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Surface Chemistry

Stabilization of Liquid Foams through the Synergistic Action of Particles and an Immiscible Liquid**

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Abstract: *Liquid foams are familiar from beer, frothed milk, or bubble baths; foams in general also play important roles in oil recovery, lightweight packaging, and insulation. Here a new class of foams is reported, obtained by frothing a suspension of colloidal particles in the presence of a small amount of an immiscible secondary liquid. A unique aspect of these foams, termed capillary foams, is the particle-mediated spreading of the minority liquid around the gas bubbles. The resulting mixed particle/liquid coating can stabilize bubbles against coalescence even when the particles alone cannot. The coated bubbles are further immobilized by entrapment in a network of excess particles connected by bridges of the minority liquid. Capillary foams were prepared with a diverse set of particle/liquid combinations to demonstrate the generality of the phenomenon. The observed foam stability correlates with the particle affinity for the liquid interface formed by spreading the minority liquid at the bubble surface.*

Liquid foams occur both in nature and in many commercial products and processes, including pharmaceutical formulation, food processing, waste water treatment, construction materials, and cosmetics.[1–3] Dried foam materials are widely used to fabricate thermally insulating materials[4] and low-weight structures, as well as in tissue engineering. Long-term stability in the liquid state is desirable for many foam-based systems, but often difficult to achieve. All foams are thermodynamically unstable because of the surface tension of the liquid and will separate into two distinct phases given enough time.[5] Therefore, stabilizers such as surfactants are commonly added to kinetically stabilize foams. Foam bubbles can alternatively be stabilized by adsorbing colloidal particles,[5–10] and the resulting “Pickering foams” can have superior long-term stability. Often, however, solid particles of a given material do not have the required wettability to stabilize gas bubbles. In that case, particle-stabilized foams can only be achieved by using a different type of particle or by adjusting the particle wettability through surface modification.[11,12]

Here, we report a new type of foam material (“capillary foams”) that dramatically expands the range of viable particles for foam stabilization, and in which gas bubbles are stabilized by the combined action of particles and a small amount of an immiscible secondary liquid. Our study focused on water-based foams with different oils as the secondary liquid. The presence of a small amount of oil led to stable foams, even when the particles could not stabilize foam bubbles by themselves (Figure 1). In the absence of oil, mechanical frothing of an aqueous suspension of polyvinyl chloride particles produced only a very small foam head, and this foam disintegrated within 24 h. However, if as little as 0.5 wt% (with respect to the water bulk) of photopolymerizable oil trimethylolpropane trimethacrylate (TMPTMA), paraffin oil, or diisononyl phthalate (DINP) was added to the particle suspension prior to frothing, a large amount of foam was formed, which showed no significant degradation over several weeks (Figure 1b). Similar behaviour was observed for other types of particles (modified cellulose, modified silica, and glass, see the Supporting Information). This synergy of oil and particulate foam stabilizers is remarkable because oils are usually considered detrimental for foam stability,[13,14] and are commonly used as defoaming agents.[15,16]

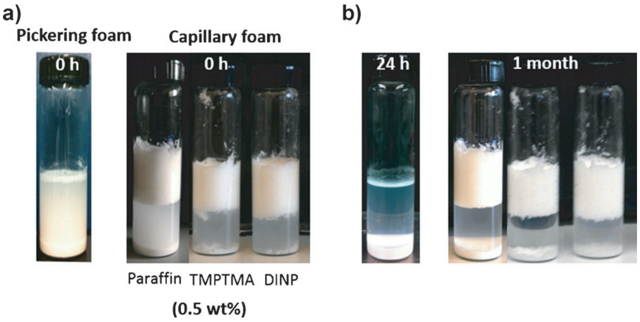

Figure 1. Stable foams requiring both particles and a secondary liquid. a) Attempts of producing a foam through frothing in the presence of PVC (Vinnolit SA 1062/7) particles only (14.16 wt%, Pickering foam), and a combination of both particles and a secondary liquid (14.16 wt% total, including 0.5 wt% of the secondary liquid, i.e. paraffin, TMPTMA, or DINP). b) Photographs of the same samples after 24 h or 1 month.

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We have prepared capillary foams with water as the bulk liquid (primary liquid) and air as the bubble phase, varying the "oil" (secondary liquid) and the particle type in a study covering a variety of particle sizes, shapes, and wettabilities (see Figures S1 and S7 and Table S2 in the Supporting Information). Oils that were explored include TMPTMA, paraffin, and DINP, and the particles that were studied include polyvinyl chloride (PVC) of different size and wettability (Vinnolit SA 1062/7 and Vinnolit P70F), polyethylene (PE), modified silica (aerosol 200), monodisperse silica spheres (SS03N), glass, aluminium oxide, and modified cellulose.

Figure 2 a–j shows SEM images of a dried capillary foam with TMPTMA as the oil (Sigma–Aldrich, treated with Al_2O_3 to remove inhibitor, and enriched with 5 wt% of the photoinitiator benzoin isobutyl ether) and either PE particles, PVC 1062/7 particles, or glass particles. Figure 2 k–m shows the location of the (dye-labelled) oil in the corresponding wet foams, as seen by confocal microscopy.

Figure 2 d–f and k–m suggests an accumulation of oil around the bubble surfaces. On the other hand, small oil bridges also connect the particles in the bulk suspension between the bubbles (Figure 2 h–j) to form a particle network. Such networks of particles connected by oil bridges are held together by capillary forces, much like the water-bridged grains of sand in a sand castle, and were already reported in 2011 for bubble-free particle suspensions that form a gel when mixed with a small amount of an immiscible liquid.[17,18] In capillary foams, the particle network appears to provide a matrix that connects and immobilizes the (particle- and oil-decorated) bubbles. We surmise that this particle network also contributes to foam stability against bubble coalescence by hindering liquid drainage. Nonetheless, the formation of particle networks in the liquid bulk does not by itself guarantee effective bubble stabilization. Figure 3 a shows a failed attempt at producing a stable capillary foam using hydrophilic silica particles and TMPTMA, a particle/oil combination that leads to networks of oil-bridged particles (Figure 3 b,c). Frothing of this suspension in the presence of oil produced no significant foam head.

We propose that the synergistic adsorption of particles and oil around the gas bubbles bears strong resemblance to the phenomenon of "particle-assisted wetting" of a macroscopic air–water interface by a drop of oil that would be

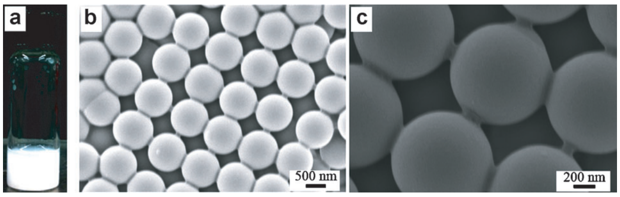

Figure 3. Network formation without foam stabilization. a) Failed attempt of producing a capillary foam from a silica particle suspension (2 wt%) in the presence of secondary liquid TMPTMA (3 wt%, with respect to the amount of bulk phase water). b,c) SEM images of a dried silica particles suspension. The secondary liquid was solidified by photopolymerization prior to water removal.

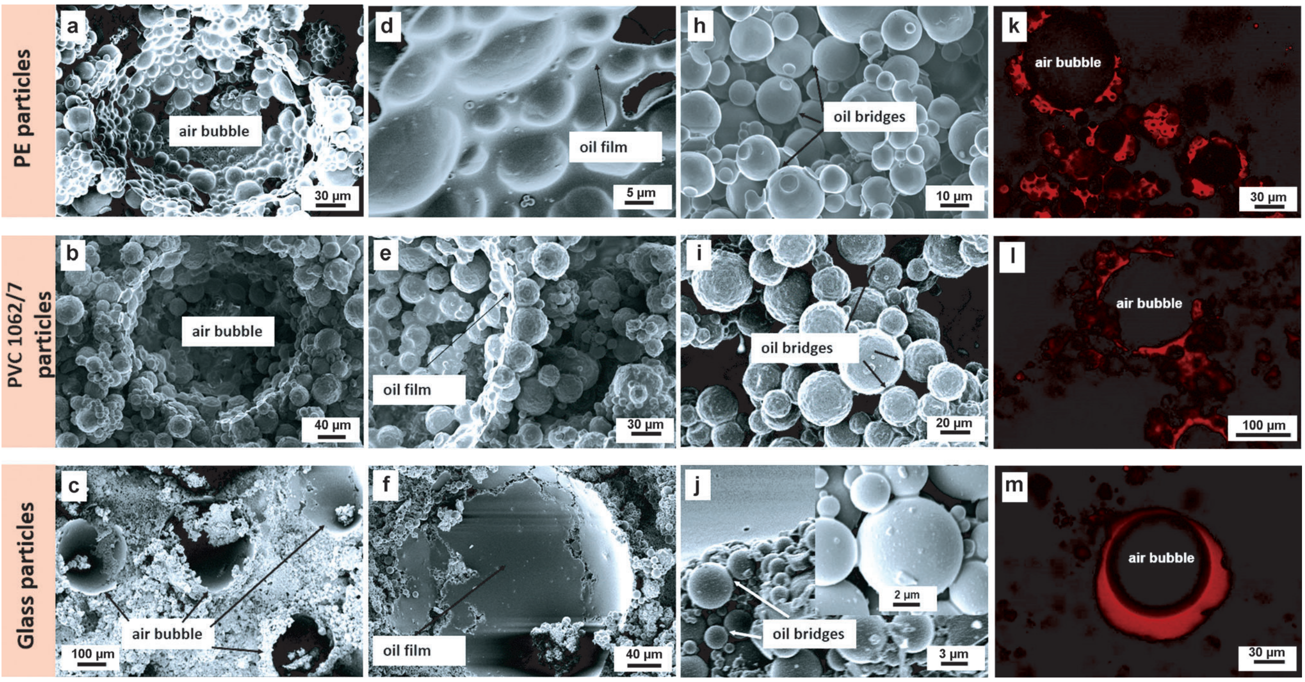

Figure 2. Combined adsorption of particles and secondary liquid at bubble surfaces of a capillary foam. a–c) SEM images of a dried capillary foam formed by addition of gas bubbles and 1 wt% TMPTMA as the secondary liquid to suspensions of PE or PVC Vinnolit 1062/7 or glass particles in water with a solids loading of 10 vol.%. The secondary liquid was first solidified by photopolymerization, and then the water was removed by drying. d–f) Close-up of particles and polymerized secondary liquid surrounding a gas bubble. h–j) Network of particles and polymerized secondary liquid bridges in the aqueous suspension bulk. k–m) Confocal microscope image of the wet capillary foam with the secondary liquid TMPTMA labelled by Nile red.

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nonwetting in the absence of particles.[19,20] This requires that particles adsorb at the oil–water interface (Figure 4b, case 1) or the oil–air interface (Figure 4b, case 2), or both, rather than at the air–water interface as in a classical Pickering foam.

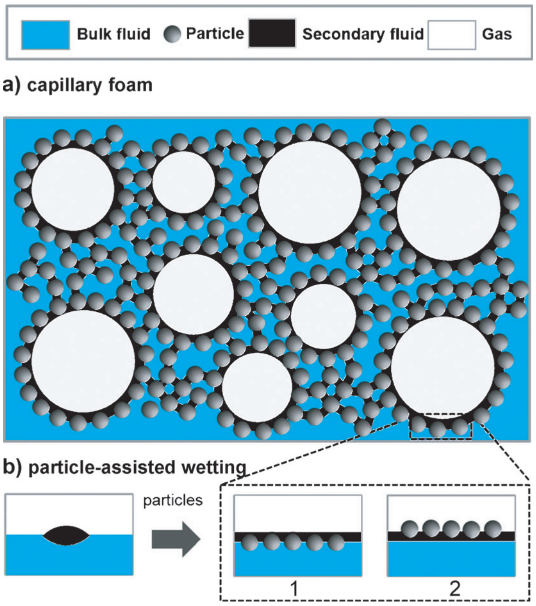

Figure 4. Schematic illustration of capillary foams. a) In capillary foams, suspension particles and the secondary liquid jointly adsorb at the interface of gas bubbles. The decorated bubbles are further entrapped in a network of excess particles in the primary liquid bridged by a secondary liquid. b) Particles adsorbing preferentially at an interface of the secondary liquid can mediate the spreading of a secondary liquid film around the gas bubbles, in direct analogy to the "particle-assisted wetting" of a macroscopic air–water interface by a drop of oil. Depending on their wetting properties, the particles can adsorb at 1) the oil–water interface, or 2) the oil–air interface (or both).

Which of these interfaces experiences particle adsorption depends on the particle wettability. The effect can be explained by the net reduction in interfacial free energy arising from the adsorption of particles at the newly formed oil–water or oil–air interface: spreading of the oil in the presence of particles becomes thermodynamically favorable for positive values of an "effective spreading coefficient" given by:

$$S_{\mathrm{eff}} = S_{\mathrm{o}} - \frac{n_{\mathrm{p}}}{A}\Delta G \qquad (1)$$

Here $S_{\mathrm{o}} = \gamma_{\mathrm{aw}} - (\gamma_{\mathrm{ow}} + \gamma_{\mathrm{ao}})$ is the spreading coefficient of the oil (as commonly defined), accounting for the energy change upon replacing the air–water interface by an oil–water and air–oil interface with respective tensions γ_{ow} and γ_{oa}, A is the total surface area of the bubbles, n_{p} is the number of particles adsorbed at the oil–water interface (Figure 4b, case 1) or the air–oil interface (Figure 4b, case 2), and ΔG is the average free energy change associated with a particle adsorption event, given by:[21]

$$\Delta G_1 = -\pi R^2 \gamma_{\mathrm{ow}} (1 + \cos\theta_{\mathrm{wop}})^2 \qquad (2)$$

for adsorption at the oil–water interface and by:

$$\Delta G_2 = -\pi R^2 [\gamma_{\mathrm{oa}}(1 + \cos^2\theta_{\mathrm{aop}}) + 2(\gamma_{\mathrm{ow}}\cos\theta_{\mathrm{wop}} - \gamma_{\mathrm{aw}}\cos\theta_{\mathrm{awp}})] \qquad (3)$$

for adsorption at the air–oil interface, where R denotes the average particle radius, θ_{wop}, θ_{aop} are the equilibrium contact angles of the particle with the oil–water and air–oil interface as measured through the oil phase, and θ_{awp} is the contact angle at the air–water interface, measured through the water phase. This description neglects effects of bubble curvature and accounts for particle interaction only indirectly through the bubble coverage (see the Supporting Information for more details).

We obtained estimates for the effective oil spreading coefficient in our capillary foams from Equations (1)–(3) with measured values for the surface and interfacial tensions γ_{ij} and for the particle contact angles θ_{ijp}, assuming an interfacial particle packing density (area fraction) $\phi = \pi R^2 n_{\mathrm{p}}/A$ of 70% based on a crude estimate from microscopic observations. Results for the oil/particle combinations of our study are shown in Figure 5a, which also indicates the experimentally achieved foam stability. All studied systems that produced stable capillary foams upon frothing have a positive effective spreading coefficient and are thus expected to experience oil

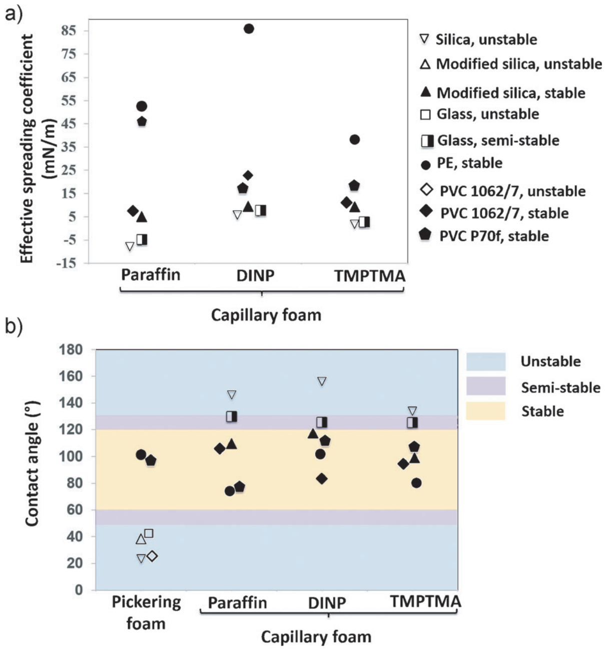

Figure 5. The effective oil spreading coefficient S_{eff} (a) and the equilibrium particle contact angle (b) at the air–water interface for Pickering foams and at the oil–water interface for capillary foams from a variety of particle/oil combinations. Full markers are used for systems that produce stable foam heads upon frothing, open markers denote patently unstable systems, and the half-open marker ("semi-stable") is used for systems developing only a very small, albeit durable, foam head and a large sediment of particles not participating in bubble stabilization. The standard spreading coefficients S_{o} of paraffin oil, DINP, and TMPTMA are $-10.17\ \mathrm{mN\,m^{-1}}$, $5.74\ \mathrm{mN\,m^{-1}}$, and $-0.11\ \mathrm{mN\,m^{-1}}$, respectively.

spreading around the air bubbles. Conversely, however, the successful spreading of the oil, either by itself ($S_o > 0$) or with the help of particles ($S_{eff} > 0$), does not guarantee good foam stability (Figure 5a). Just like oil droplets in a Pickering emulsion, the oil-coated bubbles in a capillary foam need to be stabilized by particles with a strong tendency to adsorb at the oil–water interface (the outer interface for capillary foams), where they can serve as a mechanical barrier to coalescence. The particle affinity to this interface is characterized by the contact angle θ_{wop}; it is maximal for angles close to 90°.[22]

The data shown in Figure 5b illustrate the importance of the contact angle for foam stability. In our experiments, particles with a strong affinity to the outer interface (contact angle in the range from 60° to 120°) all yielded foams that remain intact for weeks or months. Particles with intermediate contact angles from 120° to 130° stabilized only a small amount of foam, and most of these particles formed a sediment instead of participating in foam stabilization. Particles with a weak affinity to the outer interface (contact angle below 50° or above 130°) led to unstable foams that disintegrated within one or two days.

The hydrophilic PVC particles used in the foaming experiments of Figure 1 represent a case in point: their contact angle with an air–water interface mimicking the bubble surface in a classical Pickering foam is below 30° (Figure 6a), which points at a low affinity for the interface and explains their poor performance as a Pickering foam stabilizer (Figure 1). By contrast, the same particles form contact angles near 90° with oil–water interfaces (Figure 6b–d) mimicking the outer interface of oil-coated bubbles in the stable capillary foams of Figure 1.

In summary, we have reported a new class of liquid foams in which gas bubbles are stabilized by the synergistic action of particles and a small amount of an immiscible secondary liquid. The particles can promote spreading of the minority liquid around the gas bubbles, and the stabilization of the newly formed liquid–liquid interface may be easier for liquid-dispersible particles than the gas–liquid interface of a classical Pickering emulsion. The practical implications of this finding are significant: particle-stabilized aqueous foams play a role in many industrial processes, but the particle wettability requirements for bubble stabilization have so far severely limited the choice of particle stabilizers. The addition of a small amount of oil provides a convenient and timesaving alternative to surface modification and greatly broadens the range of suitable particles. Tuning and functionalization options afforded by the combined presence of particles and a secondary liquid in capillary foams make these materials extremely versatile, with expected applications ranging from drug delivery to oil recovery.

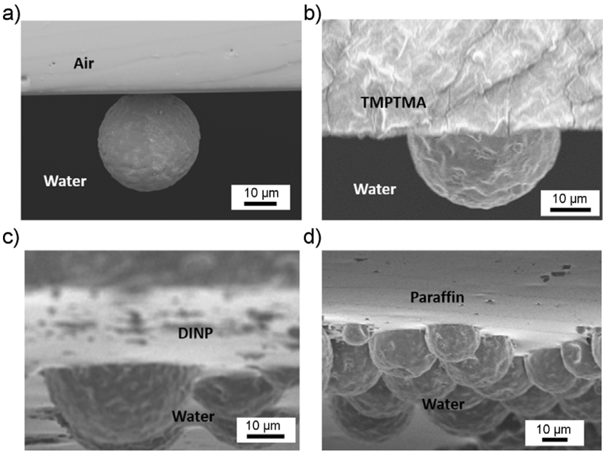

Figure 6. SEM images of PVC particles trapped in the PDMS replica of a macroscopic air–water interface (a) and of several oil–water interfaces (b–d) using the gel trapping technique (experimental details are given in the Supporting Information). The visible part of the particle originally resided in the water phase.

Experimental Section

A suspension of particles in water as the primary liquid was obtained by initially dispersing the particles through sonication; then a small amount (0.5–3.0%) of immiscible secondary liquid was added. The resulting suspension was frothed using a rotor-stator homogenizer (IKA UltraTurrax T10, stator diameter of 8 mm and rotor diameter of 6.1 mm) at 30000 rpm for 1 min (3 × 20 s with 20 s rest periods). The wet foam was characterized with respect to foam stability. The foam stability was assessed by monitoring foam height over time at ambient temperature. Confocal laser scanning microscopy (CLSM) was performed using a Zeiss LSM 510 VIS confocal microscope. Nile red (0.01 wt%) was used as a staining agent for the oil phase using excitation at 543 nm and emission above 560 nm. The wet foam containing TMPTMA was settled by exposure to UV light (Spectro-Line Longlife Filter, wavelength 365 nm) for 2 h and then dried in the oven at 70°C for 16 h. SEM images of gold-coated surfaces were taken using a Zeiss Ultra60 field emission scanning electron microscope (FE-SEM; Carl Zeiss Microscopy, LLC North America, Peabody, MA) operated at an accelerating voltage of 5 kV.

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