Soft Matter

COMMUNICATION

How do (fluorescent) surfactants affect particle-stabilized emulsions?†

Job H. J. Thijssen,* Andrew B. Schofield and Paul S. Clegg

We present the first confocal-microscopy study of synergistic effects in emulsions stabilized by both colloidal particles and a common fluorescent dye that acts as a surfactant. *In situ* microscopic imaging reveals surfactant adsorption onto the liquid–liquid interface and onto the colloidal particles, which changes the interfacial tension and the particle contact angle. This leads to emulsions that are more stable, more polydisperse and can incorporate more of the dispersed phase.

Emulsions are frequently encountered in commercial products and industrial processes ranging from foods to enhanced oil recovery. Previous investigations have primarily focused on emulsions solely stabilized by molecular surfactants or colloidal particles, even though the stability of many practical systems derives from both.[1] Intriguingly, it has been reported that emulsions with both types of emulsifier can display superior shelf life and functionality compared to those stabilized by particles or surfactants alone,[2–4] an effect referred to as *synergy*.

Several mechanisms have been proposed to explain synergistic effects. For example, particles may facilitate surfactant adsorption at the liquid–liquid interface. In addition, surfactant adsorption may affect the particles' contact angle with the droplet surface, thereby inhibiting particle desorption from this liquid–liquid interface.[2,5–7] Recently, it has been suggested that both components in mixed-emulsifier systems may also have specific functions. During emulsification, the molecular surfactant can rapidly adsorb onto the liquid–liquid interface and reduce the interfacial tension γ, *i.e.* reduce the free-energy cost per unit of liquid–liquid contact area. This promotes droplet break-up and suppresses coalescence (droplets merging), subsequently allowing the (slower) colloidal particles to cover the droplet surface and provide long-term stability.[8] At high surfactant concentrations, however, competition rather than synergy between molecular and particulate emulsifiers has been observed—depending on the type of surfactant used, it may cause particles to desorb from

the liquid–liquid interface.[9] Though plausible, the mechanisms mentioned here have not yet been backed by *in situ* microscopic observations, which could directly confirm (some of) them.

Here, we show experimentally how surfactants can affect the formation, structure, and stability of particle-stabilized emulsions using a combination of confocal fluorescence microscopy, visual inspection, and contact-angle measurements. To the best of our knowledge, we are the first to employ a *fluorescent* surfactant, enabling us to present *in situ* microscopic images of surfactant adsorption, both onto the liquid–liquid interface of the droplets and onto the colloidal particles, thereby confirming the crucial role of surfactant adsorption in emulsion synergy. Moreover, we reveal that (common) fluorescent dyes can act as surfactants and thus significantly affect particles at liquid interfaces—a valuable warning for future investigations involving fluorescent probes.

To study synergistic effects between particulate and molecular emulsifiers, we start with a reference emulsion of water and oil (*n*-dodecane), stabilized by micron-sized spheres of poly(methyl methacrylate) (PMMA, see ESI† for experimental details). These particles are fluorescently labeled with NBD, a fluorescent dye that has been chemically linked to the PMMA. Such colloidal particles can become irreversibly attached to droplet surfaces, as they reduce energy-expensive liquid–liquid contact area. This is described by

$$\Delta G_{\mathrm{d}} = \pi \cdot r^2 \cdot \gamma \cdot (1 - |\cos\theta|)^2, \qquad (1)$$

where ΔG_{d} is the free energy of detachment of a spherical particle of radius r and contact angle θ (measured through the polar phase).[1] Even if $\theta = 160° \gg 90°$, eqn (1) predicts $\Delta G_{\mathrm{d}} \sim 4 \times 10^4\, k_{\mathrm{B}} T_0$ for a 1 μm diameter colloid at a water–oil interface (k_{B}: Boltzmann constant; T_0: room temperature).[10,11]

As a molecular surfactant, we dissolve the fluorescent dye Rhodamine B (Fig. 1a) in water ([RhB] $\sim 5 \times 10^{-4}$ M),[12,13] before emulsion preparation. Fig. 1b–e justify the use of RhB as a surfactant. First, Fig. 1b demonstrates that RhB promotes foaming in water. Second, Fig. 1c shows that RhB can temporarily stabilize dodecane-in-water emulsions, as evidenced by the turbid cream and the red continuous phase at the bottom of container (A). Third, Fig. 1d reveals that RhB collects at the surface of dodecane droplets, leaving an excess of this fluorescent dye in the continuous water phase. Note that, in contrast with their particulate counterparts, molecular emulsifiers can desorb from (and re-adsorb to) liquid–liquid interfaces, courtesy of their relatively small size.[13] These images also manifest that RhB prefers water over oil, which is not surprising given its structure formula (Fig. 1a), lacking a (long)

School of Physics and Astronomy, SUPA and COSMIC, The University of Edinburgh, Mayfield Road, Edinburgh, EH9 3JZ, United Kingdom. E-mail: j.h.j.thijssen@ed.ac.uk; Web: http://www.linkedin.com/in/jobthijssen

† Electronic Supplementary Information (ESI) available: materials and experimental procedures; brightfield microscopy images of emulsions with/without Rhodamine B; movie showing gentle redispersion (by rolling) of equivalent water-in-oil/PMMA emulsions with/without Rhodamine B; image of Rhodamine B adsorbed onto PMMA colloids in samples without (added) water. See DOI: 10.1039/c1sm05968h/
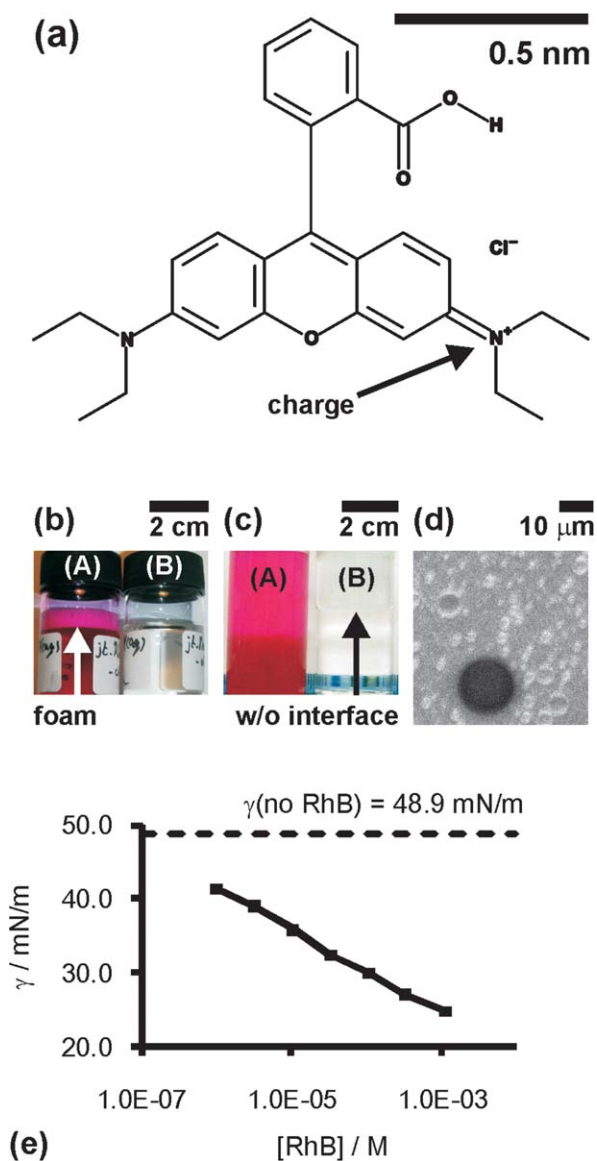
Fig. 1 (a) Schematic structure formula of Rhodamine B (RhB).[12,13] (b) Digital photograph of water with (A) RhB and (B) salt after agitation ([RhB] = 7.8×10^{-4} M and [NaCl] = 8.9×10^{-4} M); note that foaming is not due to charge. (c) Digital photograph of water/dodecane samples (54/46 vol%), 5 min after (3 × 1) min of vortex mixing; [RhB] in water is (A) 8.6×10^{-4} M and (B) 0 M. (d) Confocal RhB fluorescence micrograph of an emulsion formed from a water/dodecane mixture (30/70 vol%) by agitation in an ultrasonic bath. Note the bright edges of the droplets and the excess of RhB in the continuous water phase. (e) Water-dodecane interfacial tension γ as a function of the [RhB] in water (vertical symbol size equals error in γ).

hydrocarbon chain but featuring a positive charge. Finally, Fig. 1e shows quantitatively how the water-dodecane interfacial tension falls as the [RhB] is increased. To check the validity of these pendant-drop measurements, we repeated them with unlabeled water and obtained an interfacial tension of (48.9 ± 0.9) mN m^{-1}. This is slightly smaller than the corresponding literature value of 52.9 mN m^{-1}, which we attribute to temperature differences and polar impurities in the oil.[11,14]

Agitating the sample mixture (Fig. 2a) yields water-in-dodecane/PMMA emulsions (Fig. 2b), as evidenced by their sedimentation behavior and as expected from the hydrophobic nature of PMMA.[1,10] Fig. 2b also suggests that RhB affects emulsification by (1) adsorbing onto the colloids and (2) hindering particle adsorption at the water–oil interface,[2,3,9] leading to a (1) orange and (2) turbid supernatant. Moreover, Fig. 2c demonstrates that RhB affects emulsion structure, for a higher [RhB] leads to a more compact sediment in otherwise equivalent samples, *i.e.* the droplet volume fraction in the sediment ϕ_S increases with [RhB]. Measuring sediment/emulsion heights yields:

$$\phi_S(A) = (66.6 \pm 0.3) \text{ vol\%}$$
$$\phi_S(B) = (61.9 \pm 0.3) \text{ vol\%} \qquad (2)$$
$$\phi_S(C) = (55.8 \pm 0.3) \text{ vol\%}$$

How can RhB addition change ϕ_S? Emulsification here proceeds *via* limited coalescence,[15] in which mixing creates a surplus of liquid–liquid interface, after which the emulsion coarsens through droplets merging until their surface area can only just accommodate all the particles. As a molecular surfactant, RhB can promote the stability of (small) droplets that are not yet/only partially coated with particles,[8] *e.g. via* the Gibbs–Marangoni mechanism.[16] Hence, many droplet 'generations' can coexist and cross-coalesce, resulting in more poly-disperse emulsions. Since these pack more efficiently,[17] they form more compact sediments. In addition, the fluorescent surfactant allows small (partially coated) droplets to survive for longer without coalescing, enabling them to sweep up additional particles and thus stabilize themselves, resulting in a larger population of small droplets (see ESI†). These can sit in the interstices between large droplets, thereby increasing packing efficiency. An alternative explanation for
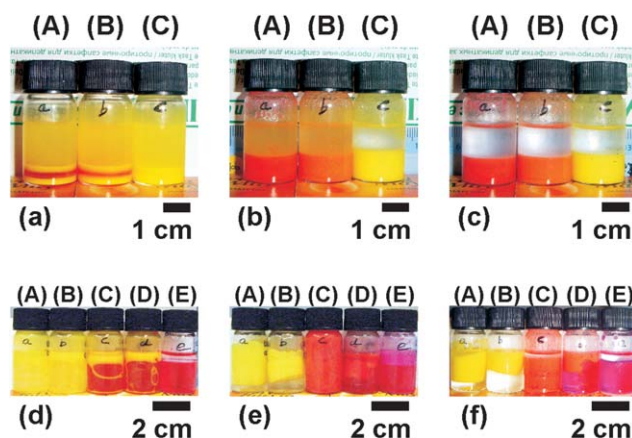

Fig. 2 (a–c) Digital photographs of equivalent water-dodecane/PMMA samples with varying concentrations of Rhodamine B [RhB]: (a) before, (b) after the 1st, and (c) ~35 min after the 3rd emulsification step. [RhB] in water is (A) 7.5×10^{-4} M, (B) 3.3×10^{-4} M, and (C) 0 M; water/liquid volume ratio is (A) 30.3%, (B) 30.6%, and (C) 30.3%. (b) RhB affords turbid supernatants and (c) more compact sediments. (d–f) Digital photographs of similar water-dodecane/PMMA samples, (A/B) without and (C/D) with RhB ([RhB] in water is 3.3×10^{-4} M), having water/liquid volume ratios of (A/C) 80% and (B/D) 90%: (d) before, (e) 5 min after the 3rd emulsification step, and (f) after overnight centrifugation at 1400 rpm (which only clarifies the situation). (f) Note that RhB allows more water to be emulsified (A/C). (E) blank sample with RhB but without PMMA.

the more compact sediments observed in particle-stabilized emulsions with Rhodamine B is that the fluorescent surfactant confers attractions between the droplets. However, we have seen no evidence of this when gently redispersing the emulsions (see ESI†).

In order to expose the synergy between our molecular and particulate emulsifiers, we prepared samples with water/liquid volume ratios λ up to 90%. Intriguingly, Fig. 2d–f show that, for mixtures with $\lambda = 80\%$ (A/C), only samples containing RhB can still form proper water-in-oil emulsions that tend to sediment to the bottom of the container (C). At $\lambda = 90\%$ (D), judging from its red color, the liquid that collects at the bottom of the vial is water. As it preferentially wets the inside of the glass wall and does not have a straight interface with the emulsion above, the latter is *not* water continuous, *i.e.* it is a water-in-oil emulsion. Apparently, the PMMA particles are so hydrophobic that they can only stabilize an oil-continuous rather than an (inverted) water-continuous emulsion, thereby forcing the system to simply expel any excess water. Confocal microscopy (not shown here) confirms that the emulsions in vials (A–D) are all water-in-oil. Here, the role of the (fluorescent) surfactant is to promote droplet stability during emulsification, thereby masking the water surplus.

Employing particles and surfactants with distinguishable fluorescence, we can separately locate the particulate and molecular emulsifiers *via* confocal microscopy. From Fig. 3a/c, it is clear that the particles form a close-packed (mono)layer around the droplets. This mechanically prevents droplets from merging (coalescence) and shrinking (Ostwald ripening),[1] courtesy of the high free-energy penalty for particle detachment (eqn (1)). Fig. 3b/d shows that the droplets contain the RhB-labeled water, *i.e.* our emulsions are water-in-oil, as previously inferred from their sedimentation behavior (Fig. 2) and as expected from the hydrophobic nature of PMMA.[1,10] Moreover, each particle is surrounded by a ring, indicating that RhB molecules have adsorbed onto the PMMA colloids, which may affect

the contact angle of the latter.‡ As RhB prefers water over dodecane (Fig. 1), its adsorption should promote the wetting of PMMA particles by water. Finally, the occasional partially coated droplet reveals that RhB also adsorbs onto the liquid–liquid interface (Fig. 3d arrow and Fig. 1d), where it reduces interfacial tension (Fig. 1).

At this point, it is worthwhile recalling that the average droplet radius $\langle R \rangle$ in our particle-stabilized emulsions is determined by the radius r and the volume fraction φ of the colloidal particles: $\langle R \rangle \propto r/\varphi$. Firstly, Fig. 2c shows that the supernatants of our emulsion sediments are clear, *i.e.* there are (virtually) no colloids in the continuous phase after emulsification. Furthermore, it also shows that there is no excess of dispersed phase, *i.e.* all the water has been incorporated into emulsion droplets. Finally, Fig. 3a/c reveals that the droplets are coated with a close-packed monolayer of particles, *i.e.* every colloid has been adsorbed at a droplet surface. All in all, this means that, even though our fluorescent surfactant may temporarily stabilize droplets that are not yet/only partially coated with particles (Fig. 1c), our emulsions coarsen until the liquid–liquid interface can just accommodate all the particles, which directly sets the average droplet size.

Having visually established that RhB adsorbs onto the surface of our droplets and particles (Fig. 1 and Fig. 3), and acts as a surfactant (Fig. 1), we now turn to tensiometry to quantitatively determine the effect of RhB addition on the particle contact angle θ. Fig. 4a and b show sessile water droplets with/without RhB, under dodecane, on
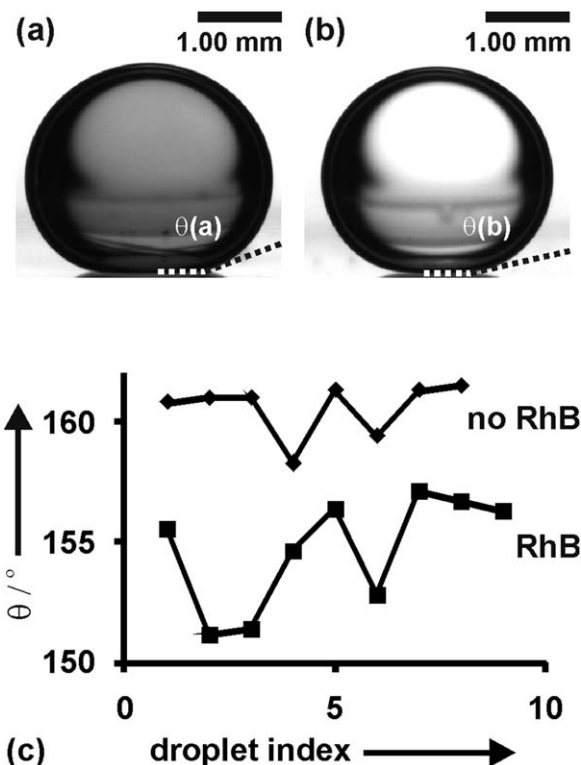
Fig. 4 (a/b) Digital snapshot of an 18 μL water droplet (a) with and (b) without Rhodamine B ([RhB] = 4.9×10^{-4} M), under dodecane, on a glass slide spin-coated with poly(methyl methacrylate) and its stabilizer. The contact angle θ has been drawn as a guide for the eye. (c) Contact angles of water droplets (■) with and (◆) without RhB, as determined from digital snapshots (a/b) of 8/9 sessile droplets at different positions on the slide, confirming the homogeneity of the PMMA/stabilizer coating.
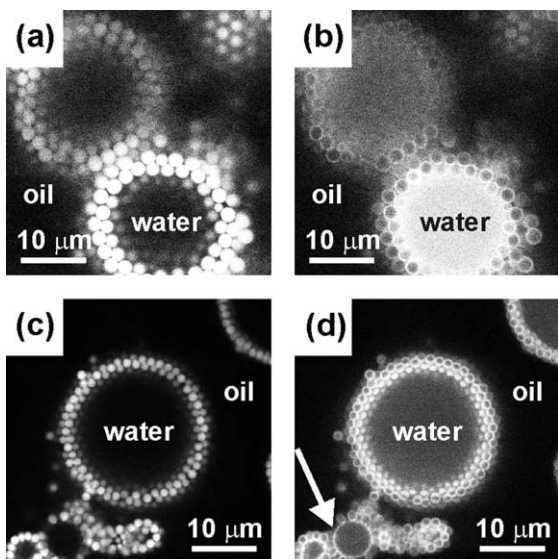

Fig. 3 Confocal fluorescence micrographs of water-in-dodecane emulsions: (a/c) NBD-labeled particles and (b/d) Rhodamine B (RhB). Note that each colloidal particle is surrounded by a ring of fluorescent surfactant (RhB). (d) Note the bright edge of the partially coated droplet (arrow). (a) Centers of colloids on the lower droplet are slightly overexposed. [RhB] in water: (a/b) 3.2×10^{-4} M and (c/d) 2.3×10^{-4} M.

solid substrates coated with PMMA and its stabilizer (poly-12-hydroxystearic acid (PHS)). Drawing tangents, it is clear that adding RhB to water lowers the solid-water-dodecane contact angle.§ Fitting tangents to 8 or 9 droplets at different positions on two separate slides yields: $\langle\theta(a)\rangle = (154.6 \pm 0.8)° < \langle\theta(b)\rangle = (160.3 \pm 0.4)°$.

Though a change in contact angle $\Delta\theta = (5.7 \pm 0.9)°$ seems small, it has a substantial effect on the free energy of detachment of a particle, which consequently increases by a factor of 2.7 (eqn (1)). Combining the effects of RhB addition on θ (Fig. 4) and γ (Fig. 1) amounts to a ΔG_d that is $1.5\times$ higher than without RhB, *i.e.* our emulsions are more stable if we add our fluorescent surfactant. It should be pointed out here that the initial [RhB] in water is $1.5\times$ larger in the samples for tensiometry (Fig. 4) than it is in the ones for confocal microscopy (Fig. 3). However, as vortex mixing during emulsification is likely to promote surfactant adsorption, an exact comparison (with the same initial [RhB]) is not possible. Hence, the numerical example above should be regarded as an illustration only.

Above, we have demonstrated that RhB acts as a surfactant in water-dodecane mixtures (Fig. 1). From a practical point of view, one might wonder how specific this behavior is. Preliminary observations imply that other (common) fluorescent dyes act similarly, *e.g.* Rhodamine 6G, Oxazine 170 Perchlorate, 1,8-ANS, and Coumarin 1; fluorescein seems to be the only exception. Hence, we attribute the surfactant-like behaviour of these molecules to their zwitter-ionic or/and charged nature. Note that this excludes many (common) fluorescent dyes from being used as non-invasive probes in particle-stabilized emulsions, a problem that may potentially have been overlooked in previous studies involving particles at liquid interfaces.[18]

To conclude, we have presented the first study of emulsion synergy that includes confocal fluorescence microscopy. Surfactant addition affects the formation and structure of particle-stabilized emulsions, resulting here in more compact water-in-oil emulsions, which can be explained in terms of increased droplet polydispersity. In addition, adding a surfactant allows more water to be emulsified, exposing its synergistic interaction with the colloidal particles. Exploiting the fluorescence of a dye that acts as a surfactant (Rhodamine B), we have shown that its adsorption, both onto the liquid–liquid interface and onto the colloidal particles, plays a crucial role: it lowers the interfacial tension and reduces the particle contact angle, leading to more stable emulsions. Though (common) fluorescent dyes should not be blindly employed as probes in particle-stabilized emulsions, some of them can be used to reveal the microscopic origin(s) of particle-surfactant synergy and related phenomena. Exciting possibilities for future research now include, for example, (high-resolution) *in situ* microscopy studies of particle-surfactant competition and particle arrangement at the water–oil interface as a function of surfactant concentration.

Acknowledgements

Notes and references

‡ Using confocal fluorescence microscopy, we have also observed RhB rings around PMMA colloids dispersed in *n*-dodecane after agitation in RhB-coated glass vials without (added) water (see ESI†).
§ In preliminary experiments, we have observed a (slight) opposite trend on glass slides spin-coated with PMMA but without its stabilizer.

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