

Foaming Mechanisms in Surfactant Free Particle Suspensions

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Physical mechanisms for foam formation in the presence of colloidal particles are poorly understood. This study is aimed at enhancing the basic understanding of the mechanisms that produce foaming in a three-phase system, containing solid, liquid, and gas, and identifying key parameters that aggravate foaming in the absence of surface-active agents. The foaming ability of a system ("foaminess") was investigated by aerating a suspension of nanosized hydrophilic silica particles. We observed that the foaminess was directly proportional to particle concentration and inversely proportional to particle size. However, even a small degree of bidispersity in particle size drastically reduced foaminess. To explain these observations, the drainage of a single foam lamella containing nanosized particles was studied using a novel capillary force balance apparatus, which incorporates the microinterferometric technique. The single foam lamella thins in a stepwise manner, as the colloidal particles self-organize into a layered structure between the gas bubbles. This layer provides a barrier against coalescence of bubbles, thereby stabilizing the foam lamella. The number of stepwise film thickness transitions increased with particle concentration and decreased with the increase in the particle size, consistent with the results from foaming experiments. Particle bimodal distribution greatly decreases the foam-lamella stability, consistent with the theoretical prediction.

Introduction

A majority of foams encountered in industry comprise two phases: gas and surfactant solutions. There are also foams, which have three phases: gas, liquid, and solid particles. Such foams incorporating finely divided solid particles are frequently encountered in the processing of solid waste, food, chemical, agricultural products, and so on (Ip et al., 1998; Calahorra et al., 1987). In many unit operations where gas-liquid contacting is required, the presence of dispersed particles alters the gas-liquid contact surface, mixing of phases (Nagy and Blickle, 1983), and also leads to foaming (Stangle and Mahalingam, 1990). Such undesirable foaming limits the gas flow rate (Mahalingam et al., 1975), restricts the range of operating conditions (Blair and Luckas, 1980), plugs filters in process vessels and vent gas monitoring systems, and causes environmental hazards, all of which translates into a financial loss of millions of dollars. In order to control such foaming, it is important to understand the key factors contributing to foaming in the presence of finely divided dispersed particles.

Many studies have been carried out to explain the role of solid particles ranging from a few to hundreds of microns in diameter on foaminess. However, these studies have been carried out in the presence of surfactants. The addition of solid particles to a foaming system has been reported to either increase (Kruglyakov and Taube, 1972; Adamson, 1982; Ralston, 1983; Hudales and Stein, 1990) or decrease the foam stability (Tang et al., 1988, and Garrett, 1979, studied using hydrophobic particles). These researchers have found conflicting results about the size and wettability of solid particles on foaminess. For example, Ralston (1983) reported that the presence of small solid particles enhances foam stability. But Hudales and Stein (1990) found that larger particles of hydrophilic glass in a cetyltrimethylammonium bromide (CTAB) solution increased foam stability (by decreasing the drainage of free vertical films), while smaller particles had no influence.

The system used in our study is an aqueous suspension of hydrophilic silica particles. Unlike other studies, no surfactant was used, either to modify surface characteristics or to create foam. Foam in our system was created by the aeration

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of nanosized silica suspension. The foam is stabilized as the nanosized hydrophilic particles form a layered structure in the confined space of the foam lamella. This layered structure provides a barrier against the coalescence of bubbles, thereby causing foaming. The layering of submicron-sized particles and micelles has been observed to stabilize foam and emulsion films (Chu et al., 1995; Xu et al., 1998). The layering occurs because nanometer-sized micelles, particles, and so on, interact via repulsive forces and are forced into the restricted volume of the thinning film (Nikolov and Wasan, 1989, 1992). This kind of layering introduces non-DLVO long-range oscillatory structural force that acts over a distance of several diameters of particles, in addition to the short-range electrostatic and van der Waals forces (Israelachvili, 1992). This produces an oscillatory energy of interaction between the two surfaces (Figure 1), with the energy peaks representing the stabilizing barriers provided by the particles. Such particle layering also produces a stepwise decrease in film thickness during the thinning process (Wasan et al., 1988; Nikolov et al., 1989; Basheva et al., 1991; Wasan and Nikolov, 1997, 1999).

Chu et al. (1995) simulated a model film consisting of monodispersed particles sandwiched between two film surfaces using the Monte Carlo method in order to understand

the particle-layering phenomena. They used both hard-sphere and Lennard-Jones pair-particle interactions. They found that as a result of layering, the disjoining pressure contributed by the particles becomes oscillatory and the period of oscillation is about the effective diameter of the particle (Figure 2). The disjoining pressure follows a similar trend as the energy of interaction shown in Figure 1. When an integral number of particle layers is present between the surfaces, both energy and disjoining pressure show repulsive interaction between the surfaces. At a lower concentration of colloidal particles or when the distance between the two film surfaces is less than the size of the particles, attractive depletion forces become important (Askura and Oosawa, 1954; Gast et al., 1983; Walz and Sharma, 1994; Mao et al., 1995). Depletion forces arise when the concentration of colloidal particles in the gap region between two macroparticles (or emulsion droplets and gas bubbles) differs from that in the bulk. At a small gap-width the colloidal particles are excluded from the gap, resulting in an attractive force due to the difference in osmotic pressure. Overall, the film-thinning process is a manifestation of long-range structural forces, which show an oscillatory decay with thickness. For the first time the role of structural forces on foaminess caused by submicellar-sized solid particles is demonstrated and discussed in this work.

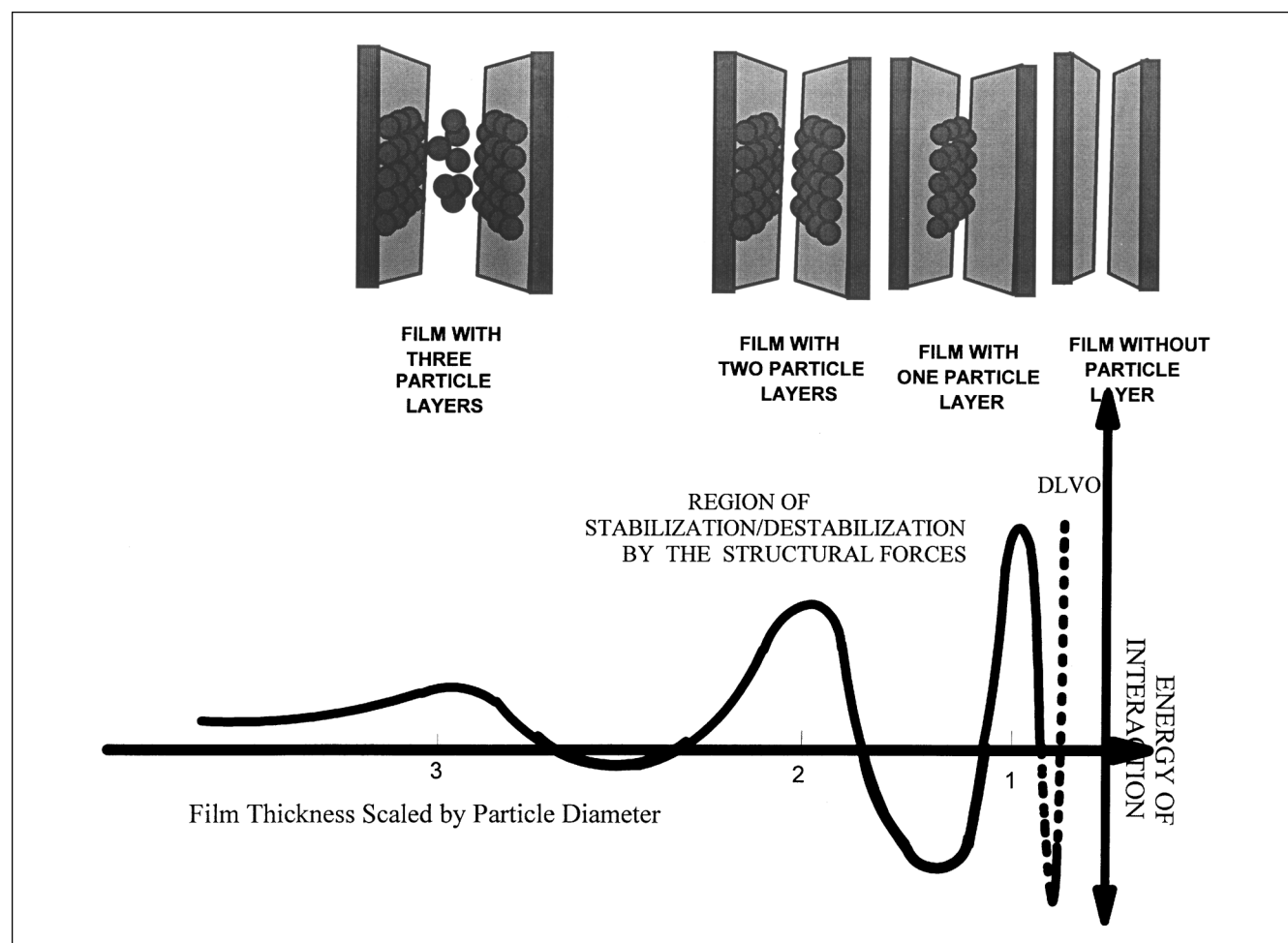


Figure 1. Long-range structural force due to layer formation.

In this article, the mechanism of foam formation due to the particle layer formation inside the foam lamella in the absence of surface-active agents is reported. A systematic study of various parameters, such as particle concentration, size, and size polydispersity that affect the particle layer formation inside the foam lamella and the foaming ability of the system ("foaminess") has been carried out.

Experiment

No surface-active agent was used in this study. The foaming ability of the system was characterized by "foaminess," which is defined as the percentage volume of air incorporated per unit volume of the suspension at steady state, under a constant rate of aeration.

Materials

The three-phase foam system used in our study was a dispersion of air in a silica-particle suspension. Silica particles of four different sizes, 8 nm, 11–14 nm, 19 nm, and 100 nm, were supplied by Nalco Chemicals, Naperville, IL, and Nissan Chemicals, Tarrytown, NY. The silica particles were hydrophilic in nature and were supplied as a suspension in water. The pH of the suspension was between 9 and 10.5 for all four particle sizes. Deionized purified water using the Milli-Q system from Millipore Corporation, Bedford, MA, was used to dilute the silica suspension, and extreme care was taken to make sure no surface-active impurities were added to the system.

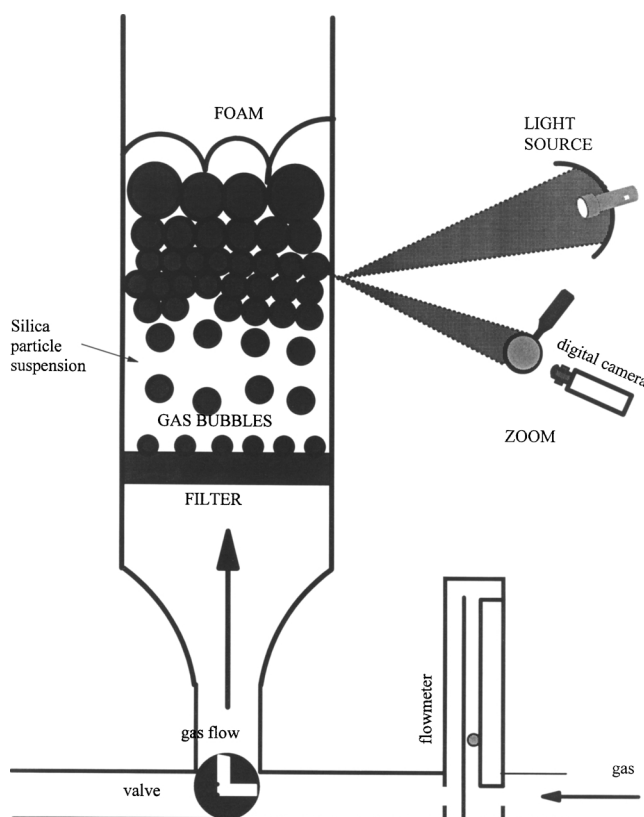


Figure 3. Experimental setup to study foaminess.

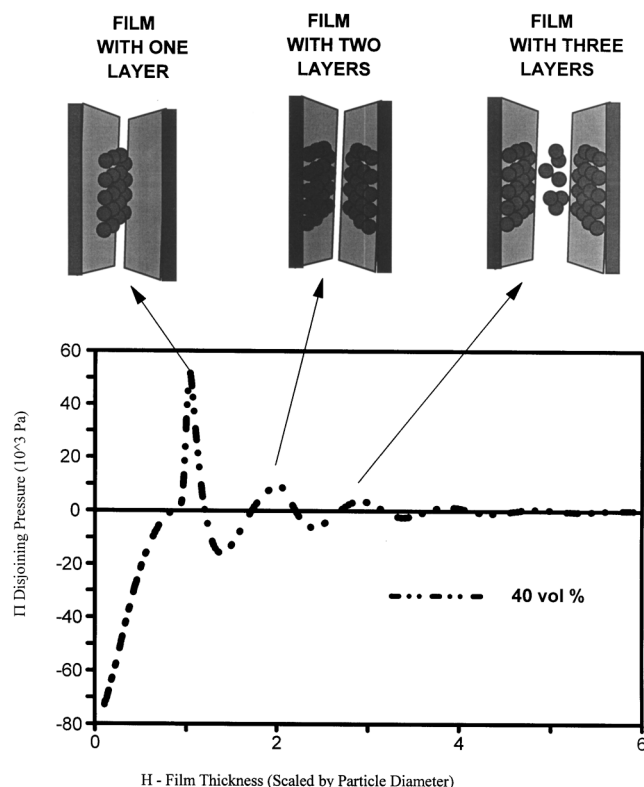


Figure 2. Disjoining pressure as a function of film thickness.

Three-phase foam generation

Three-phase foam was generated by the aeration of the silica suspension through a sintered glass filter at a controlled room temperature $25 \pm 0.5^\circ\text{C}$. The experimental setup is shown in Figure 3. It consists of a foam column, supplied by Reliance Glass Inc., Bensenville, IL, which is 61 cm in height and 1.9 cm in diameter and has a sintered glass filter at the bottom. The air flow rate was controlled with a commercial flowmeter. The flowmeter was calibrated in our laboratory by measuring the displacement of water by air. The three-phase foaminess experiments were conducted by injecting air into the fixed volume of the suspension. The volume percent of air incorporated into the system was measured for all experiments and is reported as "foaminess" in this article.

Particle interaction probed by capillary force balance

Liquid drainage from foams containing a dispersion of fine particles is determined by the film thinning of the individual lamellae separating the gas bubbles. The mechanism of film thinning of a single foam film was investigated using the capillary force balance (Nikolov and Wasan, 1992). The setup is shown in Figure 4. Microscopic thin films were formed in a cylindrical capillary with hydrophilic inner walls inside a temperature-controlled glass cell. Liquid was slowly sucked out of the drop through a capillary orifice in the tube wall to create a horizontal flat film encircled by a biconcave liquid meniscus. The entire assembly is placed on the stage of a

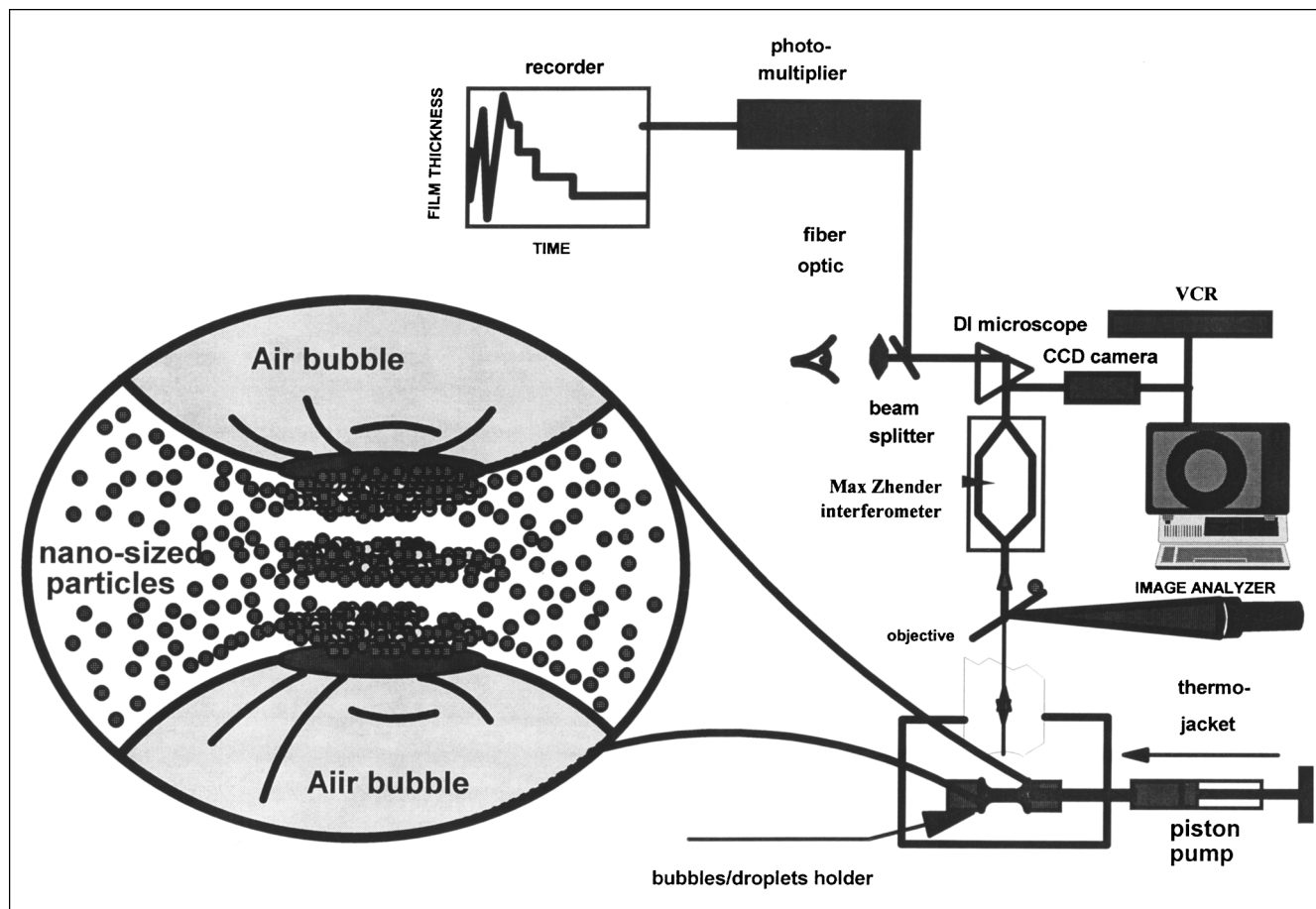


Figure 4. Capillary force balance.

differential microscope (Epival Interphako Carl Zeiss Jena, Germany), which is mounted on a vibration-free table to keep any external disturbance from affecting the film-thinning process. White light from the top incident on the film surface is reflected from the bottom and the top surface of the film, producing interference patterns (Nikolov and Wasan, 1997). The microscope was used in conjunction with a CCD camera, a video recorder, and an image analyzer to monitor the interference patterns as a function of time. From the color of the interference pattern, we can calculate the film thickness as a function of time. This allowed us to monitor the thinning process accurately. During the process of film thinning the dispersed particles are trapped between the film surfaces and this technique allows us to visually see its effects on film thinning. We used this to gain a qualitative understanding of the mechanism of film thinning in the presence of fine particles.

Results and Discussion

The effect of particle concentration and size on foaminess is discussed first, followed by a complementary study of foam-lamella thinning and stability probed by the capillary force balance. The role of bidispersity in particle size in foaminess is examined next, followed by a rationalization of these results by studies on single foam lamellae.

Effect of solid-particle concentration

In the literature, it has been mentioned that solid particles can cause foaminess if they have suitable wetting properties that allow them to go to the gas/liquid interface (Ip et al., 1998; Hudales and Stein, 1990; Tang et al., 1988; Portnaya et al., 1981). However, all these studies were carried out in the presence of surface-active agents. Therefore, we attempted first to establish that solid particles, which are hydrophilic in nature, could cause foaminess in the absence of surface-active agents. In order to prove our hypothesis, we made a three-phase foam using an aqueous silica suspension. Our observations clearly revealed that silica particles could cause foaminess when air was injected into the system (Figure 5a). To understand how the concentration of silica particles in the suspension would affect the nature and amount of foaminess, we systematically carried out foaminess studies on three different concentrations of silica particles of 8-nm size at a constant suspension volume. The air flow rate used for the study was kept constant at 8 mL/s. Foaminess, that is, the volume percent of air incorporated, increased directly with the increase in the concentration of solid particles in the range of concentration studied (Figure 5a). When the particle concentration was increased from 2.5 vol % to 10 vol %, the amount of foaminess increased from 20% to 550%. The air bubbles

were almost monodispersed in size with an approximate size of 5–6 nm.

The same concentration effect on foaminess is reported by Tang et al. (1988), but on silica particles, which were surface treated for hydrophobicity. They found that the presence of silica particles decreased the surface tension, which implies that hydrophobic particles were concentrated at the interface and the drainage process governed the foam collapse. In our system, we did not use any surface-active agents, so silica particles are not expected to accumulate at the interface and to provide any kind of stabilization. Another noteworthy observation is that foams generated by us had negligible stability, that is, the foam collapsed a few seconds after the aeration was stopped. This observation reestablishes the fact that our system had no surface-active agents.

Effect of particle size on foaminess

To investigate the effect of particle size on foaminess, 8-nm, 11–14-nm, 19-nm and 100-nm particles at 10 vol % were used. The air flow rate was kept constant at 8 mL/s. The results reveal that foaminess in a three-phase system in the absence of a surface-active agent is a strong function of particle size (Figure 5b). When the particle size was increased from 8 nm to 100 nm, the amount of foaminess decreased from 550% to 15%. The foam generated using all three particle sizes had

negligible foam stability. As soon as the aeration was stopped, the foam collapsed.

Effect of bidispersity in particle size on foaminess

To study the effect of polydispersity in particle size on foaminess, a small quantity of 100-nm particles was added to an of 8-nm silica particle suspension to produce a suspension containing 2 vol % of 100-nm particles and 8 vol % of 8-nm particles. On a number basis the ratio of 100-nm to the 8-nm particles in the bidisperse system was extremely small (1:7800). Hence, the results of the bidisperse system were compared with those of the monodisperse 10 vol % of 8-nm particles. With the addition of just 2 vol % of 100-nm particle, the foaminess decreased dramatically by about 10 times (Figure 5c).

The slower the rate of individual foam lamella thinning the higher the height of the foam in our experiments. Foaminess in these experiments is the net result of kinetic and thermodynamic factors. Kinetic factor refers to the initial stages of film thinning and is affected by the rate of liquid drainage from the film due to changes in viscosity and film elasticity (Edwards et al., 1991). On the other hand, thermodynamic factors refer to the last stages of film thinning when the rate of liquid drainage is comparatively much slower and thermodynamic parameters determine the life of the lamella, and, hence, the height of the foam column.

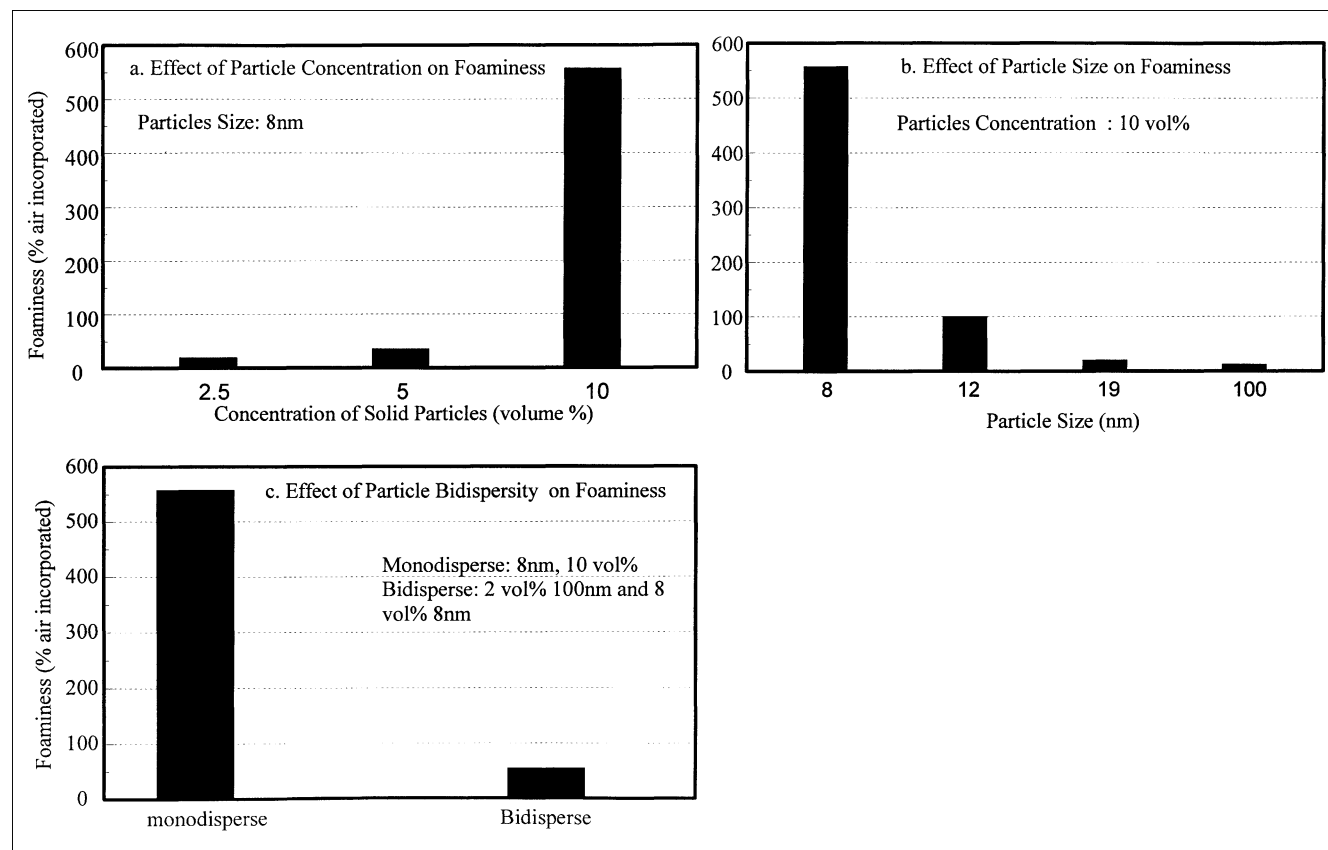


Figure 5. Effect of silica particle concentration, size, and polydispersity on foaminess.

Air flow rate: 8 mL/s; temperature: 25°C.

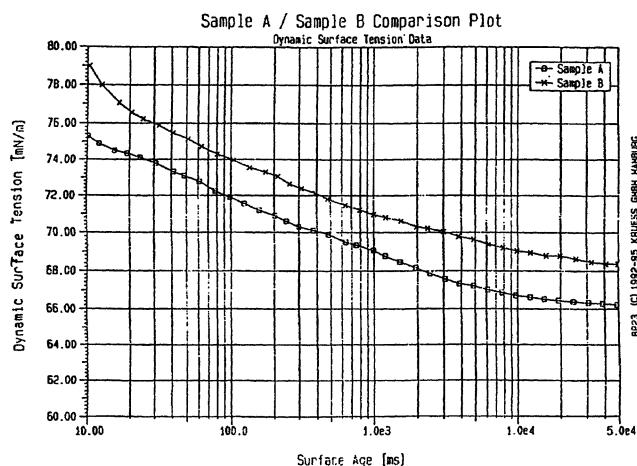


Figure 6. Dynamic surface tension for monodisperse and bidisperse systems.

The dramatic decrease in foaminess was not due to any change in film elasticity or viscosity. Elasticity affects the kinetic stability of foams by impacting liquid drainage from foam films. The greater the elasticity is, the lower the rate of film drainage and the higher the foaminess (Edwards et al., 1991). The surface elasticity of a system is defined as the relative change in surface tension with change in area ($d\sigma/dA$). This is directly proportional to the slope in Figure 6. Every point on the plot corresponds to a particular extent of surface expansion, and has a related slope. The slopes for the monodisperse (denoted as Sample A) and the bidispersed systems (denoted as Sample B) are the same at all points within experimental error. Hence, the systems have the same elasticity. Therefore, change in elasticity does not explain the observed order of magnitude difference in foaminess.

From the classic understanding of the film-thinning process, that is, according to the Reynolds model, drainage velocity $= 2\Delta Ph^3/3\mu R_f^2$. Qualitatively one could expect more viscous solutions (larger μ) to have lower rates of liquid drainage, and, hence, more foaminess. The viscosities of monodisperse and bidisperse systems were measured by a Cannon viscometer. The viscosity of the monodisperse system was found to be 1.94 cP while the viscosity for the bidisperse system was 1.57 cP. The typical Reynolds velocity (dh/dt) of film thinning, calculated at a film thickness of 1 μm , for the mono- and bidisperse systems was about 13 nm/s and 15.6 nm/s, respectively. They are only marginally different. It does not seem reasonable that about a 20% increase in viscosity (from 1.57 to 1.94) can result in a 1,000% increase in foaminess, which is what we observed. Therefore, the difference in viscosity does not explain the observed differences in foaminess.

To understand the reason behind the pronounced difference in foaminess, we studied the thinning of a single lamella made from both monodisperse and bidisperse silica particle suspensions using our capillary force balance.

Single foam-lamella thinning probed by the capillary force balance

Increasing Particle Concentration Decreases Film Thinning. The stability of the foam is influenced by the thinning of the

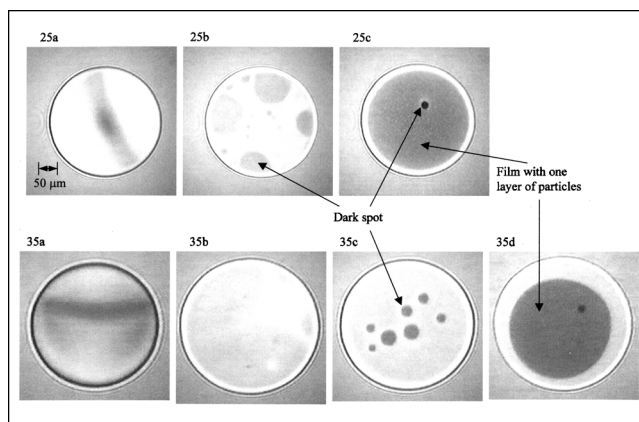


Figure 7. Stepwise film thinning of a film in the presence of 8-nm silica particles at an effective volume fraction = 0.25 (25a, 25b, 25c) and 0.35 (35a, 35b, 35c, 35d).

Total number of step transitions with an effective volume fraction of 0.25 is three and with 0.35 is four.

film separating the bubbles (Chu et al., 1995). The sequences of photomicrographs shown in Figure 7 depict the stepwise film thinning of foam lamella (with a diameter of 350–400 μm) formed from an 8-nm aqueous silica suspension at two concentrations: 5 vol %, and 10 vol %. At these concentrations and foam-lamella size, three and four stepwise thickness transitions, respectively, were observed. The foam lamella with 10 vol % particles also had a longer lifetime than with 5 vol %, as an additional particle layer had to be removed from the film for complete thinning. This correlates well with our observation of increasing foaminess by increasing the particle concentration (Figure 5a). When the film reached a thickness of less than one colloidal particle diameter, the film became unstable and ruptured in a few seconds. This was due to a lack of surface-active agents in our system.

The microscopic observation of the film-thinning phenomenon clearly shows that the stepwise film thinning occurs by the formation of dark spot(s), that is, a thinner film area with a circular shape inside the film (see Figure 7). It has been shown by Kralchevsky et al. (1990), that the formation of the spot is due to the aggregation of the dislocations or vacancies generated inside the film during the film-thinning process. The concentration of the colloidal particle inside the foam lamella is higher than that in the bulk (that is, lamella meniscus region), and when the colloidal particles diffuse into the bulk, dislocations are generated inside the film. At a sufficient concentration of dislocations, vacancies condense locally and the foam lamella decreases in thickness. Figure 8 illustrates the physics of stratification and the mechanism of aggregation of the vacancies inside the film. With an increase in particle concentration, the number of dislocations inside the film decreases and the foam lamella becomes more stable.

Bidisperse System Destabilizes Film Before all Layers have Left the Film. In the process of film thinning, as the film thickness approaches the large-particle diameter, the small particles have a tendency to pin the large particles to the walls (Figure 9a) (Trokymchuk, 2001). This constrains the diffusivity of the large particles in the film, even when the small

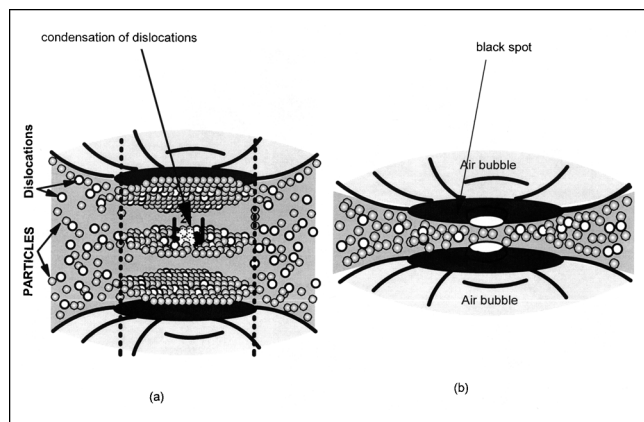


Figure 8. Mechanism of dark-spot formation (a) condensation of dislocations; (b) formation of dark spot.

particles can diffuse freely. Thus, in the last stages of film thinning one can expect that the larger particles will get trapped inside the film as the film thins all around it (Figures 9b, 9c). Such trapped large particles produce regions that are rich in large particles and are devoid of small particles. The local difference in small-particle concentration between the areas rich in large particles and the rest of the foam lamella (Figure 9b) results in differences in osmotic pressure. This sucks the water from the large particle rich region. As a result, the film surface around the large particles bends locally and tries to reduce its thickness (Figures 9c, 9e). The foam lamella at its thinner area is unstable and ruptures (Figure 9d). Based on this physical concept, it is understandable that the stability of the foam lamella is greatly reduced by bidispersity in particle size.

Summary

The influence of hydrophilic colloidal particles on foaminess was investigated. The parameters that affect the foaminess

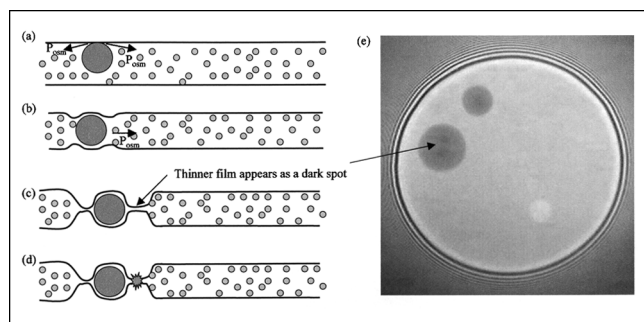


Figure 9. Effect of particle bidispersity on foam-lamella stability.

(a) Osmotic depletion pushes the large particles to the walls; (b) to reduce the osmotic depletion effect, water is sucked from the small-particle-depleted region that bends the lamella; (c) locally the film reduces in thickness (seen as a dark spot in the photograph); (d) the film at the thinner section is unstable and ruptures within a few seconds; (e) microphotograph of spot formation during foam-lamella thinning in a bidisperse suspension.

ness are solid particle concentration, particle size, and polydispersity in particle size. Foaminess studies were complemented by capillary force balance studies, where the stepwise thinning of a single foam lamella was investigated in the presence of a silica particle suspension. It is proposed that in the absence of surface-active agents, foaminess is caused by the colloidal particle self-layering phenomenon inside the confined boundaries of the foam lamella. This kind of colloidal particle self-layering provides a structural barrier against the coalescence of bubbles. The existence of particle layering is corroborated by the observed stepwise-thickness transitions (as depicted by the formation of dark spots), with each transition approximately equal to size of the particle. The strength of the structural barrier is found to be a direct function of the particle concentration. A higher concentration of solid particles leads to a better particle-layered structure inside the film, which is in turn reflected in the higher foam lamella stability and foaminess observed in these systems. It is found that foaminess is inversely proportional to the size of the particles, since a larger size implies a lower effective volume fraction (and smaller particle layering) for a constant geometrical volume fraction. The introduction of a small amount of large particles in a monodisperse system of small particles leads to a drastic reduction in the foaminess. Bidispersity in particle size leads to the local destabilization of the ordered particle structure, resulting in lamella rupture even at high thickness, which is consistent with our theoretical predictions.

Acknowledgments

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