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How Do (Fluorescent) Surfactants Affect Particle-Stabilized Emulsions? – Electronic Supplementary Information (ESI)

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Materials and Methods

Poly(methyl methacrylate) (PMMA) particles, stabilized by a layer of poly-12-hydroxystearic acid (PHS), were synthesized following Bosma *et al.*[1] They were labeled with the fluorescent dye 4-chloro-7-nitrobenzo-2-oxa-1,3-diazol (NBD), which was chemically linked to the PMMA during particle synthesis. Two different particle batches were used: a) radius 1.10 µm, polydispersity 2% and b) radius 0.575 µm, polydispersity 5% (Static Light Scattering). They were cleaned by repeated centrifugation/re-dispersion in dodecane or *n*-hexane (10×), after which they were dried under vacuum in an oven at (43 ± 3) °C. As a surfactant, Rhodamine B was used as received (RhB, Acros Organics, 99+% or Fluka 83690). Water was distilled and passed through a Millipore Milli-Q RG system (resistivity 18 MΩ·cm), whereas the oil *n*-dodecane was used as received (Sigma-Aldrich, ≥99%).

For sample preparation, the dried colloids were dispersed in *n*-dodecane using a 20 kHz 500 W ultrasonic processor set at 20% amplitude for 3×30 s (Sonics & Materials Inc), each cycle followed by 20 s of vortex mixing. Alternatively, they were dispersed using an ultrasonic bath for 3×6 min, each cycle followed by 1 min of vortex mixing. Subsequently, water was added without/with Rhodamine B at concentrations of $1.7 \cdot 10^{-4}$ to $7.5 \cdot 10^{-4}$ M ([RhB]). Typical sample composition: 2.5 to 5.0 vol-% of PMMA, 30/70 water/dodecane volume ratio and 5.0 mL total volume; all amounts were determined by weighing. Emulsions were then prepared by vortex mixing (3 to 5)×1 min, waiting 5 min in between cycles.

Digital photographs were taken using a FUJIFILM FinePix Z10fd camera. For equation (2), droplet volume fractions ϕ_S were calculated from sediment/emulsion heights, which were measured with a ruler having a mm scale; the error was calculated from four emulsions without RhB but with equivalent compositions. Microscopic images were obtained through confocal laser scanning fluorescence microscopy, for which glass cover slips were glued on top of the samples using a UV-curable adhesive (Loctite 358); emulsions were then re-agitated by vortex mixing for 1 min. A Nikon ECLIPSE TE300 or Zeiss Observer.Z1 inverted microscope was used in conjunction with a BioRad Radiance 2100 or Zeiss LSM 700 scanning system and a Nikon Plan Apo 100×/1.40 NA oil-immersion or Zeiss LD Plan-Neofluar 63×/0.75 NA objective. The 488 nm line of an Ar-ion laser was used to excite NBD in PMMA, while a 543 nm HeNe or 555 nm diode laser was employed for RhB; filters were used as appropriate. To minimize cross-talk between the two channels, frames were scanned sequentially. Image signal-to-noise was enhanced by Kalman averaging (4×).

Interfacial tensions γ and static contact angles θ were measured using a Krüss EasyDrop instrument (model FM40Mk2). Interfacial tensions γ were determined from (23.3 ± 0.3) µL pendant (RhB-labeled) water droplets under *n*-dodecane at (25 ± 1) °C. After 5 min of equilibration (10 or 15 min for low [RhB]), digital snapshots were recorded from which values for γ were extracted by fitting the Young-Laplace equation to the drop profile. Required input parameters for fitting include: the syringe needle diameter for pixel-size calibration (1.82 mm, micrometer screw), the density of water (ρ_w^{25} = 0.9970 g/mL),[2] and the density of dodecane (ρ_d^{25} = 0.7460 g/mL).[3] At each [RhB], three measurements on three different droplets were averaged to obtain the corresponding value of γ. The error bars were calculated by combining the standard deviation of the three measurements with error estimates for temperature variations, varying [RhB] and water-dodecane miscibility (main contribution).

Static contact angles θ were determined from sessile (RhB-labeled) water droplets on solid substrates under *n*-dodecane. Glass cover slips were spin-coated at 1,800 rpm for 1 min with PMMA (Aldrich, M_W ~ 996,000) from a toluene solution; layer thickness ~1.4 µm, as determined by spectroscopy.[4] Subsequently, the PMMA coated slides were similarly spin-coated with a thin layer of PHS-*graft*-PMMA.[5] Confocal

microscopy confirmed that the slides were coated with PHS on top of PMMA, the top surface featuring roughness on the micron scale. Employing software-controlled dosing, 3×6 µL pendant drops were delivered from a glass syringe and picked up by gently raising the substrate, thus forming an 18 µL sessile drop. After 5 min of equilibration, digital snapshots were recorded, from which values for θ were extracted using the "Tangent method 2". The images were calibrated via the syringe needle (0.499 mm diameter, Narishige MF-830 MicroForge). Weighted average and standard error of the mean were calculated from measurements on 8/9 droplets at different positions on the slide.

The chemical structure formula was drawn using Symyx Draw 4.0 (Accelrys); graphs were compiled using Microsoft Office Excel 2007; image processing was carried out using the ImageJ (1.42q) and CorelDraw (X4) software packages.

Droplet Size (Distribution) without/with Rhodamine B – Brightfield Microscopy

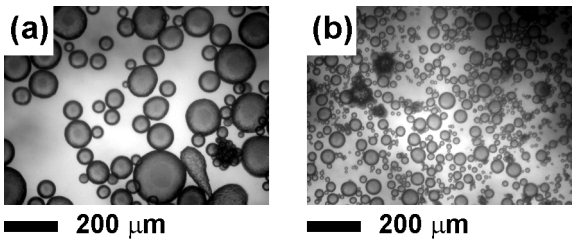

Fig. I Optical micrographs of samples of equivalent water-in-dodecane emulsions (a) without and (b) with Rhodamine ([RhB] in water: $7.5 \cdot 10^{-4}$ M). Note that RhB addition affects the droplet-size distribution, i.e. there are many more small droplets (shown here) and a few very large droplets (not shown here). Samples were transferred from the emulsion vials to glass cuvettes (Starna Scientific Ltd) using Pasteur pipettes and diluted with *n*-dodecane. Brightfield microscopy was performed on an Olympus BX50 upright microscope employing an Olympus Plan 10×/0.25 NA objective. 8-Bit images were recorded using a digital camera (QImaging MicroPublisher 3.3 RTV).

Redispersing Particle-Stabilized Emulsions with/without Rhodamine B – Movie

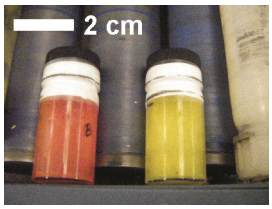

Fig. II *Thijssen_2011_DAS_MovieSIii* is a real-time movie showing no significant differences between gently redispersing sedimented water-in-oil/PMMA emulsions of equivalent composition (B, left, red) with and (C, right, yellow) without Rhodamine B ([RhB] in water is $7.5 \cdot 10^{-4}$ M). The movie has been MPEG compressed to reduce file size – the original file is available from the corresponding author upon request (85 MB).

Rhodamine B around PMMA Colloids – Confocal Fluorescence Microscopy

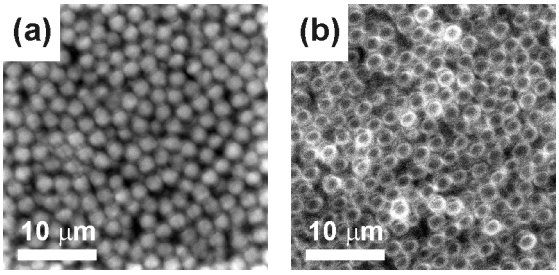

Fig. III Confocal micrographs of NBD-labeled PMMA particles dispersed in dodecane after agitation in Rhodamine B (RhB) coated glass vials without (added) water: a) NBD and b) RhB fluorescence. Note that each PMMA colloid is surrounded by a Rhodamine B ring. A Zeiss Observer.Z1 inverted microscope was used in conjunction with a Zeiss LSM 700 scanning system and a Zeiss Plan-Apochromat 63×/1.40 NA oil-immersion objective. A 488 nm diode laser was used to excite NBD in PMMA, while a 555 nm diode laser was employed for RhB; filters were used as appropriate. To minimize cross-talk between the two channels, lines were scanned sequentially. Image signal-to-noise was enhanced by Kalman averaging (2×).

Notes and References

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