for only a few minutes. These results confirm that the enhanced stability depicted in Figure 5 cannot be explained solely by an increase of the liquid viscosity in the foam lamella and is also not simply related to an increase of the gas diffusion path because of the presence of a high concentration of particles in the foam lamella.

4.5. Versatility of the Method. The high air content and stability of foams prepared with three different short amphiphiles illustrate the versatility of the foaming approach outlined here. Table 2 depicts additional examples of other colloidal particles that have been surface modified using similar short amphiphiles to produce ultrastable particle-stabilized foams. The IEPs of these powders range from 9 to 2 and the average particle sizes from 2 μm to 30 nm. All foams prepared at the conditions shown in Table 2 were stable over more than 1 day and featured air contents between 45 and 90% and average bubble sizes down to 20 μm.

5. Conclusions

We showed that inorganic colloidal particles of various surface chemistries can be partially hydrophobized with tailored amphiphiles to produce wet foams exhibiting high air contents and remarkable stability. Foams were stabilized through the adsorption of such partially hydrophobized particles at the air−water interface. Particle hydrophobization is achieved through the adsorption of amphiphiles exhibiting a functional group that efficiently anchors on the particle surface and a short hydrophobic tail which remains in contact with the aqueous phase. Short-chain carboxylic acids, alkyl gallates and alkylamines were used as amphiphiles that can in-situ hydrophobize the surface of different oxide and nonoxide particles. Other amphiphilic molecules can be envisaged on the basis of the concepts outlined here.

High concentrations of such modified particles (35 vol %) in the initial suspension enabled the stabilization of an enormous air−water interfacial area and therefore the formation of high-volume foams. Air contents between 45 and 90% and average bubble sizes between 20 and 80 μm were achieved via mechanical frothing of the initial suspension. All foams were stable against bubble growth and drainage over days because of the irreversible adsorption of the partially hydrophobized particles at the air−water interface. The adsorbed particles form an interfacial armor around the bubble surface that mechanically impedes bubble shrinkage and coalescence. The simplicity and versatility of this approach combined with the possibility to tailor the foam properties in a wide range is expected to open new opportunities in various areas, including cosmetics, flotation in mining industry, pharmaceutics, food, and materials manufacturing.

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