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Switchable Emulsions

Switchable Pickering Emulsions Stabilized by Silica Nanoparticles Hydrophobized In Situ with a Switchable Surfactant**

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Interest in switchable surfactants has been growing over the past few years.[1–13] As a switchable surfactant can undergo fully reversible interconversions between active and inactive forms, it is possible to recover and re-use the surfactant afterwards and to easily remove it from product streams by switching it to the form that is least soluble in the relevant medium. These characteristic properties make switchable surfactants sustainable chemicals and simplify many practical processes that involve such compounds, such as fuel production, oil transport, and emulsion polymerization, where, for example, the emulsions need to be stabilized only temporarily and have to be demulsified at the end.

Nevertheless, the viability of a switchable surfactant is distinctly affected by the nature of the trigger. To date, a variety of triggers have been developed that typically employ electrochemical[1–5] or photochemical approaches.[6–10] The former are based on the addition of oxidants, reductants, or acids/bases, and these methods suffer from economic and environmental costs and the potential of product contamination or modification by the additives. Photochemical approaches, however, avoid the addition of chemicals, but may be hindered by the opacity of emulsions and foams that contain the surfactant. Jessop and co-workers[11–13] have reported a switchable surfactant that employs a CO_2/N_2 trigger, wherein the hydrophobic long-chain alkyl amidines (inactive) can be protonated to become water-soluble surfactants upon the addition of CO_2 in aqueous media, and the amidinium ions (active) can then be deprotonated by bubbling N_2 or air through the solution. Both CO_2 and N_2 are inexpensive and environmentally benign.

Surface-active colloid particles adsorb onto fluid interfaces to stabilize emulsions and foams,[14,15] and they enable the preparation of novel materials, including dry water.[16] On the one hand, these particles are superior to surfactants, because they form a dense particle film that covers the oil–water or air–water interfaces, which leads to ultra-stable emulsions and foams.[14,15] On the other hand, however, demulsification or defoaming correspondingly need more effort. Switchable surface-active colloid particles are therefore of great interest in cases where emulsion or foam stability is only needed temporarily. Recently, many attempts have been made to develop stimulus-responsive surface-active particles, such as those that respond to changes in pH,[17–25] temperature,[26–29] magnetic-field intensity,[30] or specific ion concentration[31] and to dual stimuli, including pH–temperature,[32–34] magnetic-field intensity–temperature,[35,36] and pH–ionic strength.[37] Herein, we report that the CO_2/N_2 trigger of a switchable surfactant can be transferred to mineral nanoparticles through in situ hydrophobization in water. Furthermore, switchable Pickering emulsions using a CO_2/N_2 trigger can be easily obtained by using silica nanoparticles and a trace amount of the switchable surfactant as a stabilizer.

The surface activity of a nanoparticle depends on the wettability of the particle surface, and only those particles that are wetted partially by both water and oil/air are surface-active.[15] Commercially available mineral nanoparticles, such as those of silica or $CaCO_3$, are in general inert because of their extreme hydrophilicity, but they can be made surface-active by either ex situ surface coating,[14] or in situ surface activation.[38–44] The latter method, which is based on the interaction of the particles in aqueous media with suitable amphiphiles, which are typically of opposite charge to the particles,[38–44] allows the surface activity of the particles to be controlled by the selection of the molecular structure and concentration of the amphiphile,[41–43] and it has resulted in novel phenomena, such as double emulsion phase inversion.[39–43]

N′-dodecyl-*N*,*N*-dimethylacetamidine is a switchable surfactant,[11] which can be switched to its active form, *N*′-dodecyl-*N*,*N*-dimethylacetamidinium bicarbonate (amidinium/cationic), by exposure to water and CO_2 at 0–5 °C and switched back to the inactive form (amidine/neutral) by bubbling N_2 or air through the solution at 65 °C (Figure 1).[11] The interconversion can be monitored by measuring the conductivity (Supporting Information, Figure S1) or surface tension (up to 1 mM for the neutral form owing to its solubility; Supporting Information, Figure S2) of the aqueous solution. At concentrations lower than the critical micelle concentration (cmc) of the amidinium form (2.0 mM; Figure S2), either form cannot stabilize an *n*-octane-in-water (1:1) emulsion on its own (Figure S3); but when silica nanoparticles (primary diameter = 20 nm; Figure S4) were dispersed into the amidinium solutions, stable *n*-octane-in-water emulsions were formed following homogenization (Figure 2). These emulsions cream, but they do not coalesce

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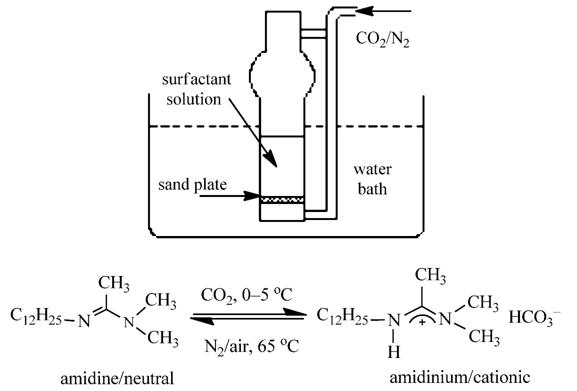

Figure 1. Interconversion between the inactive (amidine/neutral) and active (amidinium/cationic) forms of *N'*-dodecyl-*N*,*N*-dimethylacetamidine in a glass bubbling device at controlled temperatures.

at amidinium concentrations between 0.1 and 6 mM, and the droplet sizes were found to decrease with increasing concentration.

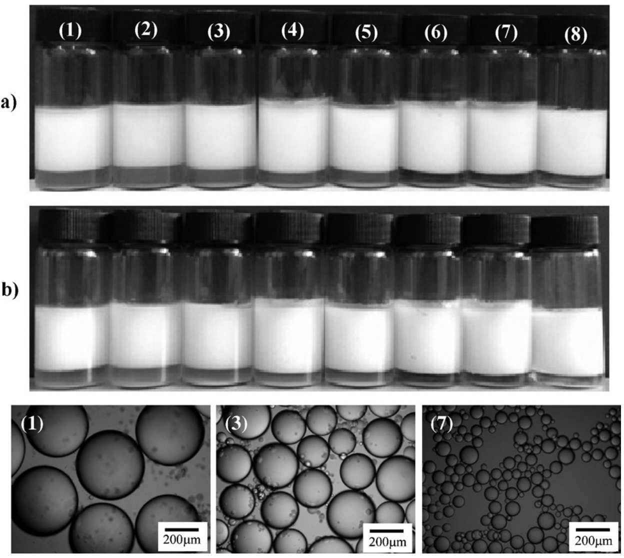

Figure 2. Digital photographs and selected optical micrographs of *n*-octane-in-water emulsions (7 mL/7 mL), which were stabilized by silica nanoparticles (0.5 wt%) and amidinium surfactant, that were taken 24 h ((a) and (c)) and one week (b) after preparation. The surfactant concentrations in water from (1) to (8) are 0.1, 0.2, 0.3, 0.6, 1, 2, 3, and 6 mM, respectively.

The bare silica nanoparticles are too hydrophilic to stabilize emulsions alone (Supporting Information, Figure S5).[39,42] However, in the presence of a trace amount of the amidinium surfactant (cationic), the negatively charged silica particles ($\zeta = -24.9 \pm 0.2$ mV for particles dispersed in pure water (0.1 wt%) at 25 °C) can then be hydrophobized in situ[42] by adsorption of the amidinium ions through electrostatic interactions, which is indicated by the variation of the zeta potential of the particles and the adsorption isotherm (Figure 3). The surfaces of the particles become partially hydrophobic because of the formation of a surfactant monolayer (for example, 4.26×10^{-2} mmol g^{-1}, or 7.8 nm^2 molec^{-1} at an initial/equilibrium amidinium concentration of 0.3/0.0426 mM) at the solid–water interface with the hydrocarbon chains protruding towards water, and the modified particles are therefore able to stabilize *n*-octane-in-water Pickering emulsions. The relatively large droplet diameters (Figure 2c) also suggest that the emulsions are stabilized by modified particles instead of by surfactant molecules.[39,42] By contrast, the zeta potentials of the particles remain negative in the presence of the amidine surfactant (neutral) at all concentrations, which indicates a much lower adsorption to particle surfaces (Figure 3).

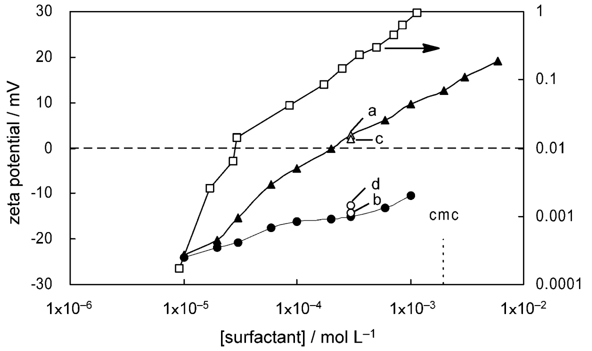

Figure 3. Zeta potentials of silica nanoparticles (0.1 wt%) that were dispersed in aqueous solutions of switchable surfactants, for both the active (cationic; ▲) and inactive (neutral; ●) forms, as a function of initial concentration; alternation at 0.3 mM after cycles of bubbling N$_2$/CO$_2$ through the dispersion (a–d, see the main text). The adsorption isotherm of the amidinium surfactant (□) at the silica–water interface is also given as a function of the equilibrium concentration.

To verify the switchable performance of the Pickering emulsions, an *n*-octane-in-water emulsion (10 mL/10 mL) stabilized by silica nanoparticles (0.5 wt%) and amidinium surfactant (0.3 mM; Figure 4a) was transferred to the bubbling device (Figure 4b). A sand plate was used as the bubble distributor, and N$_2$ was bubbled through the device at a flow rate of 160 mL min^{-1} at 65 °C. The aqueous dispersion of the precursor showed no visible signs of flocculation or sedimentation within 24 h. Following this procedure, the emulsion volume decreased slightly because of the evaporation of both water and octane, and extensive coalescence occurred with demulsification being complete after a bubbling time of approximately 80 min (Figure 4c). The separated oil–water mixture was transferred to another vessel and the conductivity of the water phase was measured to be 17.9 μS cm^{-1}, which implies that approximately 81 % of the surfactant molecules in the emulsion had been inactivated. This efficiency is very close to the maximum inactivation efficiency of 83 % obtained for an aqueous amidinium solution (1 mM), based on the conductivities before bubbling N$_2$ through the solution (316 μS cm^{-1}) and after bubbling (52 μS cm^{-1}; Supporting Information, Figure S1) and taking the conductivity as being proportional to the amidinium concentration. The conductivity before bubbling is comparable with that (320 μS cm^{-1}) of an aqueous solution of a typical cationic surfactant, cetyltrimethylammonium bromide (CTAB), at the same concen-

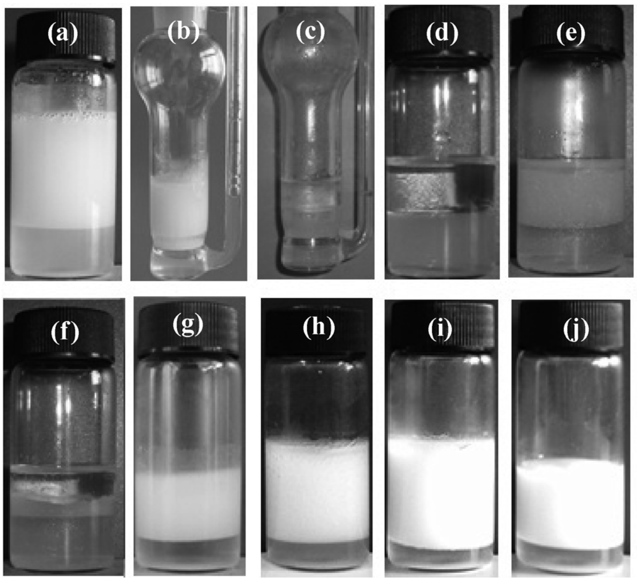

Figure 4. Digital photographs of *n*-octane-in-water Pickering emulsions that were stabilized by silica nanoparticles (0.5 wt%) and either a switchable surfactant (0.3 mM; (a)–(h)) undergoing switching or CTAB (0.1 mM; (i), (j)). a) Emulsion with amidinium (10 mL:10 mL); b) transfer to a bubbling device; c) bubbling of N_2 through the emulsion at 65 °C for 80 min; d) transfer to a vial; e) re-homogenization for 2 min, 24 h later; f) one week later; g) bubbling CO_2 through the emulsion at 0–5°C for 50 min, followed by re-homogenization for 2 min, one week later; h) emulsion (7 mL:7 mL) with amidinium kept at 65 °C for 24 h without bubbling of N_2; i) emulsion (7 mL:7 mL) with CTAB, 24 h later; j) emulsion with CTAB after bubbling N_2 through the emulsion at 65 °C for 80 min, 24 h later.

tration (1 mM), which indicates that the amidinium molecules are fully dissociated in aqueous solution.

The pH of an aqueous amidinium solution at 0.3 mM was measured to be 4.98; this value increased to 6.03 following bubbling N_2 through the emulsion, but it fell to 4.63 after subsequent bubbling through with CO_2. All these pH values are slightly lower than that of pure water (6.12). In this pH range, the silica particles are highly negatively charged,[42] and once the amidinium was inactivated, the zeta potential of the particles decreased from +2.8 mV to −15.1 mV. This is shown to be reversible for particles dispersed in the amidinium solution following bubbling N_2 through the solution and then CO_2 and N_2 again, as indicated by the points *a* (+2.8, initial)→*b* (−14.3, N_2)→*c* (+2.06, CO_2)→*d* (−12.6, N_2; Figure 3), which indicates that desorption of the switchable surfactant from the solid–water interface took place following bubbling N_2 through the solution. Thus, silica nanoparticles in emulsions lose their surface activity and return to the water phase (Figure 4c and d), and no stable emulsion can be formed after re-homogenization (Figure 4e and f). On the other hand, once CO_2 was bubbled through the mixture at 0–5°C for 50 min, the stability of the emulsions was re-established after re-homogenization (Figure 4g).

For comparison, an emulsion (7 mL/7 mL) stabilized by silica nanoparticles (0.5 wt%) and amidinium surfactant (0.3 mM) was kept at 65 °C for 24 h without bubbling of N_2 (Figure 4h), and another emulsion (7 mL/7 mL) that was stabilized by silica nanoparticles (0.5 wt%) and CTAB (0.1 mM; cmc = 0.9 mM) was bubbled with N_2 at 65 °C for 80 min (Figure 4i and j). No coalescence was observed for both emulsions, which indicates that the coalescence of droplets (Figure 4c) is not caused by a temperature increase and that the Pickering emulsion that was stabilized with silica nanoparticles, the surface of which was activated in situ by a non-switchable surfactant (CTAB), could not be destabilized by bubbling N_2 through the emulsion. It is noteworthy that only those dispersions that contain silica particles that were activated in situ with amidinium surfactant yielded stable aqueous foams (Figure S6). Details will be reported in a subsequent publication.

The optical micrographs of the various emulsions prepared indicate that the droplet sizes are similar once the emulsion has undergone a cycle of switching (Figure 5a and g). As expected, much larger droplets were observed once the surfactant had been inactivated (Figure 5e). As a comparison, no significant changes in droplet size were observed for the silica-based switchable-surfactant emulsion after a temperature increase alone (Figure 5h), or for the silica-CTAB emulsion after bubbling N_2 through the emulsion at 65 °C (Figure 5i and j).

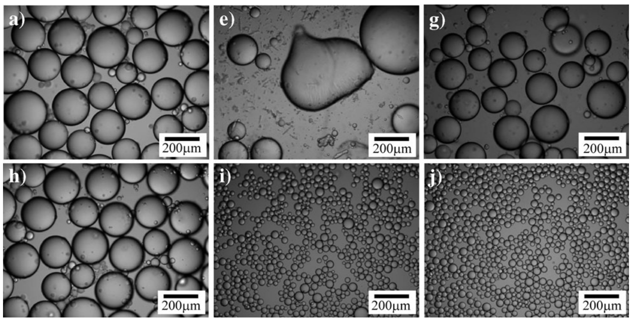

Figure 5. Micrographs of *n*-octane-in-water Pickering emulsions corresponding to those described in Figure 4.

We have thus demonstrated that switching a surfactant between its active and inactive forms can be successfully transferred to nanoparticles. Both switchable surface-active particles and switchable Pickering emulsions, which employ the same trigger, were obtained. Although switchable emulsions can be prepared using a switchable surfactant, such as *N'*-cetyl-*N*,*N*-dimethylacetamidine alone,[12] or using pH-responsive particles,[25] the former emulsions are only kinetically stable, and very high concentrations (≫ cmc) are needed, whereas the synthetic particles in the latter are quite exotic, and emulsions that contain these particles are less sensitive to the bubbling of N_2 through the solution. We have now obtained a switchable Pickering emulsion with excellent long-term stability by using only a trace amount of a switchable surfactant (cmc/10) in combination with relatively simple silica nanoparticles, and by employing the environmentally benign CO_2/N_2 trigger. The relatively low and high temperatures required for the on and off switching of the emulsions are a limitation of these systems, which may be partially overcome by a prolonged bubbling time. In fact, complete demulsification of such an emulsion may be achieved by bubbling N_2 through the emulsion at room temperature for 4 h, but a more efficient switching relies on the development of surfactants that are switchable at room temperature.

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