

Supporting Information

Detergency and its implications for oil emulsion sieving and separation

Thomas M. Schutzius,^{a,†} Christopher Walker,^{a,†} Tanmoy Maitra,^a Romy Schönherr,^a Christos Stamatopoulos,^a Stefan Jung,^a Carlo Antonini,^a Hadi Eghlidi,^a Julie L. Fife,^b Alessandra Patera,^b Dominique Derome,^c Dimos Poulikakos^{a,}*

^a Laboratory of Thermodynamics in Emerging Technologies, Department of Mechanical and Process Engineering, ETH Zurich, Sonneggstrasse 3, CH-8092 Zurich, Switzerland

^b Swiss Light Source, Paul Scherrer Institut, CH-5232 Villigen PSI, Switzerland

^c Laboratory for Multiscale Studies in Building Physics, Swiss Federal Laboratories for Materials Science and Technology, Empa, Überlandstrasse 129, CH-8600 Dübendorf, Switzerland

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[†] Denotes equal contribution

^{*} To whom correspondence should be addressed.

Prof. Dimos Poulikakos
ETH Zurich
Laboratory of Thermodynamics in Emerging Technologies
Sonneggstrasse 3, ML J 36
CH-8092 Zürich
SWITZERLAND
Phone: +41 44 632 27 38
Fax: +41 44 632 11 76
dpoulikakos@ethz.ch

Supplementary Information

Detergency mechanisms

Simulations have indicated that, after covering the water-oil interface, the excess surfactants interact with the oil molecules on the oil-substrate interface. This hydrophobic interaction of surfactant tails with the oil molecules provides the driving force for the “rolling up” effect and ultimately detachment [1]. It appears that this mechanism probably does not necessarily rely on the alteration of substrate-water interfacial energy, rather the gradual increase in the contact angle of the oil droplet can be attributed to the invasion of surfactant molecules to the oil-water interface as surfactant-laden water is able to penetrate between the oil and solid phase and ultimately provides an intermediary layer of surfactant molecules between the oil drop and the substrate.[2-4]

Alternatively, depending on the substrate characteristics, the surfactant may be adsorbed at the water-substrate interface and ultimately affect the water-substrate interfacial tension. The adsorption of surfactants at solid-liquid interfaces is however much more complex than surfactant adsorption at air-liquid or liquid-liquid interfaces due to the wider range of molecular interactions that can occur between solid and surfactant molecules [5]. In the case of ionic surfactants, which is of pertinence to SDS (due to the anionic nature of its hydrophobic head), the interactions that govern the adsorption process are not only determined by the hydrophilic/phobic nature of the substrate, but also determined by possible electrostatic forces between the surfactant and the substrate [6].

Droplet distribution

The terminal velocity of a fluid sphere of radius $d/2$, density $\bar{\rho}$, and viscosity $\bar{\mu}$ moving freely under gravity through an immiscible fluid that is otherwise undisturbed of density ρ and viscosity μ can be written as [7]

$$\mathbf{V} = \frac{1}{3} \frac{(d/2)^2}{\nu} \mathbf{g} \left(\frac{\bar{\rho}}{\rho} - 1 \right) \frac{\mu + \bar{\mu}}{\mu + \frac{3}{2}\bar{\mu}},$$

where $\nu = \mu / \rho$ is the kinematic viscosity of the surrounding fluid and $\mathbf{g} = g\hat{\mathbf{z}}$ is the acceleration due to gravity. If the surrounding fluid is flowing with a uniform velocity, $\mathbf{u} = u\hat{\mathbf{z}}$, then the above equation can be re-written as

$$V_z = \frac{1}{3} \frac{(d/2)^2}{\nu} g \left(\frac{\bar{\rho}}{\rho} - 1 \right) \frac{\mu + \bar{\mu}}{\mu + \frac{3}{2}\bar{\mu}} + u,$$

where $V_z = \mathbf{V} \cdot \hat{\mathbf{z}}$ and $u - V_z$ is the flow velocity relative to the object. For the situation where the fluid is flowing in the opposite direction of the fluid sphere ($u < 0$ and $V_z > 0$) there should be a critical sized sphere (diameter, d_c) that experiences no net motion ($V_z = 0$). This can be written as

$$\frac{d_c}{2} = \sqrt{-\frac{3u\nu}{g(\bar{\rho}/\rho - 1)} \frac{\mu + \frac{3}{2}\bar{\mu}}{\mu + \bar{\mu}}}.$$

In this study, we investigated hexadecane droplets in a water environment; therefore, the above variables have the following values: $\bar{\rho} = 0.77 \text{ g cm}^{-3}$, $\bar{\mu} = 0.03 \text{ Poise}$, $\rho = 1.0 \text{ g cm}^{-3}$, and $\mu = 8.9 \cdot 10^{-3} \text{ Poise}$ [8]. With this, we can now plot d_c vs. u , as shown by Figure 5. In order to investigate the sieving effect for our experimental conditions—mesh wire spacing, $w \approx 20\mu\text{m}$ —

we selected a value of u such that we would observe a large number of droplets, N , where $d > w$. Therefore, we chose $u \approx -0.35 \text{ mm s}^{-1}$.

Separation efficiency

The manufacturer of the commercial filter that we purchased (GxF/PSF 0.45 μm pore size, 25 mm diameter) states that to achieve a flow rate of 195 mL min^{-1} (Q_1) with water, the pressure differential across the filter should be -2.1 bar (Δp_1). To estimate the value of the pressure differential across the filter in our experiment (Δp_2)—assuming no clogging—we can use Darcy’s law, which relates flow rate, Q , to pressure differential, Δp , for flows in porous media, as

$$Q = -\frac{\kappa A \Delta p}{\mu L},$$

where κ is the permeability of the medium, A is the cross-sectional area of the filter, and L is the thickness of the filter. When comparing our experiment with the manufacturers, $\kappa A / (\mu L)$ remains unchanged; therefore, there is a linear relationship between Q and Δp . In the experiment that we conducted in Figure 7, where we demonstrated complete separation of microscale droplets from an emulsion, we had a mean flow rate of 12 mL min^{-1} (Q_2).

Substituting into Darcy’s Law using the manufacturer’s values and our values, we obtain

$$Q_1 = -\frac{\kappa A \Delta p_1}{\mu L} \text{ and } Q_2 = -\frac{\kappa A \Delta p_2}{\mu L} \text{ respectively, which can be simplified in terms of } \Delta p_2 \text{ as a set}$$

of a system of equations to $\Delta p_2 = \Delta p_1 \frac{Q_2}{Q_1}$. Substituting the manufacturer’s numerical values and

our flow rate, we calculate Δp_2 to be -0.13 bar. Based upon Q_2 , A , and Δp_2 we calculate a separation flux of $\sim 11,000 \text{ L m}^{-2} \text{ hr}^{-1} \text{ bar}^{-1}$ ($A = 491 \text{ mm}^2$).

Figures

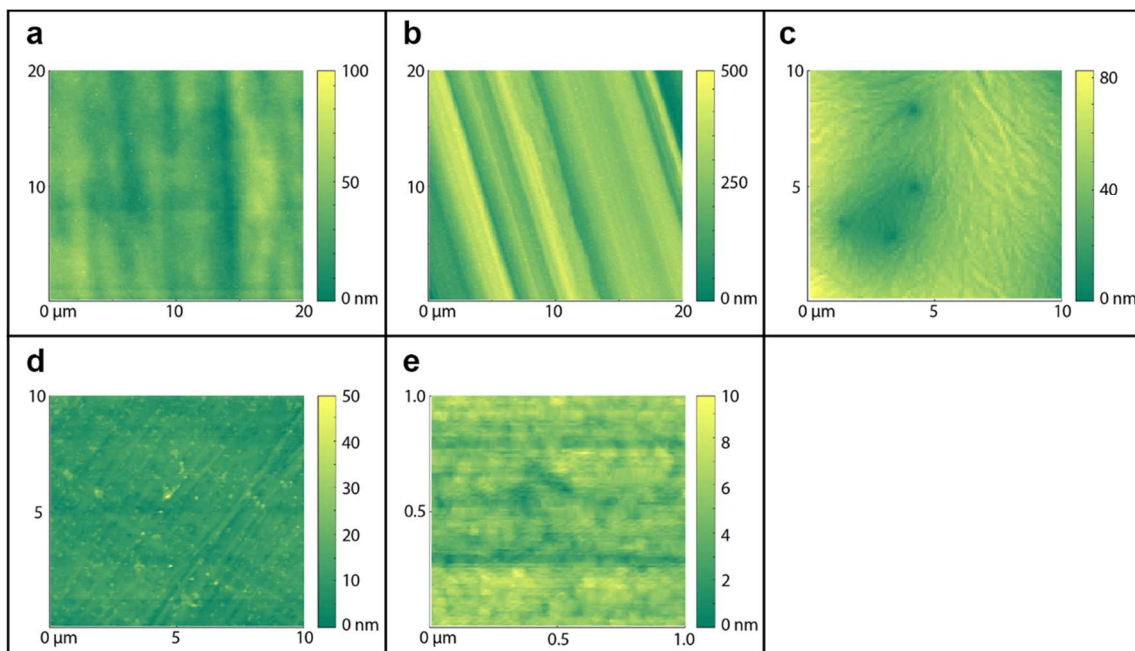


Figure S1. Micrographs obtained with atomic force microscopy (AFM) of surfaces used for contact angle measurements. The surfaces depicted in the micrographs are **a**, aluminum, **b**, stainless steel, **c**, PVDF, **d**, PMMA, **e**, glass.

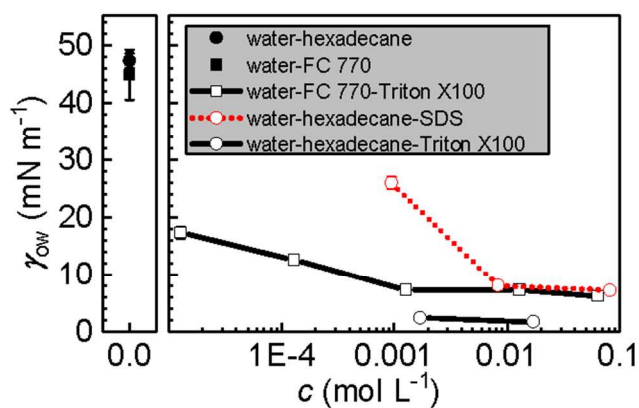


Figure S2 Effect of surfactant concentration in water (c) on the interfacial tension between oil and water. Interfacial tension, γ_{ow} , for FC 770-water (■ and □) and hexadecane-water (●, ○, and ○) interfaces without (■ and ●) and with (□ and ○, ○) surfactant. We made the following water-oil-surfactant mixtures: water-FC 770-Triton X 100 (—□—), water-hexadecane-Triton X-100 (—○—), and water-hexadecane-sodium dodecyl sulfate (SDS, --○--). The interfacial

energy was determined by the pendant droplet technique. The critical micelle concentrations (CMC) are $8\text{E-}3 \text{ mol L}^{-1}$ [9] and $0.22\text{E-}3 \text{ mol L}^{-1}$ [10] for SDS and Triton X-100, respectively.

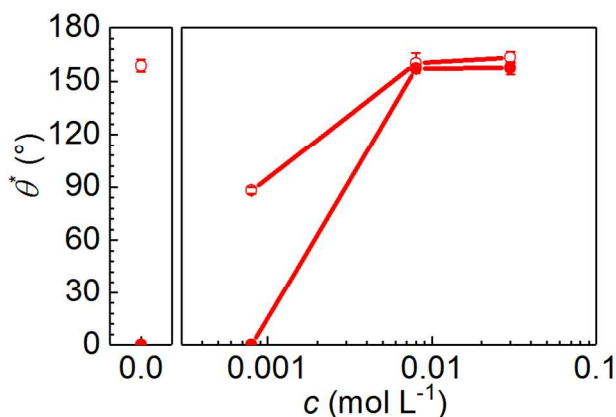


Figure S3. The effect of surfactant concentration on the underwater wetting behavior of hexadecane on aluminum. Plot of advancing (\circ) and receding (\bullet) underwater hexadecane contact angle on aluminum as a function of sodium dodecyl sulfate (SDS) concentration. The CMC concentration of SDS is $0.0082 \text{ mol L}^{-1}$.

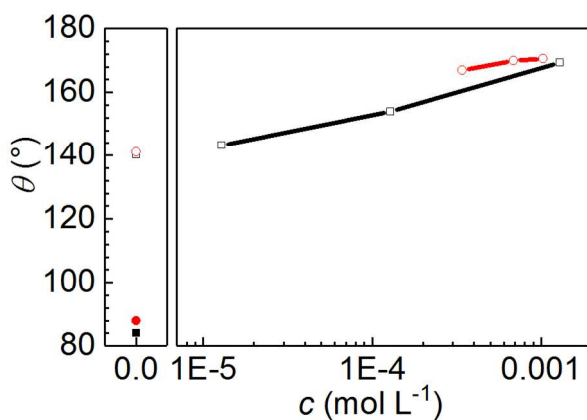


Figure S4 Effect of surfactant concentration (Triton X-100) in water on the wetting behavior of FC 770 oil droplets on metallic substrates. Square (black) data points represent stainless steel, circular (red) data points represent aluminum, non-filled data points represent advancing contact angles and filled data represent receding contact angles.

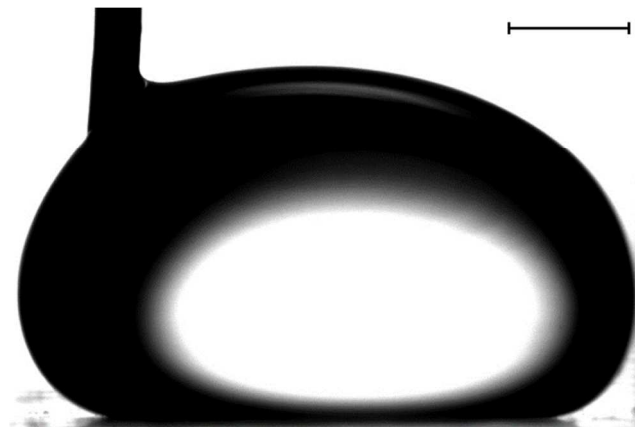


Figure S5. Underwater hexadecane contact angle measurement on PMMA (image is rotated 180° for clarity). The scale bar is 1.0 mm. SDS 0.03 mol L⁻¹.

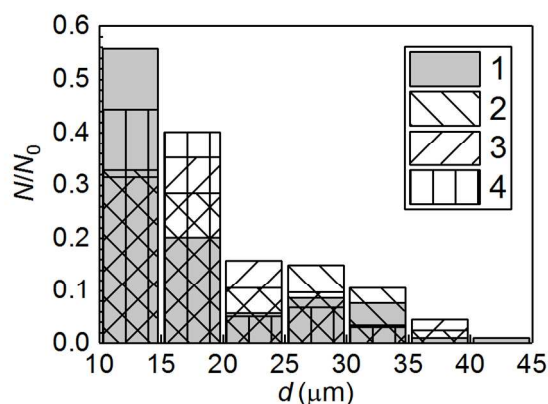


Figure S6. Plot of the relative frequency of oil droplet diameters in a surfactant stabilized oil-in-water emulsion for four separate experiments (see legend). Here, the emulsion flows in the direction opposite to that of the force due to buoyancy acting on the oil droplets ($\bar{\rho} < \rho$, where $\bar{\rho}$ and ρ are the density of oil and water, respectively). The emulsion had a concentration of ~4 wt.% hexadecane and its flow rate was 382 $\mu\text{L min}^{-1}$ in a pipe of diameter $D = 4.8$ mm; therefore, the mean flow velocity was $u = -0.35$ mm s⁻¹ and $Re_D = \rho|u|D/\mu = 1.9$, where μ is the viscosity of water. Surfactant concentration: SDS 0.03 mol L⁻¹.

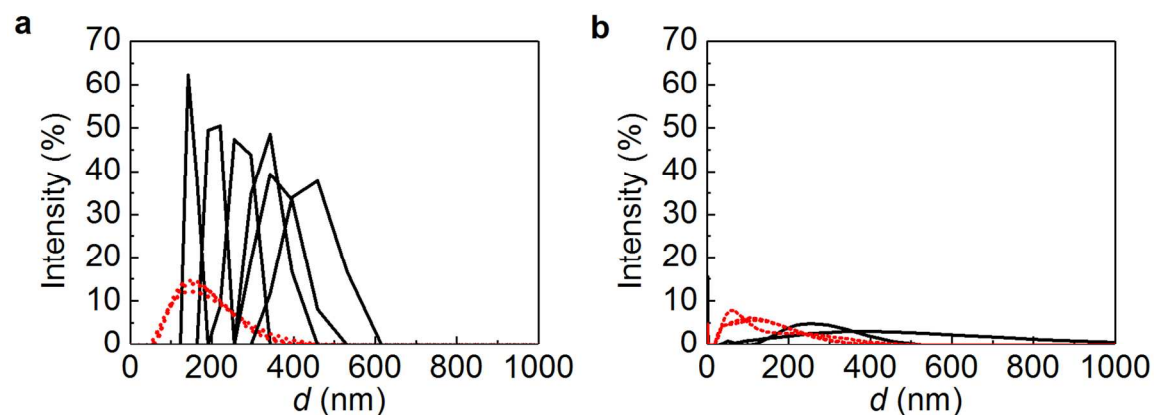


Figure S7. Dynamic light scattering characterization of surfactant stabilized oil-in-water emulsions before and after filtering (sub-micron pore size). **a**, Intensity vs. effective diameter for surfactant stabilized (SDS 0.03 mol L⁻¹) oil-in-water emulsions (5 wt.% hexadecane) before (—) and after (---) filtering with a sub-micron filter (pore size 450 nm). **b**, Control experiment: Intensity vs. effective diameter for an aqueous surfactant solution (SDS 0.03 mol L⁻¹) before (—) and after (---) filtering with a sub-micron filter (pore size 450 nm).

Videos

Suppl. Video 1. PMMA substrate initially wet with hexadecane then submerged into an aqueous surfactant solution (SDS 0.03 mol L^{-1}). Note the increase in the contact angle with time (initial contact angle was 0°). The playback rate is real-time.

Suppl. Video 2. Sieving a surfactant stabilized oil-in-water emulsion: Demonstrating droplet “blocking”. The emulsion consists of hexadecane, water, and sodium dodecyl sulfate (0.03 mol L^{-1}). The hexadecane droplets contain a fluorescent dye to facilitate imaging. Here, the droplet diameter is too large and it is blocked by the small pore size. The stainless steel mesh (635) is false colored yellow.

Suppl. Video 3. Sieving a surfactant stabilized oil-in-water emulsion: Demonstrating droplet “passing”. The emulsion consists of hexadecane, water, and sodium dodecyl sulfate (0.03 mol L^{-1}). The hexadecane droplets contain a fluorescent dye to facilitate imaging. Here, the droplet diameter is small enough to pass through the mesh pore. The stainless steel mesh (635) is false colored yellow.

Suppl. Video 4. Natural oil separation behavior from an oil-in-water emulsion (5 wt.%) due to buoyancy with and without the presence of surfactant (SDS 0.03 mol L^{-1}). Emulsion was prepared by mechanically mixing with a magnetic stir bar at 1500 s^{-1} .

Suppl. Video 5. Heavy oil droplet (FC-770) resting on an aluminum mesh (20 mesh) is initially in a water environment (20 mL) that is exposed to a water-surfactant solution (Triton X-100, 0.06 mol L^{-1}), which is being introduced into the water environment at a rate of $100 \mu\text{L min}^{-1}$.

Suppl. Video 6. Separating a surfactant (0.03 mol L^{-1} SDS in water) stabilized hexadecane-in-water emulsion ($\sim 5 \text{ wt.}\%$ hexadecane) with a commercially available filter with a minimum pore size of 450 nm. The emulsion volumetric flux was $\sim 1,800 \text{ L m}^{-2} \text{ hr}^{-1}$.

Supplementary Information References

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