

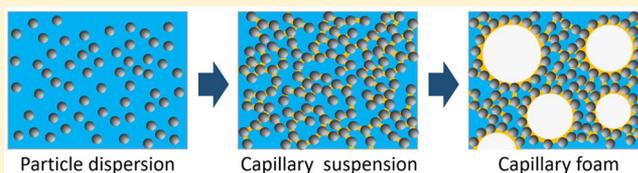
Capillary Foams: Formation Stages and Effects of System Parameters

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Supporting Information

ABSTRACT: Foams are concentrated dispersions of gas bubbles in a continuous liquid phase. They are ubiquitous in nature and familiar from beer, frothed milk, and bubble baths; moreover, they play important roles in industrial applications ranging from petrochemicals to pharmaceuticals, food, and cosmetics. Recently, we reported the discovery of “capillary foams”, a new class of stable foams obtained by frothing a suspension of colloidal particles in the presence of a small amount of oil. In this study, we explored in more detail the formation stages of capillary foams and found that particle networks are formed first, which then entrap the gas bubbles (in this case, air bubbles). We further investigated the influence of particle concentration and wettability on the formation of capillary foams. As the fraction of particles is increased, the foam volume first increases and then reaches a plateau value. Finally, capillary foams were prepared at different oil fractions, using oils with different interfacial properties. Our study shows that oil spreading has a strong effect on both the amount of oil needed to obtain stable foams and on the foam stability. A detailed understanding of the foam formation and the effects of material and process parameters lays a foundation for the targeted development of capillary foams toward future applications, which may range from the fabrication of load-bearing, lightweight porous materials, to enhanced oil recovery, advanced froth flotation, wastewater treatment, and oil spill remediation.



INTRODUCTION

Aqueous foams or froths are a common occurrence of everyday life; they also play important roles in many industrial applications, such as enhanced oil recovery, froth flotation, cosmetics, and food processing. Good foam stability is desirable for most applications.¹ However, all foams are thermodynamically unstable systems due to the large interfacial energy associated with formation of the gas–liquid interface.^{2,3} Therefore, foam stabilizers, such as surfactants, polymers, or proteins, are added to kinetically stabilize foams by slowing down film drainage, bubble coalescence, and coarsening.^{1–4}

Foams can also be stabilized by adsorbing colloidal particles, and the resulting foams, often referred to as Pickering foams, can achieve superior long-term stability.^{5–12} The transfer of particles with appropriate wettability from the liquid bulk to the gas–liquid interface tends to lower the interfacial energy so significantly that the particle attachment is practically irreversible.¹³ As a consequence, any coalescence (merging) of particle-covered bubbles results in an increase of the interfacial particle concentration. Once a sufficiently high interfacial coverage is reached, further coalescence is effectively inhibited, and the resulting foam can be stable for many months. In addition to long-term stability, certain hazardous or allergenic surfactants can be avoided and replaced by environmentally friendly, biorenewable, or even food-grade particles for applications in surfactant-free cosmetics, food technology, and pharmaceutical formulation.^{14–16} More recently, particle-based foams have become popular as precursors and templates for the assembly of novel materials, including microcapsules and lightweight materials.¹⁷ Finally,

particles offer many options to prepare stimulus-responsive foams that form or break based on external fields, chemical or mechanical stimuli.^{18–20} While the breadth of potential applications for Pickering foams keeps growing, the types of available particles to make Pickering foams are limited because of the constraints on particle wettability: aqueous Pickering foams call for particles hydrophilic enough to be dispersible in water yet also hydrophobic enough to adsorb strongly to the air–water interface. Many commercially available particles do not simultaneously meet both of these requirements and therefore fail to stabilize foams. Traditionally, such problems could only be resolved by substituting a different type of particle or by adjusting the particle wettability via surface modification,²¹ which usually involves chemical reactions and solvents and can be expensive, or time-consuming, or cause environmental concerns.

Recently, we discovered a new class of aqueous foams, which we call capillary foams.^{22,23} In these foams, the gas bubbles are stabilized against coalescence by neither surface active molecules (as in classical foams) nor particles adsorbed at the gas–water interface. Capillary foams are obtained by frothing a suspension of colloidal particles in the presence of a small amount of an immiscible oil. In the resulting foams, the bubbles are coated by a particle-stabilized oil film. Moreover, the coated bubbles are immobilized in a three-dimensional network of

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Table 1. Hydrodynamic Radius and Wettability of Silica Particles of Different Hydrophobicity^a

particle (residual silanol)	surface modification	particle hydrodynamic radius (nm) in water	contact angle (deg) at the air–water interface	contact angle (deg) at the TMPTMA–water interface
100%	none	252 ± 19	<10 ^b	18 ± 4
70%	30% methylsilyl	213 ± 2	21 ± 8	27 ± 0
50%	50% methylsilyl	209 ± 4	30 ± 10	42 ± 4
36%	64% methylsilyl	233 ± 13	46 ± 2	62 ± 8

^aIndicated uncertainties represent the standard deviation from at least three independent measurements. ^bThe contact angle of the most hydrophilic (100% SiOH) silica surface with the air–water interface is difficult to measure because the air bubble rolls off the surface easily and the angle is too small for a precise determination.

excess particles connected via oil bridges mediating a capillary attraction between the bridged particles.²²

Since oils have higher polarity than gas phases, water-dispersible particles tend to have a higher affinity to oil–water interfaces than to gas–water interfaces and are therefore often more suitable for stabilizing the oil–water interface in Pickering emulsions or the oil-coated bubbles in capillary foams than the air–water interface of aqueous Pickering foams. The addition of a small amount of oil thus provides a convenient and timesaving alternative to particle surface modification for foam stabilization and greatly broadens the range of suitable particles. The presence of the oil in capillary foams also opens up new options for the engineering of foam properties with potential benefits in diverse areas like food processing, oil recovery, and the development of high-strength porous materials.²³ A targeted development of capillary foams for future applications, however, calls for a better understanding of the foam formation process and of relevant material and process parameters. Previous work²² established two criteria for formation of stable capillary foams: (i) The oil and particles must spread spontaneously at the air–water interface. (ii) The particles must have a sufficiently high affinity for the oil–water interface. Upon the basis of these concepts, a model was developed that predicts the combinations of particles and oils that can form capillary foams based on knowledge of the particle wettability, the packing fraction at the oil–water interface, and the relevant interfacial tensions.²²

In the present study, we explore in detail the formation stages of capillary foams and investigate the influence of particle concentration and wettability. We further varied the amount of oil incorporated in the foam and the type of oil employed, using a chemically diverse set of oils with different interfacial properties. The resulting insights will provide a foundation for the rational design and optimization of capillary foams.

MATERIALS AND METHODS

Materials. Polyvinyl chloride particles (PVC, Vinnolit SA1062/7, average particle size, 14.8 μm, particle density, 1.41 g/cm³) were obtained from Vinnolit, Germany. Wacker-Chemie AG (Germany) provided amorphous fumed silica particles with various degrees of hydrophobicity: 100% SiOH (unmodified), 70% SiOH (30% methylsilyl capped), 50% SiOH (50% methylsilyl capped), and 32–36% SiOH (64–68% methylsilyl capped). The methylsilyl modification was performed by the manufacturer through reaction with dichlorodimethylsilane.^{24,25} Since the partially hydrophobic silica particles (70, 50, and 32–36% SiOH) were not wetted well by DI water, aqueous dispersions were prepared by first dispersing the particles in acetone and then transferring the particles to the DI water using repeated centrifugation and replacement of supernatant. The particle size in water was

measured by dynamic light scattering using a Malvern Zetasizer Nano ZS90. The hydrodynamic radius and wettability of the silica particles are shown in Table 1. Trimethylolpropane trimethacrylate (TMPTMA), silicone oil, and paraffin oil were purchased from Sigma-Aldrich. Surface and interfacial tensions of oils used in this study are shown in Table 2. Ultrapure water with a resistivity of 18.2 MΩ·cm (Barnstead) was used. The pure oil viscosities presented in Table 3 were provided by the manufacturers.

Table 2. Surface and Interfacial Tensions of Oils Used in This Study^a

	γ_{aw}	γ_{ow}	γ_{ao}	S_o
paraffin oil	72.0	49.2	32.9	−10.1
TMPTMA	51.74	18.99	32.86	−0.11
silicone oil	72.0	43.1	19.0	9.9

^aInterfacial tension data of TMPTMA were obtained from ref 29. Here, γ is the equilibrium surface/interfacial tension, where a, o, and w denote the air, oil, and water phases (where the oil and water phases are mutually saturated). S_o is the oil spreading coefficient; all data are in mN/m.

Contact Angle Measurement. Direct measurement of the particle contact angle, for example, by the gel-trapping method,²⁶ freeze–fracture shadow-casting cryo-scanning electron microscopy (FreSCa cryo-SEM),²⁷ or digital holography,²⁸ is challenging for fumed silica particles with a few hundred nanometers and nonspherical shapes. The wettability of these silica particles was therefore assessed in an approximate fashion by measuring the contact angle of an air bubble or an oil droplet in water against a compressed pellet of silica particles. Compressed pellets were prepared using a benchtop laboratory pellet press (Model 4350L, Carver, Inc.) at the applied load of 10 000 lbs for 2 min. The contact angle of compressed pellets was measured in a quartz-cell (filled with water) using a Ramé-Hart goniometer. The pellets were submerged in the quartz cell, and a drop of oil or an air bubble was then deposited with a 22 gauge needle. Images were taken after the sessile drop (or bubble) spread and reached equilibrium. The reported contact angles are always measured through the water phase. This method has been widely employed, possibly because of its relative simplicity. However, contact angle values obtained on compressed pellets are expected to differ slightly from those on a smooth surface of the same solid because of surface roughness. The surface roughness was characterized using AFM (atomic force microscopy) and typical images are shown in the Supporting Information.

Preparation and Characterization of Capillary Foams. Suspensions of particles in water at desired particle fractions were prepared. A small amount of oil (the reported mass percentage of oil is with respect to the water bulk unless

Table 3. Viscosity of Different Oils and the Wettability of PVC Particles at Different Oil–Water Interfaces^a

oil	viscosity (mPa·s)	PVC contact angle (deg) with the oil–water interface
TMPTMA	68.6	28 ± 4
paraffin oil	110–230	111 ± 4
silicone oil	9.3	106 ± 2

^aIndicated uncertainties represent the standard deviation from at least three independent measurements.

otherwise noted) was added to the resulting particle suspension and frothed using a rotor–stator homogenizer (IKA Ultra-Turrax T10, stator diameter of 8 mm and rotor diameter of 6.1 mm) at 30 000 rpm for 1 min or using a commercial hand-held mixer (Rival 5-Speed Hand Mixer) at the maximum speed. The rotor–stator homogenizer was used when we created foams in a small glass vial and investigated the effect of particle concentration, particle wettability, oil type and oil fraction, while the hand-held mixer was used when we created foams in a large beaker and investigated the formation stages of capillary foams. The wet foam was characterized by monitoring initial foam volume and stability, which was assessed by monitoring foam height over time at ambient temperature.

RESULTS AND DISCUSSION

Formation Stages of Capillary Foams. Previous studies have demonstrated that capillary foams can be prepared by frothing a particle suspension in the presence of a small amount of oil.^{22,23} Two primary structures are known to distinguish capillary foams from surfactant-stabilized and Pickering foams. Interconnected particle networks, stabilized by capillary or pendent oil bridges between the particles, span the space between bubbles, thus reducing bubble mobility. Moreover, particles and a thin oil film jointly cover the bubble surfaces and contribute crucially to the bubble stabilization²² (Figure 1).

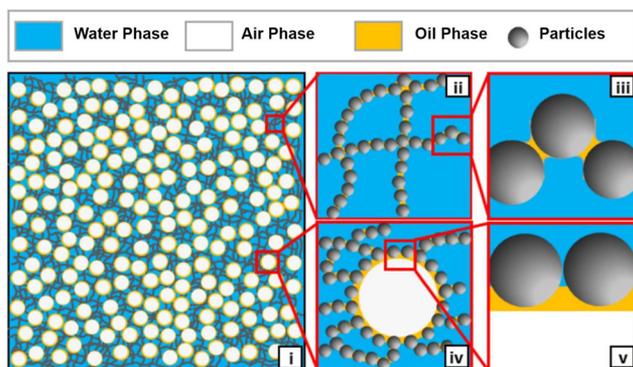


Figure 1. Structure of capillary foams. The system contains a continuous water phase, a gas phase, an oil phase, and particles (i). The agitation of the mixture results in a space-spanning network of particles in water (ii) connected by oil bridges (iii), with air bubbles embedded in the network (iv) via a joint adsorption of particles and a thin oil film (v).

However, we do not know whether the particle network formation precedes or follows the coating of bubbles in a composite film of oil and particles or whether these two processes occur simultaneously.

To address this question, we studied the formation stages of capillary foams prepared with PVC particles in the presence of a small amount of oil. PVC particles were suspended in water at a particle concentration of 10 wt %. Next, 1 wt % TMPTMA was added as the oil phase. Mechanical frothing of this mixture for 4

min generated a large amount of foam (Figure 2a). Frothing for only 40 s, by contrast, does not produce a substantial foam head; but as the center micrograph in Figure 2a suggests, a space-spanning network of liquid-bridged particles and particle clusters can be observed at this stage, i.e., a capillary suspension^{30–35} has formed. Figure 2a demonstrates that during capillary foam formation particle networks are formed before stable bubbles can be seen to accumulate. Analogous tests were carried out using the combinations of the same PVC particles with either paraffin oil or silicone oil (Figures 2b,c). They support the same qualitative conclusion that the particle networks are formed first and then the (coated) air bubbles become entrapped in the particle network (Figure 2d). Interestingly, the formation of the foam overall and even of the intermediate particle network is faster for silicone oil than for the other two oils (TMPTMA and paraffin oil). It thus appears that the contact between particles and the bridging oil droplets is established fastest in the case of silicone oil, which may indicate a difference either in the driving force for oil–particle wetting, indicated by the contact angle, or in the viscous resistance (or in both). To better understand this, we measured the PVC contact angle at different oil–water interfaces by placing an oil droplet against a pressed tablet of PVC particles immersed in water (Table 3). The measured contact angle is a little different from our previous measurement using the gel-trapping method,²² but it should serve as a rough guideline here. As Table 3 shows, silicone oil is found to have a contact angle with the PVC surface and water similar to that of paraffin oil, which does not support the notion of a particularly strong driving force for particle wetting by silicone oil. This oil does, however, have the lowest viscosity by far of the sampled oils (Table 3), and the associated low resistance to dynamic changes in the droplet shape and wetting configuration thus offers the most plausible explanation for the fast network and foam formation observed with silicone oil as the minority liquid.

Mechanical frothing of a particle suspension (Figure 3a) in the presence of a small amount of oil is expected to generate air bubbles and oil droplets throughout the suspension (Figure 3b). One might expect that the particles in the suspension could at this point adsorb directly to the air–water interface, forming particle-coated bubbles (Figure 3c). However, the contact angle of PVC particles in the air–water interface is below 30°,²² which points to a low thermodynamic affinity for this interface. Moreover, particles approaching the air–water interface would likely face a larger kinetic barrier to adsorption than particles approaching the oil–water interface because the van der Waals interaction across water between particles and air is repulsive whereas that between particles and oil is attractive. Experimentally, neither particle-stabilized bubbles nor discernibly large particle-stabilized oil droplets were observed. For the case of silicone oil with its positive spreading coefficient, the encounter of bubbles and oil droplets would be expected to yield oil-engulfed bubbles,³⁶ which should not be colloiddally stable in the absence of adsorbed particles; however, oil-coated

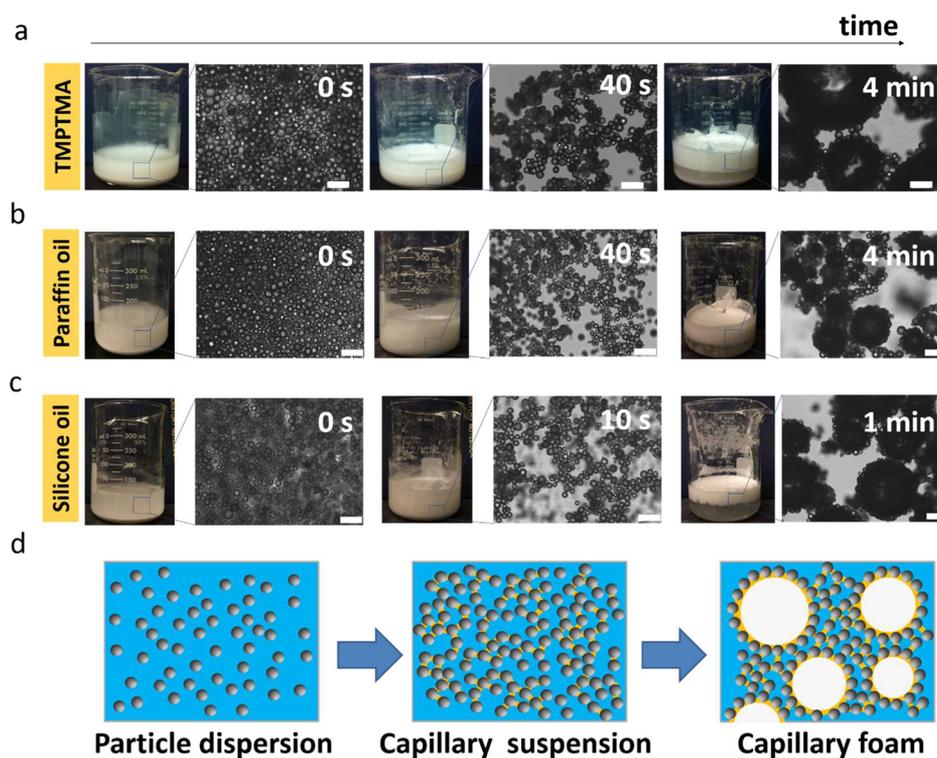


Figure 2. Formation stages of capillary foams. Photographs and corresponding microscope images of PVC particle suspension in the presence of 1 wt % (a) TMPTMA, (b) paraffin oil, and (c) silicone oil during several stages of frothing. Scale bars are 110 μm . (d) Schematic illustration of suspension morphologies during formation of capillary foams.

bubbles with or without particles were not observed initially (Figure 3e). Instead, observations exemplified by the micrographs in Figure 2 clearly suggest that the PVC particles employed here, when combined with oils of rather different interfacial properties (Table 2), preferentially form networks of oil-bridged particles characteristic of water-continuous capillary suspensions.^{30–35} In a previous study, we concluded that the connection of particle networks by oil bridges is not by itself sufficient to entrap bubbles in a stable foam; moreover, stable capillary foams also require the particle-assisted spreading and stabilization of an oil coat around the bubbles.²² Here, we identify the network formation as the first step observed in the foam formation process.

Effect of Particle Concentration. Particle concentration has been found to have a strong effect on the formation and stability of Pickering foams and emulsions.^{37,38} We investigated the role of particle concentration in capillary foams and found a pronounced effect on foamability. The PVC particle concentration was varied in the range of 5–40 wt %, as shown in Figure 4. In all of the capillary foams prepared here, the oil phase was TMPTMA and its amount was kept constant at 1 wt %. As the fraction of particles increased from 5 to 20 wt %, the foam volume increased. However, upon a further increase of the particle concentration to 30 or 40 wt %, the suspension became solid-like; thus, it was difficult to disperse and entrap gas bubbles. This was indicated by solid, nonflowing suspensions without significant presence of bubbles, in Figure 4. These results suggest that as the number of available particles in the bulk phase initially increases up to 20 wt % gas bubbles are incorporated into a tenuous network of particles connected by oil bridges. However, beyond a particle fraction of 30 wt %, the increasingly solid-like gelled suspensions were too viscous to allow the generation of bubbles by using mechanical

frothing. Photographs of capillary foams stabilized with different concentrations of PVC particles after 5 months are shown in Figure 4b, indicating the stability of the capillary foams.

Effect of Particle Wettability. The wettability of particles is crucial for the preparation of stable capillary foams.^{22,23} To study the influence of particle wettability on the formation of capillary foams, a series of dichlorodimethylsilane-modified silica particles with systematically varied hydrophobicity, were used ranging from completely hydrophilic (100% SiOH) to partially hydrophobic (32–36% SiOH). We also compared the foamability of foams stabilized only by particles (Pickering foams) to foams stabilized by both particles and oil (capillary foams). In all capillary foams, the oil phase was TMPTMA, kept constant at 1 wt %, and the particle concentration was 3 wt % (Figure 5). In all Pickering foams, the particle concentration was also kept constant at 3 wt %. For foams stabilized only by particles (Pickering foams), the most hydrophilic particles, 100 and 70% SiOH, cannot stabilize foam bubbles that form during frothing. With further increase of particle hydrophobicity to 50 and 32% SiOH, air bubbles are stabilized, and the foam volume increases progressively with the increase of particle hydrophobicity. The maximum initial foam volume was achieved for the most hydrophobic particles with 32% SiOH (Figure 5). This is consistent with our measurements of the silica contact angle with the air–water interface: As the wettability of the solid is varied from hydrophilic (100% SiOH) to hydrophobic (36% SiOH), the contact angle increases and gets closer to 90°, which means the affinity of particles to the air–water interface increases. Thus, air bubbles are increasingly well-stabilized by the particles.¹⁵

The addition of a small amount of oil (1 wt %) to even the most hydrophilic particles (100 and 70% SiOH) enables the

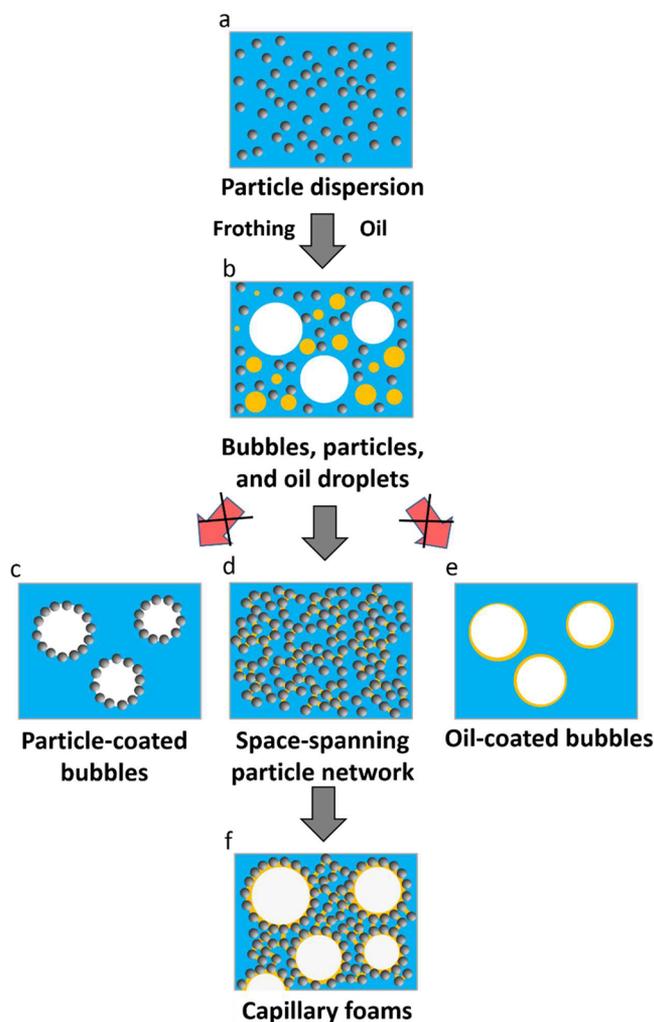


Figure 3. Possible formation stages of capillary foams. (a) Particle dispersion. (b) Mixture of generated air bubbles, oil droplets, and particles in water. (c) Particle-coated bubbles. (d) Space-spanning particle network in a capillary suspension. (e) Oil-coated bubbles. (f) Capillary foams.

formation of stable foams. In capillary foams, oil spreads on bubble surfaces, and the original air–water interface is replaced with air–oil and oil–water interfaces.²² Since oil is more polar than air, hydrophilic silica particles have a stronger affinity to the oil–water interface in capillary foams than to the air–water interface in Pickering foams. For capillary foams, the initial foam volume increases progressively with the increase of particle hydrophobicity from 100 to 50% SiOH (Figure 5). The initial foam volume drops slightly with a further increase of particle hydrophobicity to 32% SiOH, while contact angle measurements suggest that foam stability should keep increasing (Figure 5). This should not necessarily be surprising, since there is no compelling reason to expect a perfect correlation between the initial foam volume and foam stability (or contact angle).

Effects of Oil Type and Fraction. We have established that stable capillary foams can be prepared using particles of different wettability and a small amount of oil, whose wetting behavior also allows for some variation. One question that has not yet been answered concerns the amount of oil needed to produce stable capillary foams and how this oil demand depends on the type of oil chosen. To answer this question, we

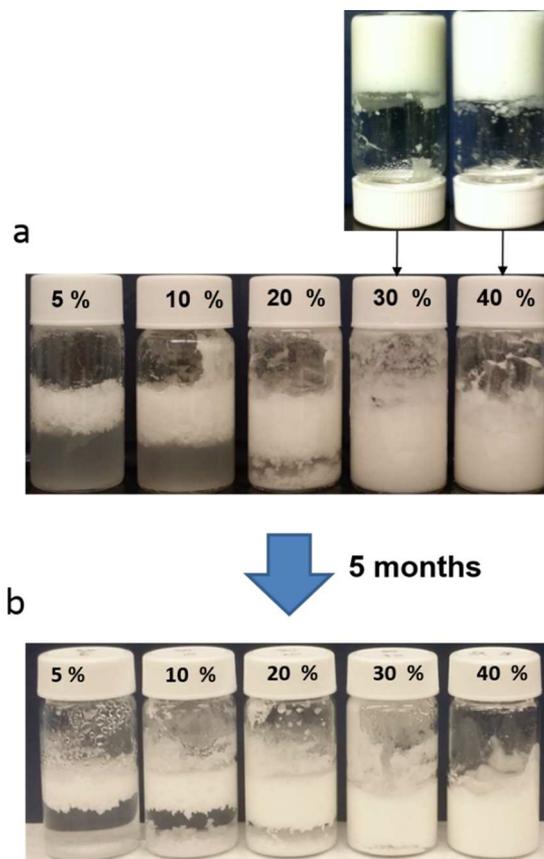


Figure 4. Photographs of capillary foams stabilized with different concentrations of PVC particles. The photograph was taken (a) initially and (b) 5 months after preparation. The upside-down vials are solid-like capillary suspensions.

prepared capillary foams with oils of different interfacial properties and at varied oil concentrations. The interfacial properties of the oil phase can be distinguished by the spreading coefficient of the oil at the air–water interface. Three types of oils, paraffin oil, TMPTMA, and silicone oil, were used in this study. The spreading coefficients of paraffin oil, TMPTMA, and silicone oil are -10.1 , -0.11 , and 9.9 mN/m, respectively (Table 2). For PVC particle suspensions, we varied the amount of oil from 0.025 to 5 wt % (Figure 6). For low oil concentrations, excess particles are seen to form a sediment at the bottom of the container, whereas at high oil concentrations, no such sediment is found. The drained water phase below the foam becomes clearer from left to right, suggesting that an increase in oil content leads to the incorporation of more particles in the foam head as one might expect. Similarly, at a fixed oil concentration, the spreading coefficient of the oil appears to correlate positively with the extent of particle incorporation in the foam. Samples with silicone oil as the oil with the highest spreading coefficient display the smallest particle sediment at low oil content and the clearest water phase at high oil content. Photographs of foams after 5 months, shown in Figure 6b,d,f, further indicate a difference in long-term foam stability: In the foams stabilized with paraffin oil ($S_o = -10.1$ mN/m), some foam degradation is observed after 5 months, and particles or particle aggregates settle on the bottom of the container. Figure 6 suggests that while capillary foams can be prepared with oils of very different spreading

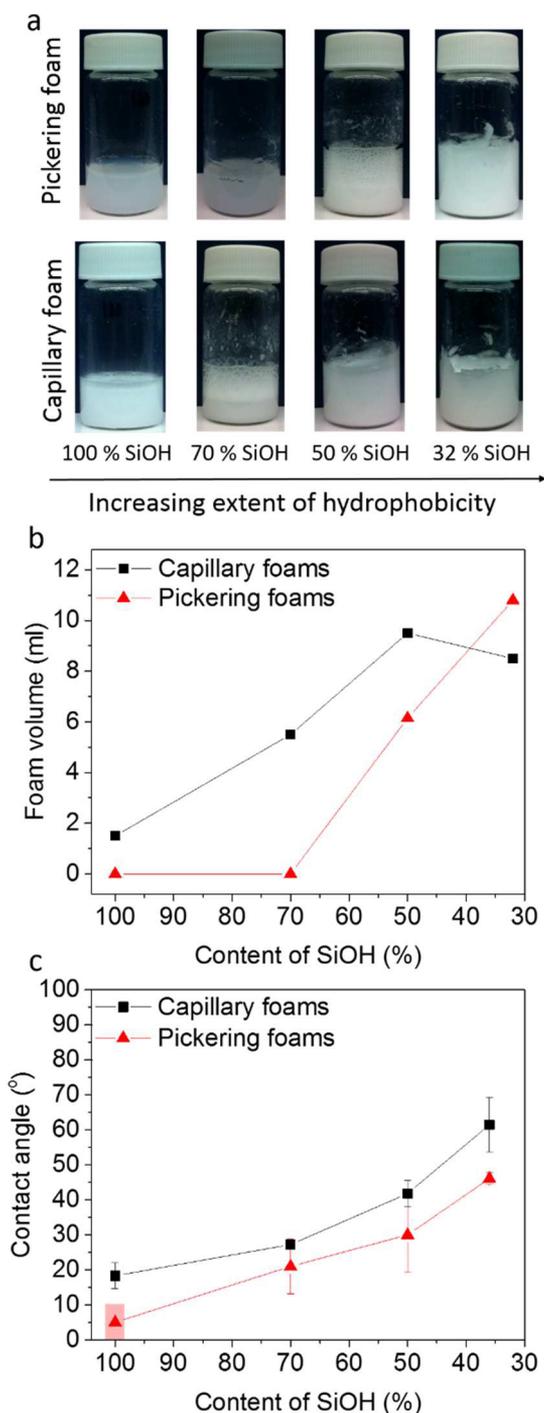


Figure 5. Effect of particle hydrophobicity on the formation of Pickering and capillary foams. (a) Photographs of foams prepared by using particles with various hydrophobicity. (b) Initial foam volume as a function of particle wettability. (c) Silica contact angle with the air–water interface and oil–water interface as a function of silica wettability. For reasons of availability, the most hydrophobic particles (32% SiOH) used in the foaming experiments (a, b) were substituted by very similar but slightly less hydrophobic particles (36% SiOH) in the contact angle study (c).

characteristics at the air–water interface a higher oil spreading coefficient may provide benefits for foaming ability.

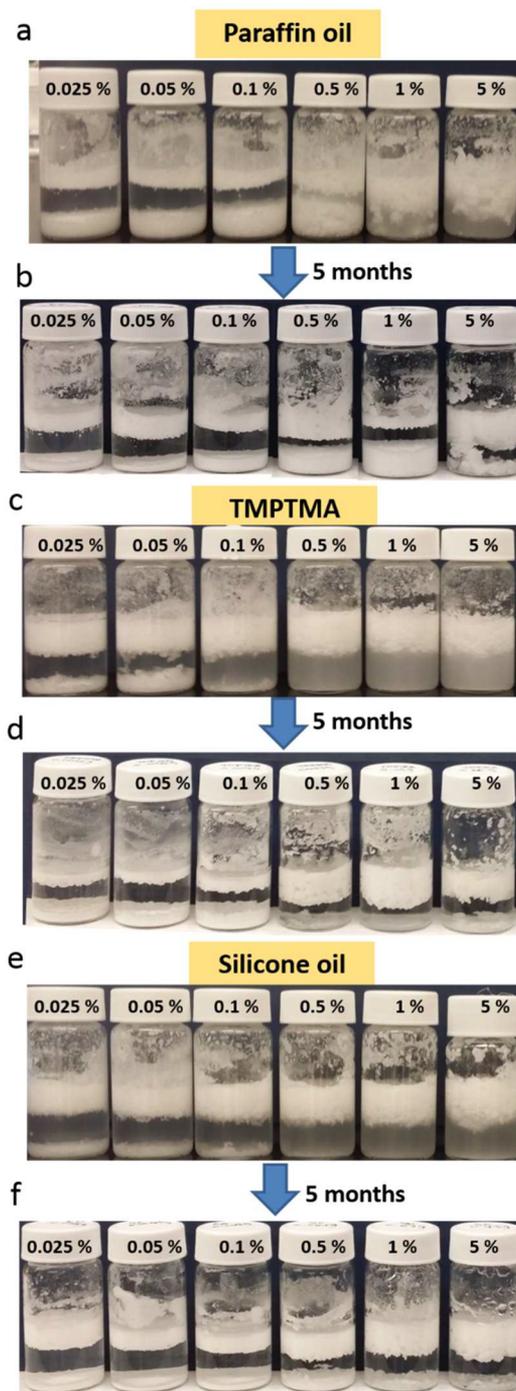


Figure 6. Effects of oil type and oil fraction on the formation and stability of capillary foams. Capillary foams prepared with 10 wt % PVC particles in the presence of (a) paraffin oil, (c) TMPTMA, and (e) silicone oil. (b, d, f) Appearance of the foams after 5 months. The equilibrium spreading coefficients S_o of paraffin oil, TMPTMA, and silicone oil are -10.1 , -0.11 , and 9.9 mN/m, respectively.

CONCLUSIONS AND OUTLOOK

In this study, we examined the formation stages of capillary foams and found that upon frothing particle networks are first formed which can then entrap gas bubbles. In addition, we have systematically investigated the influence of the particle concentration and wettability on the preparation of capillary foams. As the particle concentration was increased, the foam volume first increased and then reached a plateau where the

system became too viscous to readily accommodate air bubbles. Finally, to illustrate the effects of oils, capillary foams were prepared using a set of oils with markedly different interfacial properties. Capillary foams can be prepared with a diverse set of oils. The spreading coefficient of the oil for the gas–water interface appears to correlate positively with the foamability. Understanding the foam formation and the effects of material and process parameters lays the foundation for the targeted development of capillary foams toward future applications, which may range from the fabrication of load-bearing, lightweight porous materials to enhanced oil recovery, advanced froth flotation, wastewater treatment, and oil spill remediation.

■ ASSOCIATED CONTENT

Supporting Information

The Supporting Information is available free of charge on the ACS Publications website at DOI: 10.1021/acs.iecr.7b02180.

Particle pellet surface roughness characterization, contact angle measurement, characterization of particle morphology before and after the homogenization process (PDF)

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Notes

The authors declare no competing financial interest.

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