Electronic Supplementary Material (ESI) for Soft Matter.

Supplementary Information for "Steady-state droplet size in montmorillonite stabilised emulsions"

1 Calculation of Flow Parameters for the Ultra Turrax Mixer

To characterise the flow regime within which the emulsions are formed the bulk and droplet Reynold numbers (Re and $\mathrm{Re_d}$), the energy dissipation rate (ϵ) and Kolmogorov microscale (λ) were calculated.

The Reynolds number is defined by equation 1:

$$\mathrm{Re} = \frac{\rho v L}{\eta} \tag{1}$$

where ρ, v and η are the fluid density, velocity and viscosity respectively and L is a characteristic distance.

The continuous phase is composed mostly of water so $\rho = 1000$ kg m^{-3} and $\eta =$ 1 mPa s. The droplet phase is hexadecane where $\rho = 770$ kg m^{-3} and $\eta = 3.3$ mPa s [1]. The Ultra Turrax IKA T18 with a S18-10G dispersing element was operated at a tip speed of 8.6 m s^{-1} and the rotor diameter is 7.5 mm [2]. Substituting these values into equation 1 gives Re = 64500 and $\mathrm{Re_d} = 10.0$ where $L = 7.5$ mm and 10 μm respectively.

The energy dissipation rate for a slotted rotor-stator was estimated by Brocart *et al.* [3] and Fradette *et al.* [4] to be:

$$\epsilon = \frac{(2\pi D N)^3}{4a} \tag{2}$$

where D is the rotor diameter, N is the rotation speed and a is the distance between two slots in the stator. Using values $D = 7.5$ mm, $N = 22000$ rpm and $a = 2$ mm equation 2 gives an energy dissipation rate of 6.45×10^5 W kg^{-1}.

Using this information the Kolmogorov microscale can be calculated. This is the smallest size (corresponding to the highest energy density) of eddy present in a turbulent flow and is given by [5]:

$$\lambda = \frac{\eta^{\frac{3}{4}}}{\rho^{\frac{3}{4}}\epsilon^{\frac{1}{4}}} \tag{3}$$

where symbols are as defined above. Equation 3 therefore gives $\lambda = 1.1$ μm.

2 Calculations of Adsorption Energy and Kinetic Energy in Turbulent Flow

During mixing the kinetic energy of the fluid is transferred to the various components of the emulsion. If this kinetic energy could at any point exceed the energy of adsorption of platelets at the droplet interface then desorption during mixing could occur.

The energy of adsorption of a platelet at a planar oil-water interface is given by:

$$E_{\mathrm{ads}} = A_p \gamma_{\mathrm{ow}} (1 - |\cos(\theta)|) \tag{4}$$

where A_{p} is the area the platelet occupies at the interface, γ_{ow} is the oil-water interfacial tension and θ is the three-phase contact angle between oil, water and particle. A_{p} is approximated by assuming a disk-like particle with a radius of 150 nm [6], γ_{ow} is known to be approximately 0.05 N m^{-1} [7] and θ is not known but a range of energies can be calculated assuming θ lies between 50^{o} and 90^{o}. This gives a range in E_{ads} of 1.3×10^{-15} J to 3.6×10^{-15} J.

Given $\epsilon = 6.45 \times 10^5$ W kg^{-1} the power input to a typical droplet (10 μm diameter) in the high energy dissipation region can be estimated as being $\sim 10^{-7}$ W. Naively assuming that all of this power may go into causing particle desorption, a rate can be estimated as $\frac{10^{-7}\ \mathrm{W}}{E_{\mathrm{ads}}} \sim 10^8\ \mathrm{s}^{-1}$ (similar conclusions were reached by Phipps and Gittins [8]). Since the mechanisms of desorption under turbulent flow are unknown this is an absolute upper bound as there are many possible energy dissipation pathways in this system and, for instance, the model in the main text predicts a rate 3 orders of magnitude lower. It does show however that there is sufficient energy present under the experimental flow conditions for the particles to be forced off as well as on to the oil/water interface.

3 Continued Coalescence at Lower Oil Volume Fraction

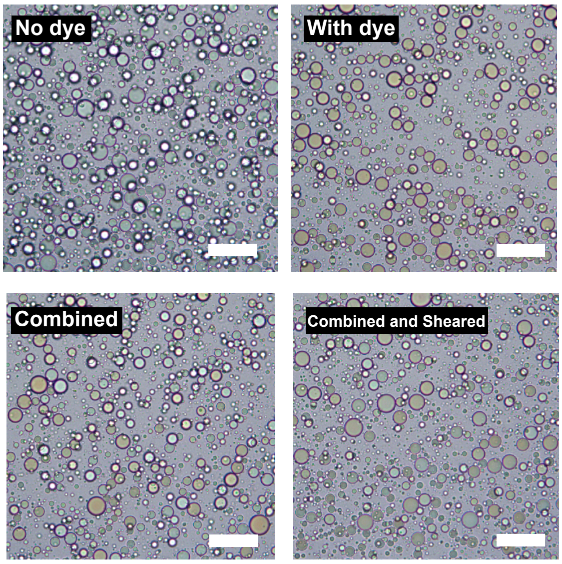

Figure S1: BF microscopy of emulsions ($\phi_o = 0.128$, $\phi_p = 0.0098$) where some droplets were dyed with Sudan II. Top shows undyed (left) and dyed (right) emulsions. Bottom shows that the dye does not redistribute upon simple mixing (left) but does upon high shear mixing (right).

Figure S1 shows continued coalescence experimental similar to that shown in figure 7 in the main paper but at $\phi_o = 0.128$.

4 Wide Angle X-ray Scattering of an Emulsions

Small angle X-ray scattering in figure 2 of the main text shows an absence of correlations related to particle stacking but a slight deviation from the $I(Q) \propto Q^{-2}$ at high Q in the emulsion sample. This was investigated by probing the sample at wider angles and figure S2 shows X-ray scattering of an emulsion at two sample to detector distances.

The $I(Q) \propto Q^{-2}$ scaling at low Q is characteristic of two dimensional plate-like objects. The feature at $Q = 1.46$ Å^{-1} is characteristic of hydrocarbon chain to chain

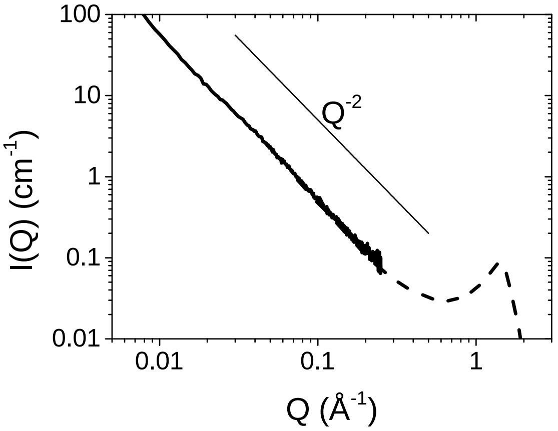

Figure S2: X-ray scattering of montmorillonite stabilised hexadecane-in-water emulsion (ϕ_o = 0.358, $\phi_{\mathrm{p}=0.0048}$). Different line styles correspond to different sample-to-detector distances.

separation [9]. The lack of any features below Q = 0.628 Å^{-1}, corresponding to distances larger than the platelet thickness of 1 nm through the relation $Q = \frac{2\pi}{D}$, indicates that there is no stacking of platelets and hence they form a monolayer at the oil-water interface and are fully exfoliated in suspension.

5 Polarising Optical Microscopy of Sodium Dodecyl Sulphate Stabilised Emulsion

As a control experiment 1 mL hexadecane was emulsified into 9 mL of a 10 mM solution of sodium dodecyl sulphate(SDS) by vortex mixing at something rpm for 30 s. Figure S3 shows microscopy of this emulsion using differential interference contrast and polarising optical microscopy. There is an absence of features under polarising optical microscopy for emulsion droplets that do not have montmorillonite platelets at the interface.

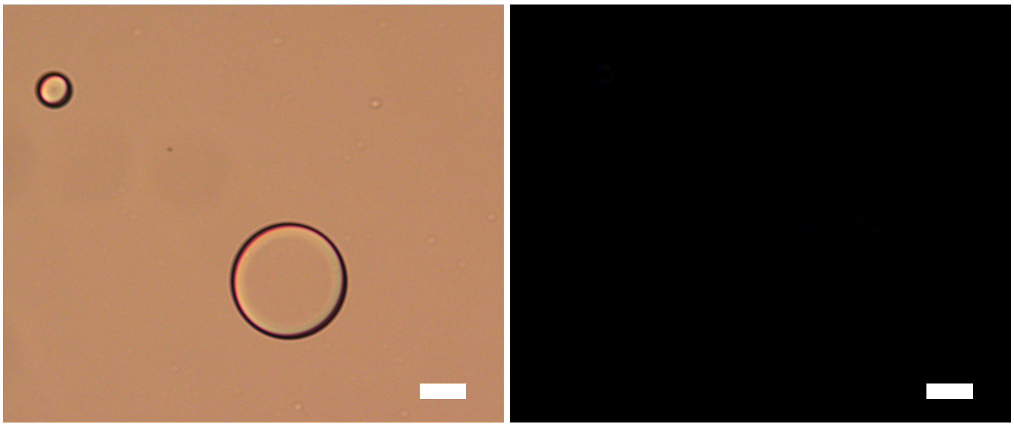

Figure S3: DIC (left) and POM (right) of hexadecane-in-water emulsion ($\phi_o = 0.1$), aqueous phase contains 10 mM SDS and scale bars represent 20 μm.

6 Droplet Size Histograms

Figures S4 to S6 show droplet size histograms corresponding to data points in figures 5 and 6 in the main text. At least 100 droplets were measured for each with the help of the Linear Intercept software package (TU Darmstadt). Microscopy images can be found in data repository.

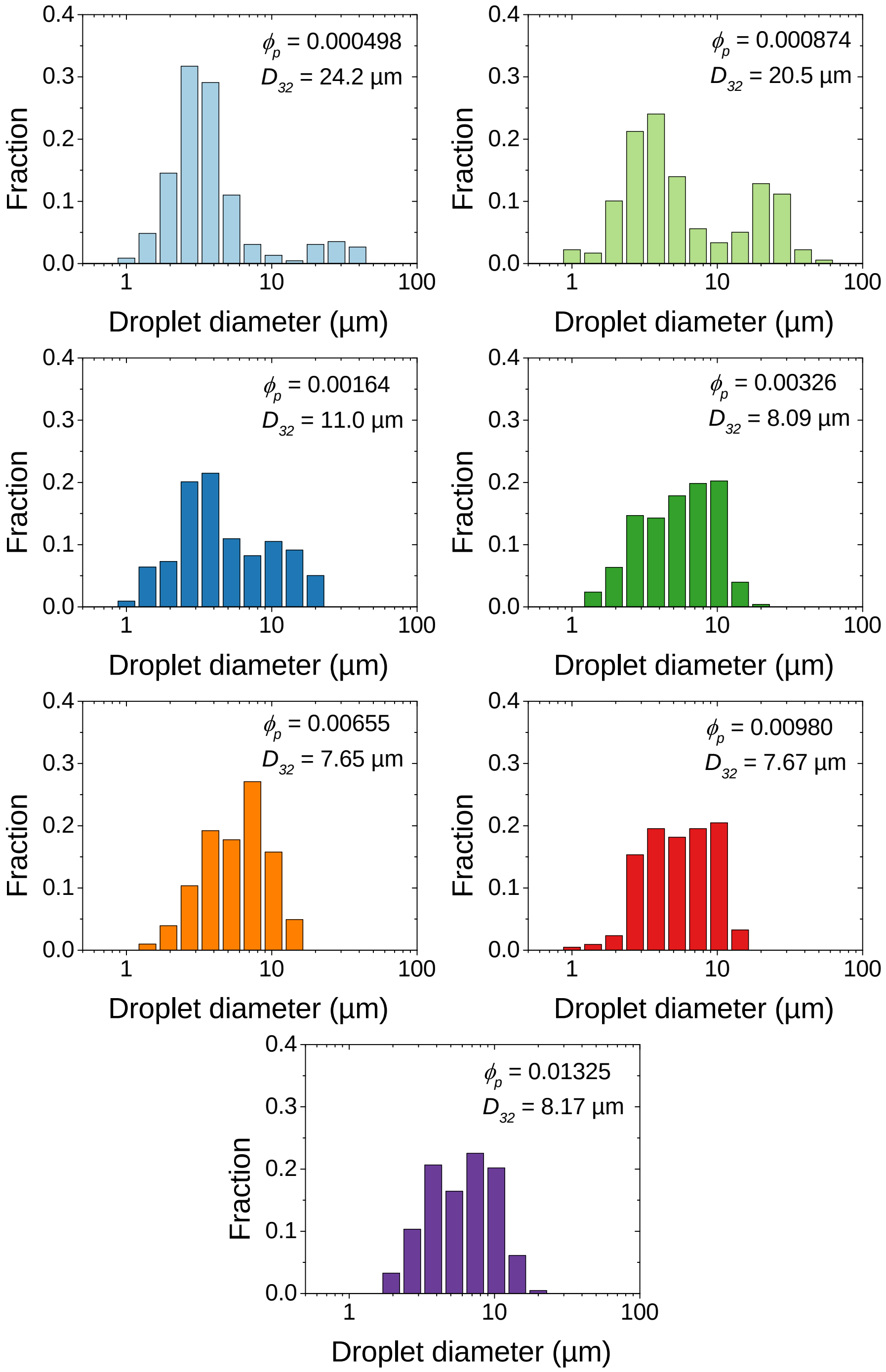

Figure S4: Droplet size histograms for emulsions prepared at $\phi_{\mathrm{o}} = 0.13$.

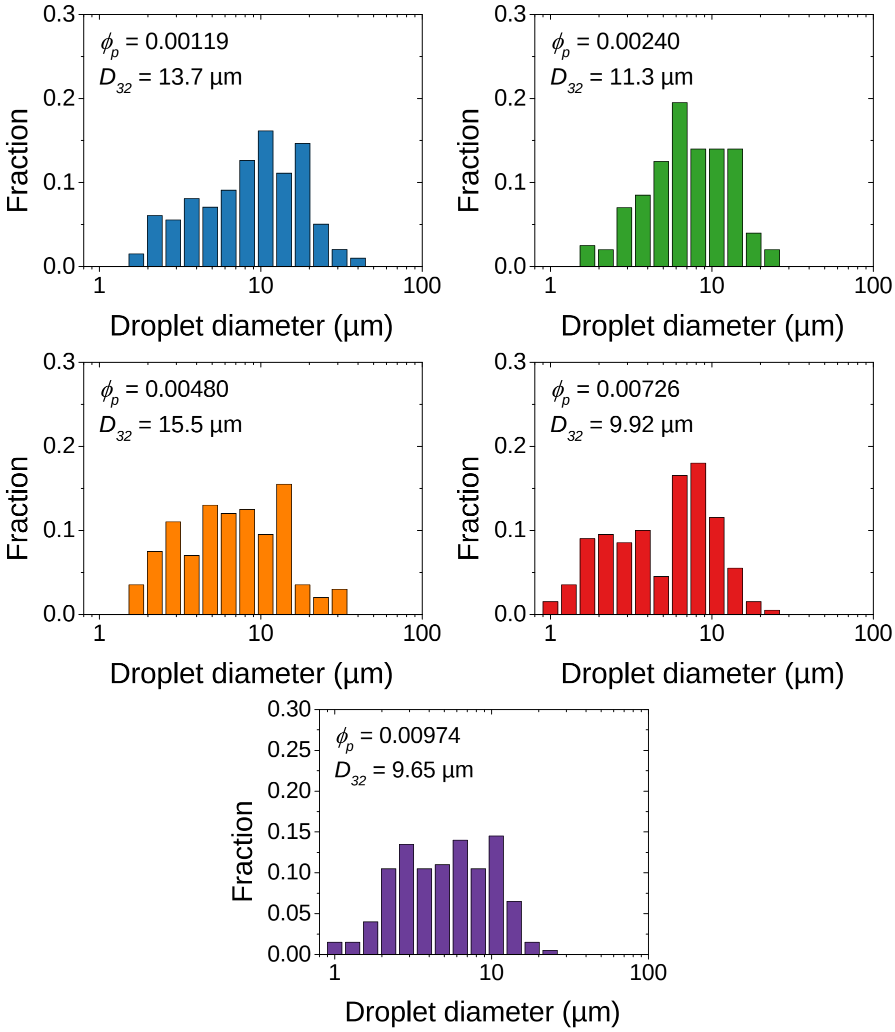

Figure S5: Droplet size histograms for emulsions prepared at $\phi_o = 0.36$.

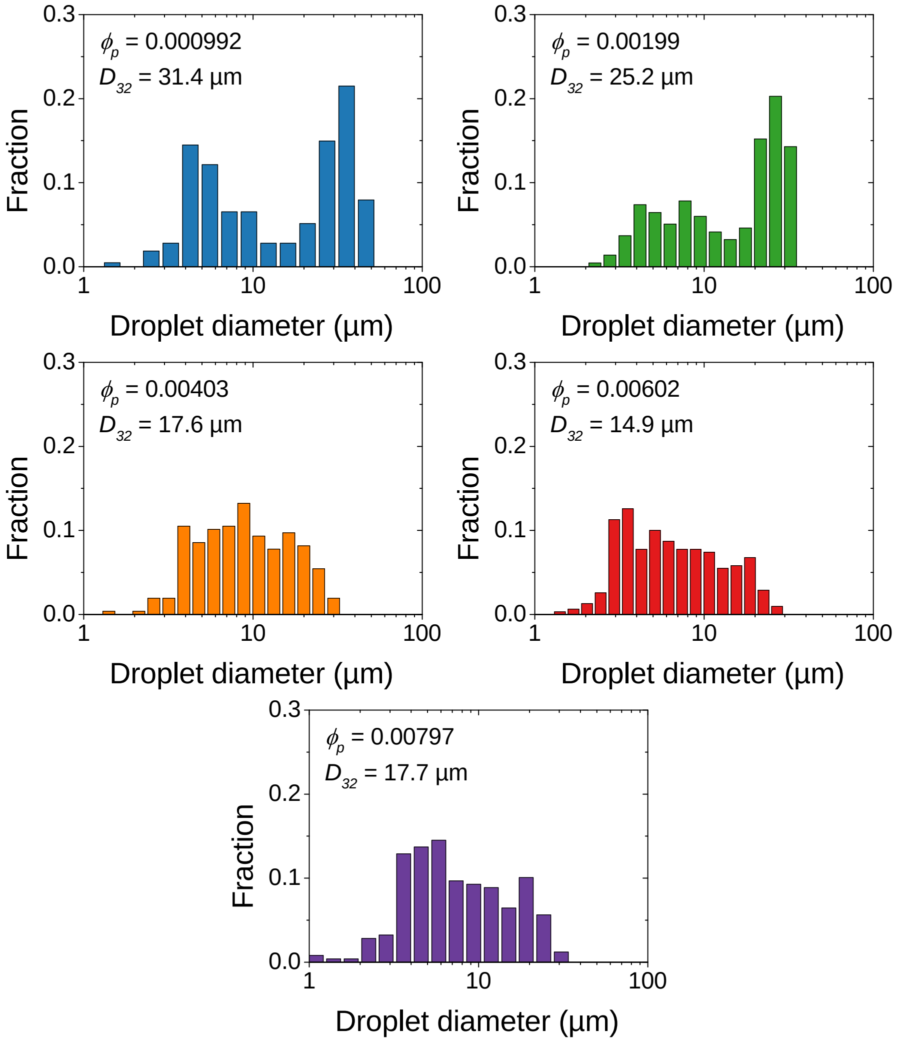

Figure S6: Droplet size histograms for emulsions prepared at $\phi_o = 0.47$.

References

[1] Hexadecane ReagentPlus® 99% (2015). `http://www.sigmaaldrich.com/catalog/product/sial/h6703` [Online; accessed 30-August-2015].

[2] T 18 digital ULTRA-TURRAX®(2015). `http://www.ika.com/owa/ika/catalog.accessory_data?iProduct=3720000` [Online; accessed 30-August-2015].

[3] B. Brocart, P. A. Tanguy, C. Magnin, J. Bousquet, *Journal of Dispersion Science and Technology* **23**, 45 (2002).

[4] L. Fradette, B. Brocart, P. Tanguy, *Chemical Engineering Research and Design* **85**, 1553 (2007).

[5] P. Walstra, P. Smulders, *Modern Aspects of Emulsion Science* (Royal Society of Chemistry, Cambridge, 1998).

[6] L. J. Michot, *et al.*, *Langmuir* **20**, 10829 (2004).

[7] A. Goebel, K. Lunkenheimer, *Langmuir* **13**, 369 (1997).

[8] J. S. Phipps, D. I. Gittins, *Agro FOOD Industry Hi Tech* **27**, 60 (2016).

[9] G. Stewart, *Physical Review* **31**, 174 (1928).