Tailoring the Microstructure of Particle-Stabilized Wet Foams

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Received August 23, 2006. In Final Form: October 23, 2006

Inorganic colloidal particles which are in situ hydroph obized upon adsorption of short-chain amphiphilic molecules can be used as foam stabilizers. In this study, we tailor the microstructure of particle-stabilized wet foams, namely, the foam air content, average bubble size, and bubble size distribution, by changing the composition of the initial colloidal suspension. Wet foams featuring average bubble sizes between 10 and 200 μm and air contents between 45% and 90% were obtained by adjusting the amphiphile and particle concentration, pH, ionic strength, and particle size in the initial suspension. The influence of these parameters on the bubble size was satisfactorily described in terms of a balance between the shear stress applied during mixing and the counteracting Laplace pressure of the air bubbles. This model, originally developed for oil droplets in emulsions, can therefore be used to deliberately tailor the microstructure of particle-stabilized wet foams.

1. Introduction

Wet aqueous foams are used in numerous different applications ranging from food and cosmetics to oil recovery and fire extinguishing.1 Additionally, wet foams can be used as intermediate structures to fabricate solid porous materials applied as thermal insulators, low-weight structures, and scaffolds for drug delivery and tissue engineering, among others.2–4 The use of wet foams for the manufacture of porous materials upon drying and sintering has been extensively investigated in recent years as a simple and low-cost approach to prepare macroporous monoliths with tailored microstructure and chemical composition.4–8

However, wet foams are thermodynamically unstable and show limited resistance against bubble coarsening as a result of bubble coalescence, Ostwald ripening, and drainage. To improve the stability of wet foams, surfactants are used to lower the surface tension of the gas-liquid interface and thus increase the lifetime of gas bubbles. However, these surfactants are not able to completely avoid bubble growth due to their low energy of attachment to the gas-liquid interface, which is only a few kT’s for a single surfactant molecule (k being the Boltzmann constant and T the temperature).

In order to improve the stability of wet foams, particles have been used to adsorb on the surface of gas bubbles to stabilize the gas-liquid interface9–14 based on the original observations of Ramsden15 and Pickering.16 Upon adsorption, particles lower the overall free energy of the system by replacing part of the high-energetic gas-liquid interfacial area with less energetic interfaces. As opposed to surfactants, the energy of attachment of a particle at a gas-liquid interface can reach thousands of kT’s.9 Therefore, particles can irreversibly adsorb at gas-liquid interfaces, in contrast to the constant adsorption and desorption of surfactants. Particles adsorbed at the interface impede bubble coalescence and form an interfacial armor that hinders gas diffusion outward the bubble (Ostwald ripening). As a result, particle-stabilized foams exhibit enhanced stability in comparison to foams stabilized by surfactants.

Recently, we developed a very versatile method to prepare high-volume wet foams stabilized by partially hydrophobized particles.14,17,18 In situ hydrophobization of initially hydrophilic particles enabled the attachment of particles to the gas-liquid interface. Short amphiphilic molecules containing less than eight carbons in the hydrocarbon tail were adsorbed on the particles to impart surface hydrophobicity. Particles of various surface chemistry have been used as foam stabilizers by deliberately choosing the anchoring group of the adsorbing amphiphiles.18

The surface hydrophobization of a high concentration of particles and their adsorption to air-water interfaces enabled the stabilization of high-volume wet foams. These wet foams showed neither bubble growth nor drainage over more than 4 days.14,17

The formation of stable wet foams using modified particles as stabilizing agents opens many opportunities in a number of areas where foams are used either as an intermediate or end product, including food, pharmaceutics, cosmetics, oil recovery, textile manufacture, and materials fabrication. In these applications, microstructural features of the wet foam such as the average bubble size, the bubble size distribution, and the air content are of major importance, since they determine the rheological behavior of the wet foam and the functional properties of the final product. The size and content of gas bubbles in food foams, for example, have a marked effect on the sensorial quality and texture of the final food product.19,20 Likewise, the air content, of Ramsden15 and Pickering.16 Upon adsorption, particles lower the overall free energy of the system by replacing part of the high-energetic gas-liquid interfacial area with less energetic interfaces. As opposed to surfactants, the energy of attachment of a particle at a gas-liquid interface can reach thousands of kT’s.9 Therefore, particles can irreversibly adsorb at gas-liquid interfaces, in contrast to the constant adsorption and desorption of surfactants. Particles adsorbed at the interface impede bubble coalescence and form an interfacial armor that hinders gas diffusion outward the bubble (Ostwald ripening). As a result, particle-stabilized foams exhibit enhanced stability in comparison to foams stabilized by surfactants.

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bubble size, and bubble size distribution of wet foams used to produce porous materials also have a remarkable influence on the final mechanical and physical properties of porous solid structures.\textsuperscript{4,21}

Given the importance of the foam microstructure in various applications, we evaluate here the effect of the composition of the foam precursor suspension on the final microstructure of particle-stabilized wet foams. The concentration of surface modifier, salt, and particles, as well as the particle size and the pH of the initial precursor suspension, are the main parameters investigated. These parameters are expected to change some of the factors that control foam formation, such as the viscosity and surface tension of the suspension. A deliberate control of these parameters should therefore enable one to tailor the final microstructure of particle-stabilized wet foams. The principles investigated here should also be relevant for the microstructural control of particle-stabilized emulsions.\textsuperscript{22,23}

2. Materials and Methods

2.1. Materials. Submicrometer-sized alumina powders were used as model colloidal particles in this study. The powders were acquired from the following suppliers: $\text{Al}_2\text{O}_3$, $d_{50}$ ~ 28 nm, Nanotechnologies (Austin, TX); $\text{Al}_2\text{O}_3$, $d_{50}$ ~ 70 nm, Nanophase Technologies Co. (Romeoville, IL); $\text{Al}_2\text{O}_3$, $d_{50}$ ~ 116 nm (grade TM-DAR) Taini Chemicals Co. (Tokyo, Japan); $\text{Al}_2\text{O}_3$, $d_{200}$ nm (grade Ceralox HPA-0.5), Sasol North America Inc. (Tucson, AZ); $\text{Al}_2\text{O}_3$, $d_{1800}$ nm (grade CL2500SG), Alcoa (Ludwigshafen, Germany). Table 1 depicts the physical properties of these powders. If not supplied by the manufacturer, the particle size was measured on an X-ray disk centrifuge sedigraph (XDC, Brookhaven Instruments, Worchestershire, Great Britain) and confirmed by scanning electron microscopy. The specific surface was obtained by BET adsorption measurements (Nova 1000 Series, Quantachrome, Odelhausen, Germany).

The short-chain amphiphilic molecules used in this work were propionic acid and valeric acid (Fluka AG, Buchs, Switzerland). Other chemicals used in the experiments were deionized water, hydrochloric acid (2 N, Titrisol, Merck, Germany), sodium hydroxide (1 N, Titrisol, Merck, Germany), sodium hydroxide (1 N, Titrisol, Merck, Germany), and sodium chloride (Fluka AG, Buchs, Switzerland).

2.2. Suspension Preparation. Suspensions were prepared by adding the dry powder stepwise to water upon continuous stirring. During powder addition, the pH was kept at values below 5 using 2 N HCl in order to electrostatically stabilize the alumina particles. The initial solids content of suspensions prepared with 28, 70, 116, 200, and 1800 nm sized particles was set to 25, 30, 20, 50, and 45 vol %, respectively, before ball-milling. In the case of 70 and 28 nm particles, 20 mM NaCl was also added to the initial suspension to partially screen the particles’ surface charge and enable the addition of powder until the above-mentioned solids content. Homogenization was then added.

2.3. Foaming and Foam Characterization. Foaming of 150 mL suspensions 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 plastic cylindrical cup with small holes on the bottom and a massive sliding stamp on top. The foam was carefully filled into the cup and then slightly compressed with the stamp to remove possible air pockets introduced during filling. 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 foams was evaluated using an optical microscope in transmission mode (Polyvar MET, Reichert-Jung, Austria) connected to a digital camera. The bubble sizes were measured with the linear intercept method using the software Linear Intercept (TU Darmstadt, Germany). The average bubble size ($d_{50}$) was determined from the resulting cumulative bubble size distribution, as the size corresponding to a number cumulative percentage of 50%.

2.4. Surface Tension Measurements. The surface tension of the suspensions was measured using the pendant drop method (PAT1, Sinterface Technologies, Berlin, Germany). Suspensions were prepared as mentioned above by adding the carboxylic acid dropwise, adjusting the pH to 4.75, and diluting the suspension to the desired solids content. Depending on the surface tension, the drop volume was set to a constant value within the range of 12–35 mm$^3$.

2.5. Foam Rheology. Foam rheology was evaluated in a stress-controlled rheometer (model CS-50, Bohlin Instruments, Cirencester, U.K.) using profiled parallel plates (diameter: 25 mm) with a gap of 1 mm. Measurements were performed under steady-shear conditions by applying a stepwise stress increase until a shear rate of at least 500 s$^{-1}$ was reached.

3. Results and Discussion

The influence of the composition of the initial suspension on the microstructure of wet foams was investigated by characterizing the foams with regards to air content, average bubble size, and bubble size distribution. Figure 1 shows two typical wet foam
microstructures obtained, one with small average bubble sizes and a narrow bubble size distribution (Figure 1a) and the other with large bubble sizes and a wide size distribution (Figure 1b). The parameters evaluated were the amphiphile concentration, pH, ionic strength, particle concentration in the initial suspension, and particle size. Valeric acid was used as amphiphile to hydrophobize the alumina particles’ surface in most experiments, except for the study concerning the influence of ionic strength where propionic acid was used. Trends similar to the ones described here were observed for several other short-chain amphiphilic molecules with hydrocarbon tails containing 3–8 carbon atoms.18

It should be noted here that the wet foams investigated in this study are quite complex systems. A series of events is involved in the stabilization process, including the adsorption of amphiphiles on the particle surface, the adsorption of amphiphile-coated particles on the gas bubbles, and the adsorption of free amphiphiles on the gas bubbles. Therefore, changes in the initial foam composition often affect more than one of the parameters relevant for foam formation and stabilization. Varying the particle concentration at a constant amphiphile addition, for instance, also changes the hydrophobicity of the particle surface, as discussed below. Therefore, the parameters investigated in sections 3.1–3.5 should be regarded as practical variables that can be changed in the initial suspension composition rather than factors that have been independently adjusted in the experiment. Remarkably, in spite of such complexity, we show in section 3.6 that the combined effect of all the investigated parameters can be rationalized in terms of one single scaling number that allows us to predict the foam microstructure based on the composition of the initial suspension.

3.1. Initial Amphiphile Concentration. The amphiphile concentration in the initial suspension directly affects the hydrophobicity of the colloidal particles.14,17 An increase in the initial amphiphile concentration leads to a higher adsorption onto the particles, enhancing the surface hydrophobicity. Above a critical concentration of absorbed amphiphiles, the particles are sufficiently hydrophobic to adsorb to air–water interfaces and to stabilize freshly introduced air bubbles. Therefore, foam formation and their resulting microstructure depend strongly on the initial amphiphile concentration in the suspension.

Figure 2a shows the effect of the initial valeric acid concentration on the air content and average bubble size of suspensions containing 35 vol % of 200 nm alumina particles at pH 4.75. The discrete bubble size distribution of wet foams prepared with 10 and 40 mmol/L of valeric acid is depicted in Figure 2b. No stable foam is formed below the critical valeric acid concentration of 5 mmol/L (Figure 2a). At this concentration, the particles are not sufficiently hydrophobic to absorb to the air–water interface. With increasing valeric acid concentration, the particles become hydrophobic enough to attach to the surface of air bubbles, resulting in stable wet foams (Figure 2a). The air content in the wet foam remains nearly constant at approximately 80% for valeric acid contents between 10 and 40 mmol/L. The addition of valeric acid concentrations higher than 40 mmol/L leads to a considerable increase in the suspension viscosity (>2 Pa s at 100 s⁻¹), hindering the incorporation of air and foam formation (Figure 2a). This viscosity increase is caused by the enhanced screening of the particles’ surface charge resulting from the high amphiphile concentrations (section 3.3).14,17

Even though the air content of the wet foams remained nearly constant at 80%, the average bubble size decreases from 108 to 16 μm with increasing the valeric acid concentration from 10 to 40 mmol/L. Foams with lower average bubble size also exhibited a narrower bubble size distribution, as shown in Figure 2b.

3.2. Suspension pH. Besides the amphiphile concentration, the pH of the suspension also significantly influences the wet foam microstructure. Figure 3 shows the effect of pH on the air content, average bubble size, and bubble size distribution of wet foams prepared from suspensions containing 35 vol % of 200 nm alumina particles and a constant valeric acid concentration of 30 mmol/L.

The results show a constant air content in the wet foam of approximately 82% between pH 2.5 and 7 of the initial suspension. Below pH 2.5, no stable foam was formed, and above pH 7, the air content decreases due to an increase in the viscosity of the initial suspension as the pH approaches the isoelectric point of alumina (pH 9.4).

The pH also has a pronounced effect on the average bubble size and the bubble size distribution (Figure 3). Interestingly, highly aerated foams with small average bubble size and narrow bubble size distributions were achieved at a pH range between 3.5 and 5. For pH values in the range of 5–7 and below 3, foams feature relatively large bubbles (Figure 3a) and a wide bubble size distribution (Figure 3b).

3.3. Ionic Strength. The concentration of salt in the initial suspensions directly affects the interactions between the partially hydrophobized colloidal particles and is therefore also expected to affect the microstructure of wet foams. The addition of salt to the suspension increases the medium ionic strength, screens the particle surface charge, and reduces the electrostatic repulsive forces between particles. In order to investigate the influence of ionic strength on the foam properties, suspensions with different
NaCl concentrations were prepared. In this case, the particle concentration was set to 35 vol % and 176 mmol/L propionic acid was added to hydrophobize the particles at a pH of 4.1.

Figure 4 shows the effect of the salt concentration in the initial suspension on the microstructural features of the resulting wet foams. An increase in NaCl concentration from 1 to 500 mmol/L decreases the average bubble size from 65 to 20 μm and narrows the foam bubble size distribution. These effects were accompanied by an increase in the suspension initial viscosity from 0.013 to 1.92 Pa s (at 100 s⁻¹). The viscosity of the initial suspension for different concentrations of added salt was experimentally measured and added in Figure 4 as an upper x-scale. The air content in the wet foam remains constant at a level slightly above 80% up to a salt concentration of 100 mmol/L which corresponds to a viscosity of 0.18 Pa s. The addition of more NaCl leads to a strong decrease in the air content of the foam, as a result of an increased initial viscosity of up to 2 Pa s (at 100 s⁻¹).

3.4. Particle Concentration. The microstructure of the wet foams can also be tailored by the particle concentration in the suspension. The influence of particle concentration on the microstructure of wet foams was determined by varying the solids content in an alumina suspension containing 200 nm particles at pH 4.75 and a valeric acid concentration of 0.134 wt % to alumina (Figure 5). This condition corresponds to an amphiphile concentration of 30 mmol/L in a suspension containing 35 vol % alumina.

The results depicted in Figure 5a show a strong decrease in average bubble size from 161 to 16 μm upon increasing the suspension solids content from 10 to 50 vol % alumina. On the other hand, the foam air content changes only from 85% to 71% within this range of solids concentration. The drop in air content above a solids content of 50 vol % results from the strong increase in the viscosity of the initial suspension. The minimum particle concentration required for the formation of stable foams is 5 vol % in this case. The bubble size distribution in the foam is wide at low solids content and becomes narrower with increasing particle concentration (Figure 5b).

3.5. Particle Size. Figure 6 shows the effect of particle size on the average bubble size, air content, and bubble size distribution of foams prepared from 15 vol % alumina suspensions containing particle sizes ranging from 28 to 1800 nm. In this case, valeric acid concentrations resulting in stable foams with high air content (>80%) combined with small average bubble size (<60 μm) were chosen for foam preparation. Valeric acid contents of 0.834, 0.527, 0.191, 0.134, and 0.150 wt % to alumina were used in suspensions containing 28, 60, 116, 200, and 1800 nm particles, respectively. The higher valeric acid contents (in wt %) required to obtain stable foams with smaller particle sizes is directly related to the higher specific surface area of the smaller particles. When normalized with respect to the particle specific surface area, the valeric acid contents used were 0.162, 0.153, 0.147, 0.142, and 1.614 mg/m² for suspensions containing 28, 60, 116, 200, and 1800 nm particles, respectively. Except for the coarser particles, the normalized valeric acid concentrations used for foaming are quite similar for the particle sizes investigated here.

Air contents of approximately 90% were obtained for all the foams prepared with different particle sizes (Figure 6a) except for the foam which was stabilized with 1800 nm particles. This foam showed an air content slightly below 80%. With increasing the particle size from 28 to 1800 nm, the average bubble size...
in the foam increases from 56 to 140 μm (Figure 6a). Additionally, the use of smaller particles as foam stabilizers leads to wet foams with slightly narrower bubble size distributions, as indicated in Figure 6b.

It is important to note that in the case of the 1800 nm particles, the valeric acid concentration per surface area needed to obtain stable foams was approximately ten-fold higher compared to that required for smaller particles. Even though foam formation with 1800 nm particles was also observed at lower amphiphile concentrations, coalescence and drainage could not be prevented at these conditions. These results suggest that the preparation of wet foams that are stable against bubble coarsening and drainage at these conditions. These results suggest that the preparation of wet foams that are stable against bubble coarsening and drainage requires particle sizes not larger than a few micrometers in diameter. Theoretical calculations based on the adsorption energy of particles at the gas—liquid interface and the maximum capillary pressure developed at the interface showed that particles larger than ~3 μm are not able to stabilize foams for long periods of time. These results are in the same order of magnitude as our experimental findings.

### 3.6. Influence of Mechanical Shearing on the Wet Foam Microstructures

In order to understand the influence of the investigated parameters on the final microstructure of the wet foams, one has to consider in detail the influence of mechanical shearing on the development of the foam microstructure. The bubble size, in particular, is significantly influenced by the stresses applied on the bubble surface during shearing. Even though qualitative predictions of foam bubble sizes are rather scarce in the literature, a number of models have been suggested to describe the influence of mechanical shearing on the size of oil droplets in emulsions. In the 1930s, Taylor introduced a model to predict the final droplet size of a viscous fluid dispersed in a second immiscible fluid. According to this model, the final droplet size is achieved through a series of breakup steps of larger droplets during shearing. To understand this idea, let us consider an isolated spherical droplet of radius \( R \), viscosity \( \eta_d \), and surface tension \( \sigma \) that deforms into an ellipsoid or an elongated cylinder when sheared in a fluid of viscosity \( \eta_f \). Droplet deformation only takes place if the applied shear stress \( \tau_{\text{applied}} \) overcomes the interfacial stress \( \tau_{\text{interfacial}} \). The ratio between these two counteracting stresses is defined as the capillary number \( Ca = \frac{\tau_{\text{applied}}}{\tau_{\text{interfacial}}} \). When \( Ca \) exceeds a critical value \( Ca_{\text{crit}} \), the elongated droplet ruptures into smaller droplets. Ca depends on the viscosity ratio \( p \) between the dispersed and the continuous phase (\( p = \frac{\eta_d}{\eta_f} \)) as well as on the type of flow. By assuming the interfacial stress \( \tau_{\text{interfacial}} \) to be proportional to the Laplace pressure \( \sigma R \) of the droplet, one can estimate the droplet size \( R \).

at the critical condition as follows:

\[ R \propto \frac{C_{\text{crit}} \sigma}{\tau_{\text{applied}}} = \frac{C_{\text{crit}} \sigma}{\eta \dot{\gamma}} \]  

(3.1)

where \( \dot{\gamma} \) is the shear rate applied during mixing.

In order to use eq 3.1 to describe the shearing rupture of oil droplets in concentrated emulsions, several authors have suggested that the viscosity of the continuous fluid \( \eta_c \) has to be replaced by the effective viscosity of the concentrated emulsion itself, \( \eta_{\text{eff}} \).\textsuperscript{27–29} Even though this simple equation does not take into account the complex mechanisms involved at the microscopic level, it indicates the key physical parameters that control the final droplet size. Thus, this model was used here to understand the effect of the initial suspension composition on the final bubble size of the investigated foams. For that purpose, we assumed the effective viscosity \( \eta_{\text{eff}} \) to be proportional to the final viscosity of the foam after mixing (\( \eta_{\text{foam}} \)).

The surface tension of the initial suspension (\( \sigma \)) and the apparent viscosity of the wet foams (\( \eta_{\text{foam}} \)) were thus measured for compositions containing different valeric acid and particle concentrations. The rheological measurements showed that the wet foams are viscoelastic materials with a strong yielding behavior. Foam fracturing was observed for stresses higher than the yield point, leading to inhomogeneous flow patterns. Bubble rupture was assumed to occur predominantly before the fracturing phenomenon. Therefore, the effective viscosity that leads to bubble rupture (\( \eta_{\text{eff}} \)) was assumed to be proportional to the foam apparent viscosity before the fracturing point (\( \eta_{\text{foam}} \)). Since no fracturing was observed at a shear rate of 0.01 s\(^{-1}\) for all the evaluated compositions, the apparent viscosity at this shearing condition was arbitrarily taken as \( \eta_{\text{foam}} \).

Parts a and b of Figure 7 show the influence of the suspension initial amphiphile concentration on the surface tension, apparent viscosity, and critical capillary number of wet foams prepared with 35 vol% of 200 nm alumina particles.

The increase in amphiphile concentration from 10 to 40 mmol/L led to a decrease of the suspension surface tension from 72 to approximately 54 mN/m (Figure 7a). This decrease in surface tension is mainly due to an enhanced adsorption of the partially hydrophobic particles at the air–water interface. Higher amphiphile concentrations in the initial suspension result in a higher amount of adsorbed molecules on the particle surface, increasing the hydrophobicity of particles and favoring their adsorption at the air–water interface. The surface tension is also decreased by the adsorption of free amphiphilic molecules at the air–water interface.\textsuperscript{14} This effect also increases for higher amphiphile concentrations.

Figure 7b shows that the foam viscosity increases with increasing amphiphile concentration in the initial suspension. This increase is due to the more pronounced screening of the particle surface charge achieved for higher concentrations of amphiphilic molecules adsorbed on the particle surface or free in the liquid medium.\textsuperscript{17} As a result of this screening effect, the thickness of the electrical double layer around the particles is reduced, decreasing the repulsive forces between them. The interparticle attraction due to van der Waals forces is thus favored, leading to an increase in foam viscosity.

The critical capillary number \( C_{\text{crit}} \) depicted in Figure 7b was calculated based on the viscosity of the foam (\( \eta_f = \eta_{\text{foam}} \)) and the viscosity of air (\( \eta_a \)), assuming simple shearing conditions and an air viscosity of 1.85 × 10\(^{-5}\) Pa s. The \( C_{\text{crit}} \) value increases for a lower viscosity ratio \( p = \eta_f/\eta_a \). Since the viscosity of air remains constant, \( C_{\text{crit}} \) increases as a function of the amphiphile concentration due to the increase in foam viscosity and a resulting decrease in the viscosity ratio \( p = \eta_f/\eta_a \).

According to eq 3.1, the final bubble size (\( R \)) should be proportional to the ratio \( C_{\text{crit}} \sigma/\eta_{\text{foam}} \). This ratio was therefore calculated from the rheology and surface tension data shown above and compared in Figure 7c with the experimentally measured average bubble size \( R \) obtained at different amphiphile concentrations. The results show a remarkably good agreement between the measured bubble size and the ratio \( C_{\text{crit}} \sigma/\eta_{\text{foam}} \) for wet foams containing different initial amphiphile concentrations.

Based on this analysis, we conclude that the average bubble size decreases with increasing amphiphile concentration as a result of the decrease in surface tension (Figure 7a) and the increase in foam viscosity (Figure 7b). These two effects compensate for the less pronounced increase in the critical capillary number obtained for increasing amphiphile concentrations (Figure 7b).

The effect of the particle concentration on the average bubble size can also be interpreted on the basis of eq 3.1. Figure 8 shows the influence of the particle concentration on the surface tension, foam viscosity, and critical capillary number.

The surface tension of the initial suspension decreases with increasing particle concentrations (Figure 8a). This can be
explained by an increase in surface hydrophobicity of particles with increasing particle concentration. Earlier investigations have shown that the adsorption of propionic acid on alumina particles increases from 0.50 to 1.11 μmol/m² by changing the suspension particle concentration from 10 to 35 vol %. A similar behavior can be expected for valeric acid. The higher amount of amphiphiles adsorbed on the surface enhances the particles’ hydrophobicity and thus their adsorption to the air–water interface, leading to a lower surface tension. The amphiphilic molecules that do not adsorb on the particle surface and remain free in the liquid medium might also decrease the suspension surface tension. However, this effect is believed to be of minor importance due to the low concentrations of free amphiphiles in the suspension for the valeric acid concentrations evaluated here.

Figure 8b shows that higher particle concentrations in the initial suspension also increase the viscosity of the foams, as would be expected for any colloidal suspension. This increase in foam viscosity leads to higher critical capillary numbers, as indicated in Figure 8b.

The experimentally measured bubble size $R$ and the calculated ratio $\frac{C_{\text{crit}}}{\eta_{\text{foam}}}$ for foams with different solids content are compared in Figure 8c. The results show that the decrease in average bubble size for higher particle concentrations is accompanied by a decrease of the ratio $\frac{C_{\text{crit}}}{\eta_{\text{foam}}}$, confirming the good agreement between the experimentally measured data and the predictions from the model. As in the case of the effect of amphiphile concentration, the decrease in average bubble size with increasing particle concentration is caused by a decrease in the suspension surface tension and an increase in foam viscosity.

The effect of pH, ionic strength, and particle size on the average bubble size can also be interpreted on the basis of this model. Even though not shown here, an excellent agreement between the average bubble size and the ratio $C_{\text{crit}}/\eta_{\text{foam}}$ was also obtained for these parameters. In case of the pH, the suspension surface tension shows a minimum around pH 4.5, resulting in smaller average bubble sizes at this condition. This minimum possibly results from an increased adsorption of valeric acid around the $pK_a$ of the molecule, which is at pH 4.84.

From the results shown here, we conclude that the final average bubble size of wet foams is indeed controlled by shearing and rupture of single bubbles during the frothing process. The suspension surface tension, the foam viscosity before fracturing, and the critical capillary number were the main factors determining the final bubble size of the wet foams. Even though it was not the subject of this work, the shear rate should also influence the final bubble size as predicted in eq 3.1. Besides the parameters investigated here, other changes in the composition of the initial precursor suspension would also affect the final bubble size of wet foams by influencing the factors depicted in eq 3.1. Therefore, this simple physical model can be a powerful tool for tailoring the microstructure of particle-stabilized wet foams.

3.7 Tailoring the Wet Foam Microstructure. Figure 9 shows the average bubble size and the air content of wet foams prepared by direct foaming with surfactants (+, dark gray) and with particles (from this work, light gray). For the particle-stabilized foams, the microstructure can be tailored by changing the amphiphile concentration in suspension (●), pH of the suspension (○), ionic strength (□), particle concentration (△), and particle size (■). Foams prepared using long-chain surfactants were set by a number of different gelling reactions described in the literature (ref 4).

According to Figure 9, the microstructure of particle-stabilized foams can be tailored in a wide range by adjusting some of the
experimental parameters investigated here such as amphiphile concentration, pH, ionic strength, particle concentration, and particle size. The air content of the resulting foams can vary between 45% and 90%, whereas the average bubble size can be tailored within the range from 10 to 200 μm.

4. Conclusions

We showed that the microstructure of wet particle-stabilized foams can be tailored in a wide range by adjusting the composition of the initial colloidal suspension, namely, the short amphiphile content, particle concentration, pH, ionic strength, and particle size. In order to form stable high-volume foams, the particles need to be sufficiently hydrophobic to adsorb to the surface of air bubbles. Foam formation also requires suspensions with initial viscosities lower than approximately 2 Pa s (at 100 s⁻¹) to allow for the incorporation of air during mechanical frothing. The effect of the suspension composition on the final bubble size of the wet foam was interpreted with the help of a model that describes the rupture of bubbles as a balance between interfacial stresses and shearing stresses applied during the mixing process. According to this model, the final bubble size can be tailored by changing the suspension surface tension, the foam viscosity, and the shearing rate applied during mixing. A scaling number containing these three variables was successfully employed to explain the effect of the suspension initial composition on the average bubble size of wet foams. An increase of the amphiphile content and particle concentration, for instance, led to foams with smaller average bubbles mainly due to a decrease in the suspension surface tension and an increase in the effective foam viscosity. The ability to control the microstructure of wet foams in a wide range combined with the high stability in the wet state opens the possibility to use these foams in many different areas ranging from pharmaceuticals, food, and cosmetics, to health care, medicine, and materials’ manufacture.

Acknowledgment. The authors thank CIBA Specialty Chemicals (Switzerland) for their funding as well as Rahel Nägeli, Claudia Strehler, Lorenz Bonderer, and David Steinlin for their contribution to the experimental work.

LA0624844