Effect of surfactant concentration on diffusion and microstructure in water-in-oil emulsions studied by low-field benchtop NMR and optical microscopy

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Supporting Information

Rheological measurements

Continuous tests on water solutions and emulsions were carried out at room temperature using a stress-controlled rheometer (Anton Paar Physica MCR 301 Instruments) equipped with a titanium double-gap measuring system (DG 26.7/TI-SN9317). Measurements were performed imposing a shear stress ranging from approximately 10^{-2} to 5 Pa for Brij 58 aqueous solutions and from 10^{-3} to 300 Pa for soybean oil. Flow curves were recorded using 30 measurement data points with a sampling time of 10 s. Both viscosity curve of surfactant and soybean oil exhibit a Newtonian behaviour with the viscosity constant as a function of the shear rate. In particular, soybean oil shows a viscosity of about 60 cP, while surfactant water solutions exhibit a viscosity slightly higher than pure water, around 1.2-1.5 cP. Emulsion flow curves exhibit a slight shear thinning around 1 s^{-1} followed by a plateau value over the entire range of shear rates investigated. For the sake of brevity only two emulsions, at highest surfactant concentrations, are investigated (see Supplementary Information, Figure S1).

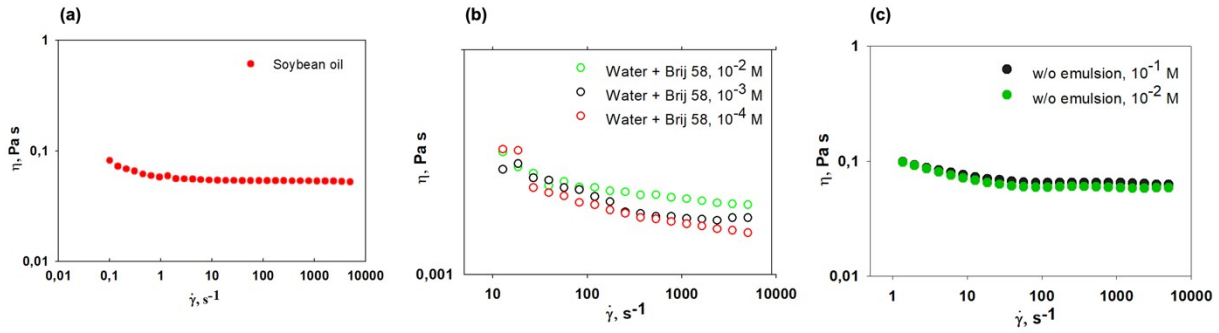

Figure S1. Steady shear measurements of viscosity η as a function of the shear rate $\dot{\gamma}$ for (a) Soybean oil, (b) Brij 58 aqueous solutions at 10^{-2}, 10^{-3} M and 10^{-4} M and (c) w/o emulsions at 10^{-1} M and 10^{-2} M.

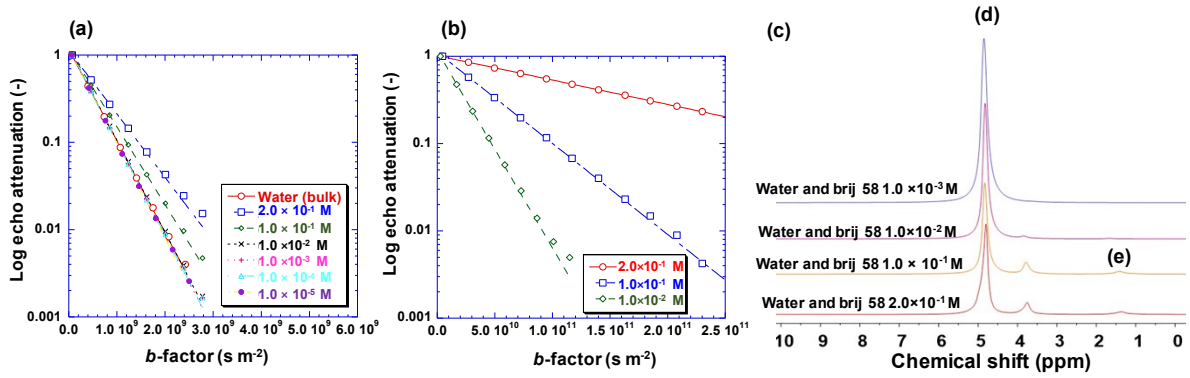

Figure S2. (a) PGSTE plot for bulk liquid (water) and solutions at different concentration of Brij 58. (b) PGSTE plot for NMR signal for Brij 58. (c) ^{1}H spectra of solution water plus Brij 58 peak (d) represents water, peak (e) represents Brij 58.

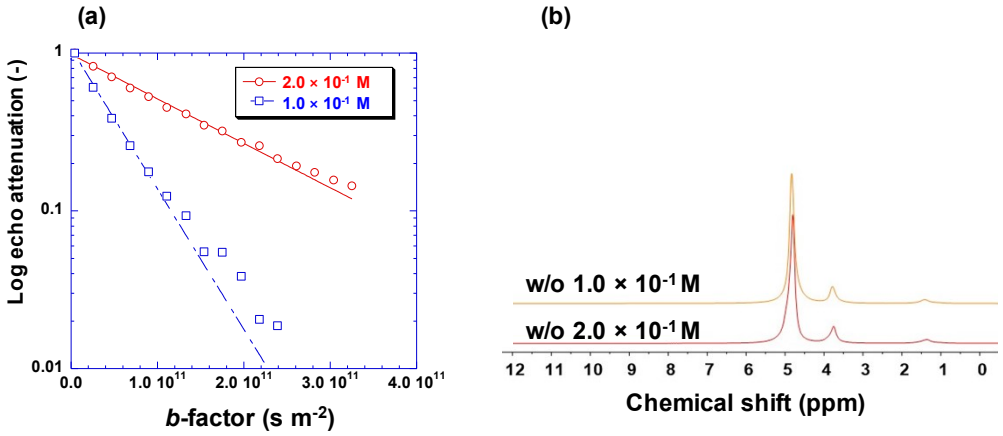

Figure S3. (a) PGSTE for Brij 58 in the emulsions 2×10^{-1} M and 10^{-1} M, respectively. (b) ^{1}H spectra of Brij 58 in water mixtures with the region between 3.5-4 ppm represents the NMR signal for Brij 58.

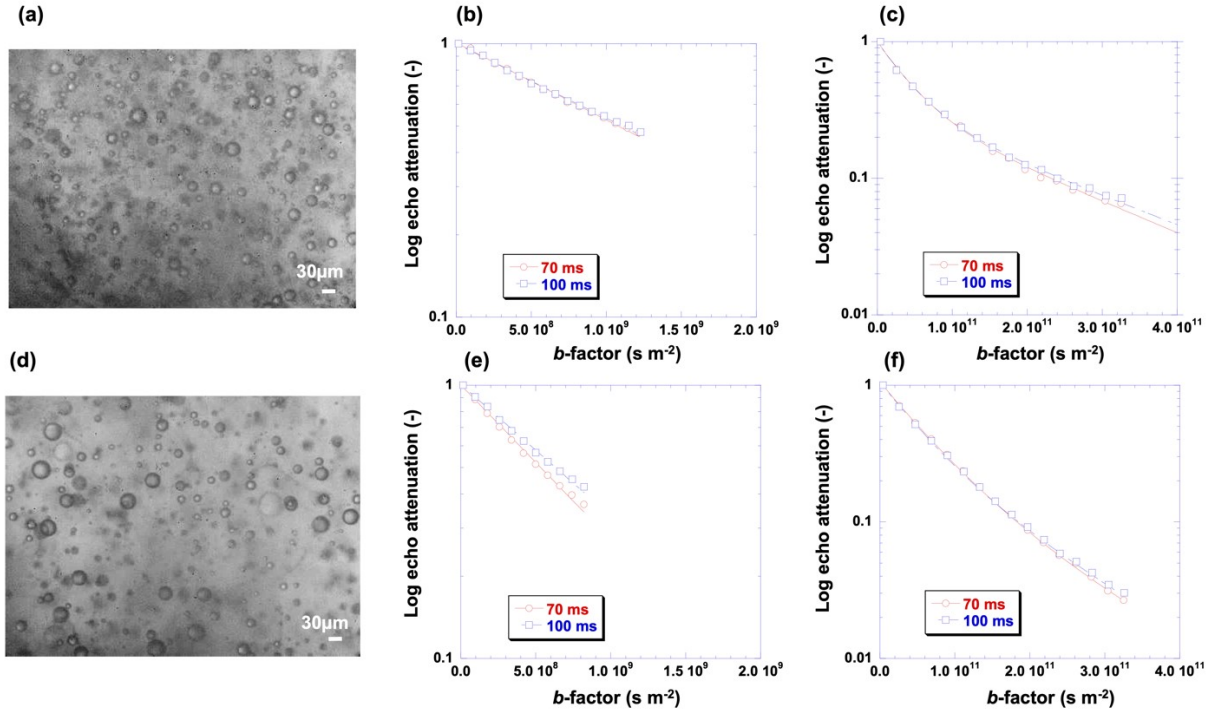

Figure S4. (a) Optical microscopy image at 10^{-1} M surfactant concentration and associated PGSTE plots at (b) data at low *b*-factor values and (c) data at high *b*-factor values; (d) optical microscopy image at 10^{-4} M surfactant concentration and associated PGSTE plots at (e) low *b*-factor values and (f) high *b*-factor values. Solid lines are fittings to Equation (1) with n = 1 for (b) and (e) and n = 2 for (c) and (f). The scale bar is 30µm.

Table S1
Self-diffusion coefficient for pure water, water in solution with Brij 58 and for Brij 58 in emulsions and in solution with water.

Sample	Water Diffusion coefficient [$m^2 s^{-1}$] $\times 10^9$	Brij 58 in solution Diffusion coefficient [$m^2 s^{-1}$] $\times 10^{11}$	Brij 58 in emulsion Diffusion coefficient [$m^2 s^{-1}$] $\times 10^{11}$
Water (bulk)	2.42	-	-
Water + Brij 58 2×10^{-1} M	1.67	0.64	0.65
Water + Brij 58 10^{-1} M	2.05	2.40	2.05
Water + Brij 58 10^{-2} M	2.43	5.19	-
Water + Brij 58 10^{-3} M	2.47	-	-

Table S2
Average droplet size for the emulsions studied in this work.

Emulsion concentration [M]	Droplet size *d* [µm]
2×10^{-1}	10
10^{-1}	10
10^{-2}	20
10^{-3}	30
10^{-4}	30
10^{-5}	35

Table S3
Self-diffusion coefficient values for oil, water slow component and water fast component.

Emulsion concentration [M]	**Observation time [ms]**	**Diffusivity [$m^2 s^{-1}$] $\times 10^{11}$** Oil	**Diffusivity [$m^2 s^{-1}$] $\times 10^{10}$** Water Fast component	**Diffusivity [$m^2 s^{-1}$] $\times 10^{11}$** Water Slow component
2×10^{-1}	70	2.30 ± 0.04	4.15 ± 0.04	0.21 ± 0.01
10^{-1}	70	2.20 ± 0.04	6.49 ± 0.14	0.19 ± 0.02
10^{-2}	70	2.11 ± 0.03	8.40 ± 0.20	0.44 ± 0.02
10^{-3}	70	1.98 ± 0.03	3.40 ± 0.22	0.71 ± 0.20
10^{-4}	70	1.74 ± 0.03	13.00 ± 0.78	0.76 ± 0.02
10^{-5}	70	1.76 ± 0.21	8.88 ± 0.73	0.87 ± 0.06