

Supporting information for:

Interfacially-adsorbed particles enhance the self-propulsion of oil droplets in aqueous surfactant

Seong Ik Cheon¹, Leonardo Batista Capaverde Silva², Aditya Khair³, Lauren D. Zarzar^{*1,2,4}

1. Department of Chemistry, The Pennsylvania State University, University Park, PA 16802
2. Department of Materials Science and Engineering, The Pennsylvania State University, University Park, PA 16802
3. Department of Chemical Engineering, Carnegie Mellon University, Pittsburgh, PA 15213
4. Materials Research Institute, The Pennsylvania State University, University Park, PA, 16802

*Correspondence to ldz4@psu.edu

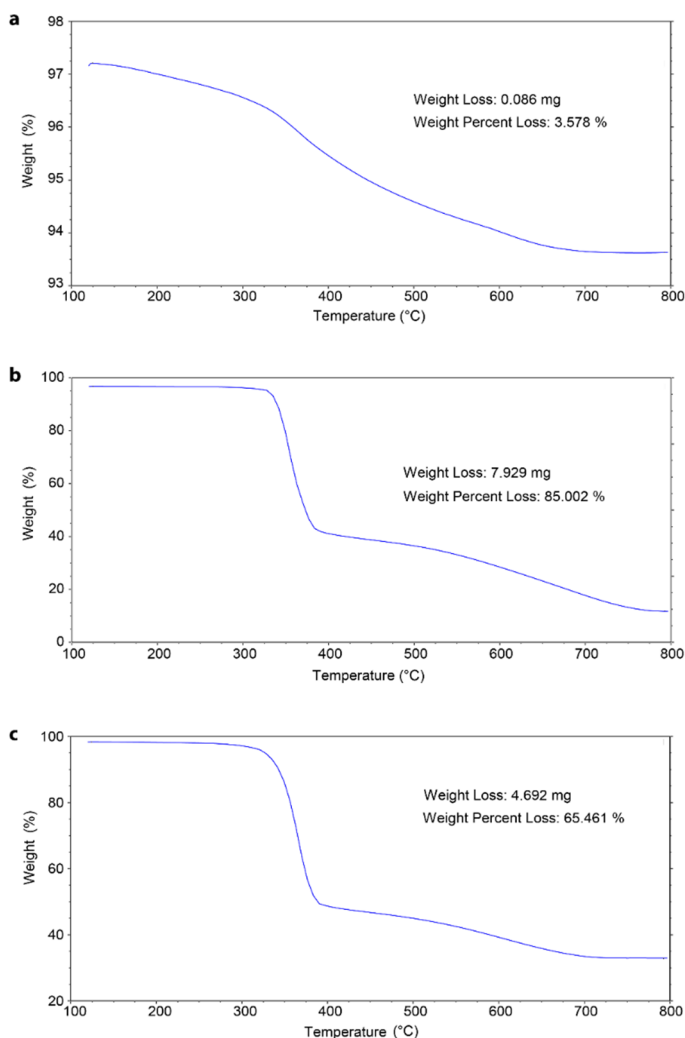


Figure S1. Thermogravimetric analysis traces of particles produced during the different steps of fluorescent particle synthesis. The silica particles were heated in air from 25 °C to 120 °C at 10 °C/min and held in isotherm for 10 minutes to remove residual solvent. Particles are then heated to 800 °C at 20 °C/min. The normalized weight loss was then calculated from mass change between 120 °C and 800 °C. **a**, Analysis of amine-terminated S13 silica, functionalized with aminopropyl triethoxysilane. **b**, Analysis of particles after carbodiimide coupling of fluorescein onto amine terminated S13. **c**, Analysis of fluorescent particles after surface functionalization with hexadecyltrimethoxysilane to render the particles more hydrophobic.

Table S1. Speeds of bromodecane droplets containing various silica (H13L) concentrations dispersed in different Triton X-100 concentrations were measured. For a given droplet, the highest speed reached during the imaging was assigned as the droplet's speed. For each experimental condition, at least 25 droplets were measured. This data is plotted in **Figure 1**.

0.1 wt% Triton X			0.5 wt% Triton X			1.0 wt% Triton X		
Particle wt%	Speed ($\mu\text{m/s}$)	Stdv	Particle wt%	Speed ($\mu\text{m/s}$)	Stdv	Particle wt%	Speed ($\mu\text{m/s}$)	Stdv
0.00	3.4	1.0	0.00	48.9	17.1	0.00	125.0	24.7
0.05	74.8	12.7	0.05	167.56	21.8	0.05	231.5	17.2
0.20	66.9	10.1	0.20	232.0	21.5	0.20	256.4	17.9
0.40	53.6	15.4	0.40	233.6	12.3	0.40	285.3	30.2
0.50	48.3	15.1	0.50	244.0	31.4	0.50	265.5	37.7
0.60	49.8	11.1	0.60	243.9	22.9	0.60	280.5	22.5
0.80	49.4	16.3	0.80	213.7	21.1	0.80	251.0	29.5
1.00	49.8	3.1	1.00	166.0	35.6	1.00	234.4	29.5
1.50	3.7	1.3	1.50	110.3	51.7	1.50	175.8	40.0
2.00	4.1	1.8	2.00	48.9	40.8	2.00	159.8	52.5

Table S2. Speeds of bromodecane droplets in various surfactant concentrations, with and without 1 wt% fluorescent silica particles. To keep particle surface coverage as constant as possible across all conditions, droplets with surface coverage in the range of 30% to 50% ($\theta_c = 66$ to 90°) were used in these measurements. At least 6 droplets were measured and averaged for each condition. This data is plotted in **Figure 5a**.

Surfactant	Speed ($\mu\text{m/s}$)		Speed ($\mu\text{m/s}$)	
	With Particles	Stdv	No Particles	Stdv
1 wt% SDS	5.9	1.4	2.8	1.56
10 wt% SDS	117.3	15.8	3.7	1.2
15 wt% SDS	288.6	48.0	6.6	0.8
1 wt% SDS, 0.25 M NaCl	345.9	74.4	11.2	5.1
1 wt% CTAB	11.9	3.2	5.4	1.0
2.5 wt% CTAB	189.5	41.45	15.5	10.2
1 wt% CTAB, 0.25 M NaCl	251.6	42.9	16.9	8.0
0.5 wt% Triton X-100	256.9	29.5	48.9	17.1
0.5 wt% Triton X-100, 0.25 M NaCl	278.9	23.9	41.9	15.4
1 wt% Triton X-100	351.8	48.8	125.0	24.7

Table S3. Speeds of various brominated oil droplets with and without 1 wt% fluorescent silica particles in 0.5 wt% Triton X-100. To keep particle surface coverage as constant as possible across all conditions, droplets with particle surface coverage in the range of 30% to 50% ($\theta_c = 66$ to 90°) were used in these measurements. At least 6 droplets were measured and averaged for each condition. This data is plotted in **Figure 5b**.

Brominated oil	Speed ($\mu\text{m/s}$)		Speed ($\mu\text{m/s}$)	
	With Particles	Stdv	No Particles	Stdv
Brominated vegetable oil	9.2	3.9	2.5	0.5
Bromohexadecane	99.3	24.7	4.4	2.1
Bromododecane	241.3	14.8	69.7	12.0
Bromodecane	256.9	29.5	48.9	17.1
Bromooctane	223.5	23.8	12.4	5.8

Table S4. Solubilization rates of various brominated oils in Triton X-100 and bromodecane in various surfactants. Solubilization rates were quantified by measuring the change in droplet diameter over an hour in each surfactant condition. Surfactants labeled with an * indicate that the solution was supersaturated and the solution was handled carefully to not induce crystallization and no significant crystallization occurred during the measurement. Each measurement was collected for one droplet. Although we could not measure a significant change in the bromohexadecane droplet diameter within one hour, literature¹ indicates that hexadecane does solubilize in Triton X-100; we thus believe that the bromohexadecane is still solubilizing, just slowly. In comparison, we expect the brominated vegetable oil, which is highly viscous, solubilizes at a slower rate than the bromohexadecane.

Brominated oil	Surfactant concentration	Solubilization rate ($\mu\text{m/min}$)
1-Bromodecane	1 wt% SDS	0.035
1-Bromodecane	5 wt% SDS	0.095
1-Bromodecane	1 wt% SDS with 0.25 M NaCl	0.091
1-Bromodecane	5 wt% SDS with 0.25 M NaCl *	0.112
1-Bromodecane	1 wt% CTAB *	0.068
1-Bromodecane	2.5 wt% CTAB *	0.163
1-Bromodecane	1 wt% CTAB with 0.25 M NaCl	0.131
1-Bromodecane	2.5 wt% CTAB with 0.25 M NaCl	0.424
1-Bromooctane	0.5 wt% Triton X-100	0.412
1-Bromodecane	0.5 wt% Triton X-100	0.237
1-Bromododecane	0.5 wt% Triton X-100	0.136
1-Bromohexadecane	0.5 wt% Triton X-100	≤ 0.01
Brominated vegetable oil	0.5 wt% Triton X-100	< 0.01

Video S1. Transmission optical microscopy video of bromodecane droplets with 0.5 wt% H13L particles in 0.1 wt% Triton X-100. Video is played back in 6x speed.

Video S2. Fluorescence microscopy video of bromodecane droplets containing 2 wt% fluorescent particles dispersed 0.5 wt% Triton X-100 immediately after preparation by vortex mixing and added to an imaging chamber containing surfactant. The particles are initially dispersed inside the droplets, but over time, the particles accumulate at the droplet surface and aggregate in a cap at the rear pole of the droplet. Droplets begin to move when the interfacial particle cap forms. Video is played back in 2x speed.

Video S3. Fluorescence microscopy video of bromodecane droplets with 2 wt% fluorescent particles dispersed in 0.5 wt% Triton X-100. Video is played back in 2x speed.

Video S4. Side-view transmission optical microscopy video of a bromodecane droplet in 0.1 wt% Triton X-100, without interfacially-adsorbed particles. Particles in the continuous phase are tracer particles used to visualize the flow around the droplet. The solubilizing droplet pumps fluid from top to bottom, and the drop does not move laterally. Video is played back at 3x speed.

Video S5. Side-view transmission optical microscopy video of a bromodecane droplet, with 1 wt% fluorescent particles, in 0.1 wt% Triton X-100. The droplet self-propels with the particle cap oriented perpendicular to the substrate. Occasionally the droplet translates perpendicular to the imaging plane so continuous refocusing is needed to follow the droplet motion. Video is played back at 3x speed.

Video S6. Side-view transmission optical microscopy video of a bromodecane droplet, with 1 wt% fluorescent particles, in 0.1 wt% Triton X-100. While similar to Video S5, here a droplet is seen where the cap orients largely parallel to the substrate, causing fluid pumping from top to bottom and preventing lateral motion. The rotation of the particle cap is critical to the droplet lateral translation. Video is played back at 3x speed.

Video S7. Bright field transmission optical microscopy video of bromodecane droplets with 0.5 wt% fluorescent particles in 2.5 wt% CTAB. Video is played back at 2x speed.

1. Zhong, H. *et al.* Aggregate-based sub-CMC solubilization of hexadecane by surfactants. *RSC Adv.* **5**, 78142–78149 (2015).