Electronic Supplementary Material (ESI) for Soft Matter.

Supplementary Information for:

Minimum Surfactant Requirements for Inducing Self-shaping of Oil Droplets and Competitive Adsorption Effects

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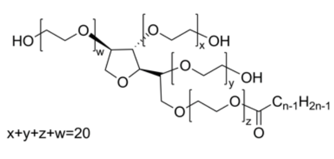
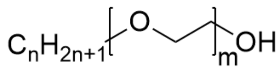
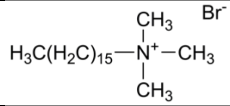
<u>Table S1.</u> Source (Sigma-Aldrich) and properties of the surfactants studied.

Non-ionic surfactants	**Non-ionic surfactant (trade name)**	**Number of C atoms, n**	**Number of EO groups, m**	**HLB**	**Structural formula**
Polyoxyethylene Sorbitan monoalkylate $C_nSorbEO_{20}$	Tween 20	12, 14, 16	20	16.7	
	Tween 40	16, 18	20	15.5	
	Tween 60	16, 18	20	14.9	
Polyoxyethylene alkyl ethers C_nEO_m	**Brij C10**	**16**	**10**	**12**	
	Brij S10	**18**	**10**	**12**	
	Brij 58	**16**	**20**	**15.7**	
	Brij S20	**18**	**20**	**15.3**	

Ionic surfactant	Abbreviation	Number of C atoms, n	Hydrophilic head group	Purity	Structural formula
Cetyltrimethyl-ammonium bromide	$C_{16}TAB$	16	$N^{+}(CH_3)_3Br^{-}$	> 99%	

Appendix

Composition of adsorption layer

Tween 20 and Tween 60 mix ideally in the micelles. Under this assumption we can calculate the free concentration of molecules of Tween 20 and Tween 60 in the solution by using eqs. (12) and (9) from Clint[1] together with the experimentally determined values for CMC of Tween 20 and Tween 60:

$$C_1^{\text{monomer}} = CMC_1 \frac{\sqrt{\left[\frac{C_{\text{tot}}}{CMC_1} - \left(\frac{CMC_2}{CMC_1} - 1\right)\right]^2 + 4x_1 \frac{C_{\text{tot}}}{CMC_1}\left(\frac{CMC_2}{CMC_1} - 1\right)} - \left[\frac{C_{\text{tot}}}{CMC_1} - \left(\frac{CMC_2}{CMC_1} - 1\right)\right]}{2\left(\frac{CMC_2}{CMC_1} - 1\right)}, \qquad (1a)$$

$$C_2^{\text{monomer}} = \left(1 - \frac{C_1^{\text{monomer}}}{CMC_1}\right) CMC_2 \qquad (1b)$$

Here, C_1^{monomer} and C_2^{monomer} are the free monomer concentration of Tween 20 and Tween 60 in the aqueous solution, x_1 is the molar fraction of Tween 20 and C_{tot} is the total surfactant concentration. Assuming that the molecular masses of Tween 20 and Tween 60 are 1228 g/mol and 1298 g/mol, we can calculate the free concentration of monomers in the solution. In order to estimate the ratio between Tween 20 and Tween 60 on the oil-water interface we used the expression for competitive adsorption on the interface assuming a Langmuir mixed adsorption isotherm[2]:

$$y_2 = \frac{\Gamma_2}{\Gamma_1 + \Gamma_2} = \frac{K_{A2} C_2^{\text{monomer}}}{K_{A1} C_1^{\text{monomer}} + K_{A2} C_2^{\text{monomer}}} \qquad (2)$$

where y_2 is the mole fraction of 2nd component (Tween 60) on the interface, Γ are the interface adsorptions of the respective components and K_A are the adsorption constants on the drop-water interface of the surfactant molecules, and C_1^{monomer} and C_2^{monomer} are the free monomer concentration of Tween 20 and Tween 60.

From interfacial tension isotherms we determined that CMC for Tween 20 is 0.0167 mM, whereas CMC for Tween 60 is 0.0108 mM. From the best fit of the experimental data around CMC we determined that Γ_{CMC} are 4.3 μmol/m^2 and 4.4 μmol/m^2 for Tween 20 and Tween 60, respectively. From the measured interfacial tensions below CMC by using the Langmuir adsorption isotherm we determined that the adsorption constants are 2200 m^3/mol and 1900 m^3/mol for Tween 20 and Tween 60, respectively. Using these values we determine the composition of adsorption layers given in Table S2.

The obtained results showed that the composition of the aqueous phase is close to the composition of the interface which is related to the fact that the determined CMC and adsorption constant of Tween 60 and Tween 20 do not differ significantly, which means that there is a significant fraction of long chain surfactants in Tween 20 which are able to adsorb on the solution surface and to decrease Tween-20's CMC.

Table S2

Wt. ratio in aqueous solution [Tween60]/[Tween20]	% Tween60	Free monomer concentration of Tween 60 in μM	Surface occupation by Tween 60 (%) From Eqn. 2	Appearance of self-shaping
1:73	1.35%	0.14	0.72	No
1:6.6	13.2%	1.3	7.4	No
1:3.28	23.4%	2.4	14	No
1:1	50%	5.2	35	Yes
2:1	66.7 %	7.1	51	Yes

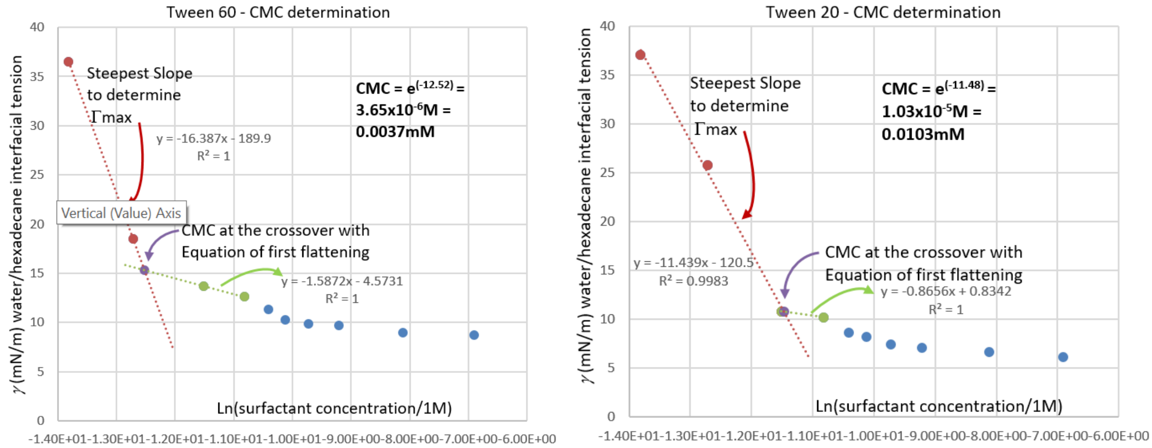


Figure S1. Adsorption isotherms for Tween 20 and Tween 60 at hexadecane-water interface at 20 °C.

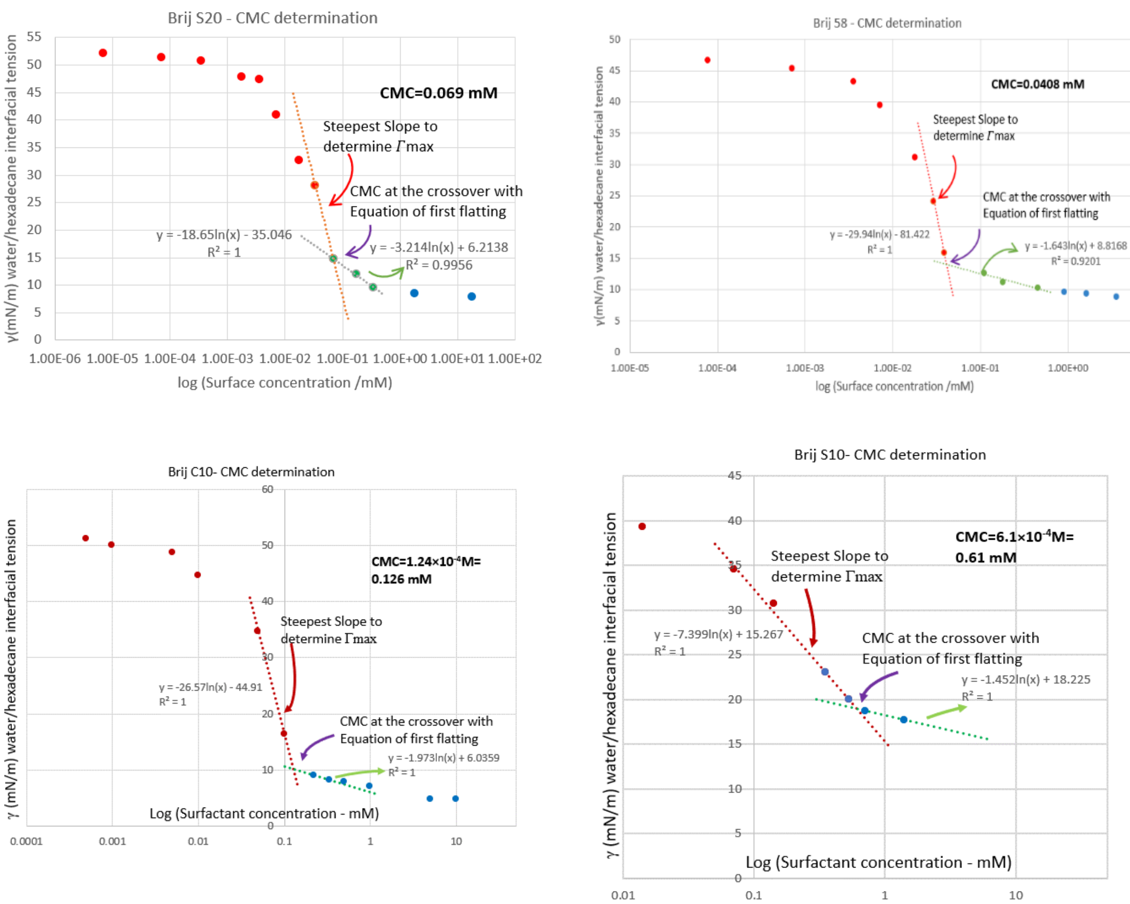


Figure S2. Adsorption isotherms for Brij S20, Brij 58, Brij C10 and Brij S10 at hexadecane-water interface at 20 °C.

Table S3

Surfactant	Concentration (mM)	Multiple of CMC	Appearance of self-shaping
Brij S20	0.21	3	Yes
	0.13	1.9	Yes
	0.034	0.49	Yes
	0.0093	0.13	No
Brij 58	0.41	10	Yes
	0.3	6.5	Yes
	0.06	1.3	Yes
	0.03	0.65	No
Brij S10	0.7	1.15	Yes
	0.5	0.86	Partially self-shaping
	0.35	0.57	Partially self-shaping
	0.14	0.23	No
Brij C10	0.5	3.96	Yes
	0.3	2.6	Yes
	0.2	1.7	Yes

	0.1	0.7	No

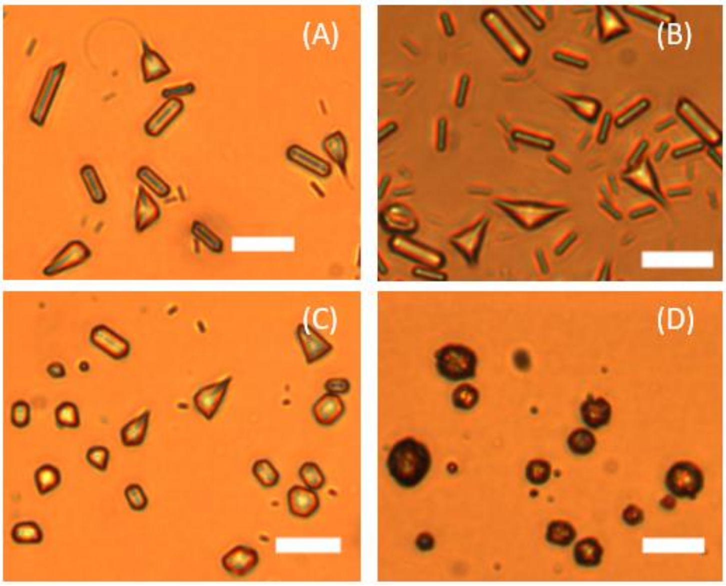


Figure S3: **Drop shape transformations for emulsions of** hexadecane drops in water stabilized by Brij S20. Cooling rate is 0.5 K min^{-1}. The total surfactant concentration in the emulsion is (A) 0.21 mM, (B) 0.13 mM, (C) 0.034 mM, (D) 0.0093 mM Scale bars: 20 µm.

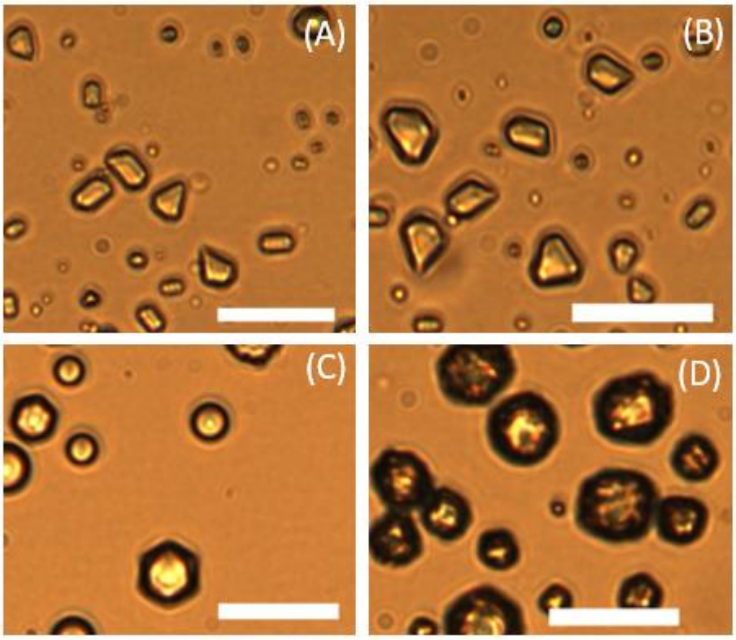


Figure S4: **Drop shape transformations for emulsions of** hexadecane drops in water stabilized by Brij 58. Cooling rate is 0.5 K min^{-1}. The total surfactant concentration in the emulsion is (A) 0.41 mM, (B) 0.3 mM, (C) 0.06 mM, (D) 0.03 mM Scale bars: 20 µm.

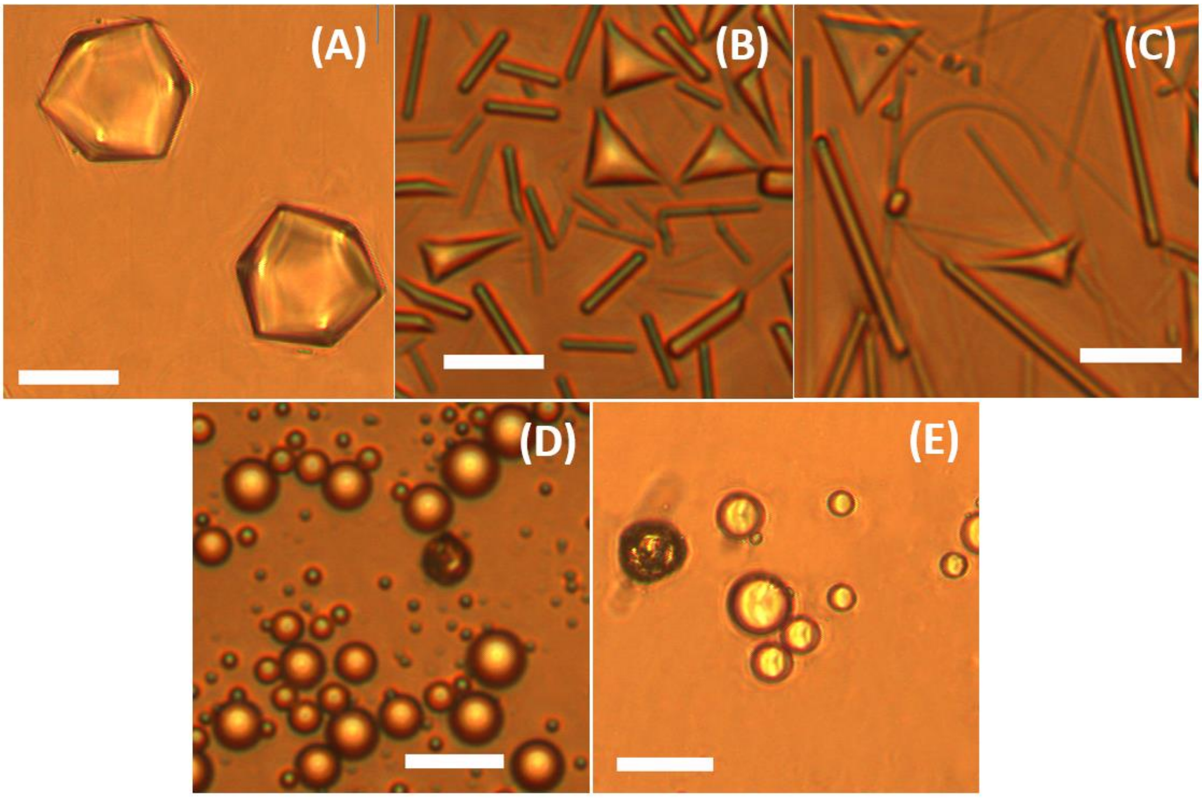


Figure S5: **Drop shape transformations for emulsions of** hexadecane drops in water stabilized by Brij C10. Images on the **first row** are obtained with emulsions prepared by the double syringe emulsification technique. Droplets d_{ini} ≈ 15 µm and the cooling rate is 0.5 K min^{-1}. The total surfactant concentration in the emulsion is (A) 0.5 mM, (B) 0.3 mM, (C) 0.2 mM, (D) 0.1 mM and (E) 0.05 mM. Scale bars: 20 µm.

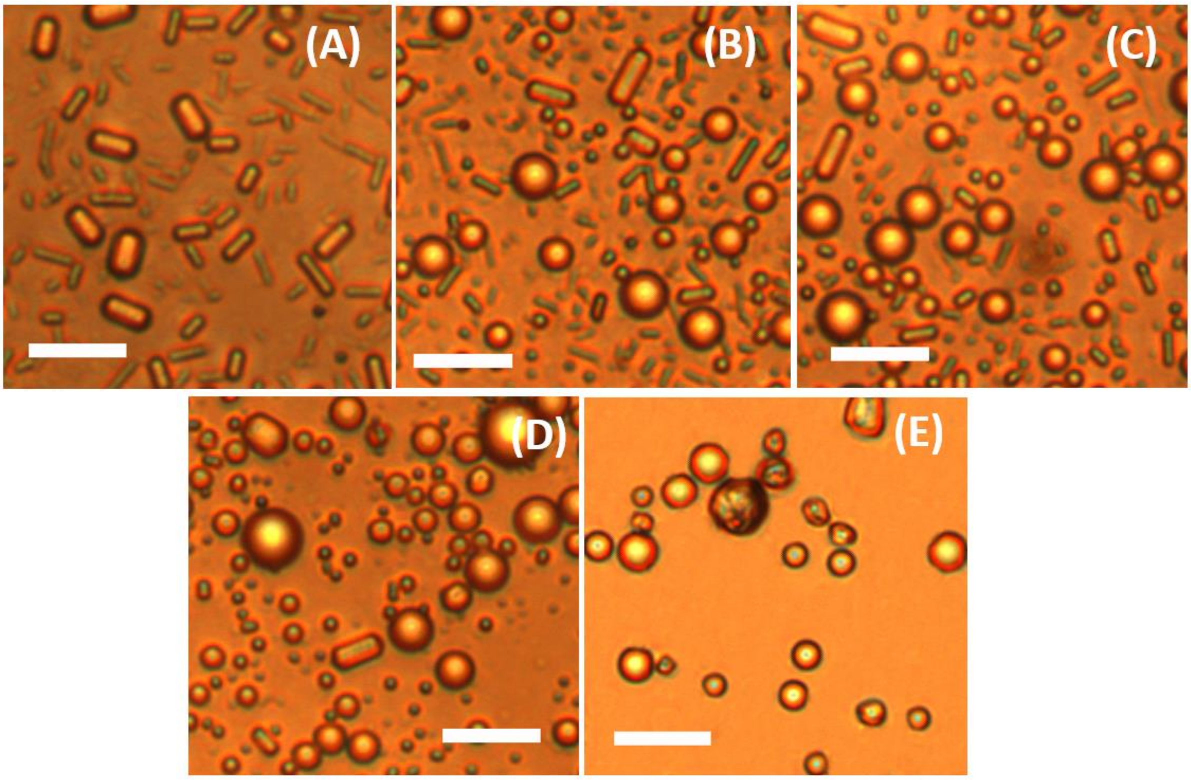


Figure S6: **Drop shape transformations for emulsions of** hexadecane drops in water stabilized by Brij S10. Images on the **first row** are obtained with emulsions prepared by the double syringe emulsification technique. Droplets d_{ini} ≈ 15 µm and the cooling rate is 0.5 K min^{-1}. The total surfactant concentration in the emulsion is (A) 0.7 mM, (B) 0.5 mM, (C) 0.35 mM, (D) 0.14 mM and (E) 0.07 mM. Scale bars: 20 µm.

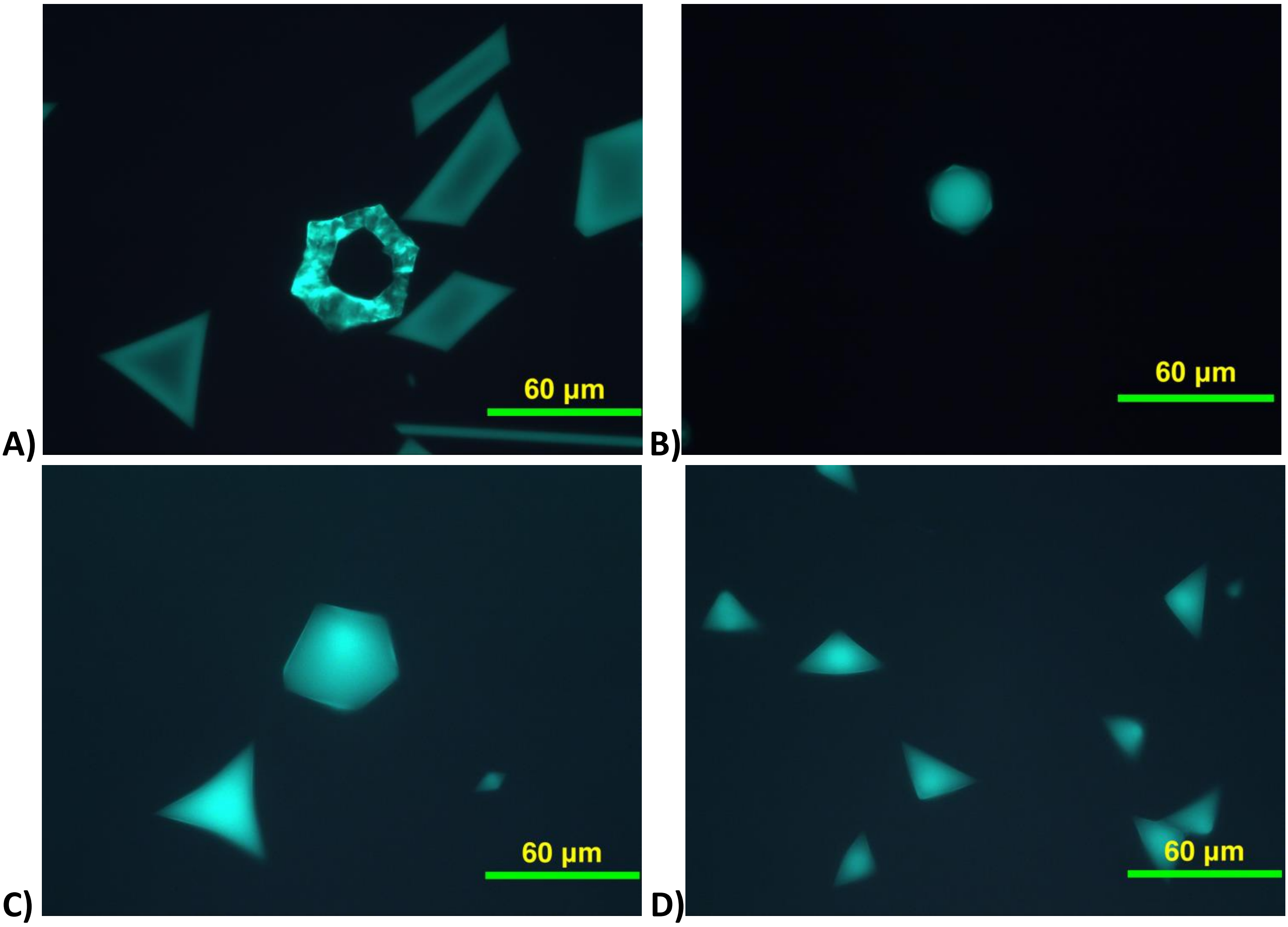


Figure S7. Fluorescence micrographs of hexadecane droplets containing 0.001% fluorescent dye (Solvent Green 5), in aqueous solutions with various non-ionic surfactants. All solutions contained 1.5 wt.% of surfactant in the water phase and were cooled at 0.2 K/min. (A) Tween 40. Frozen hexagonal droplet surrounded by liquid droplets of other shapes. B) Brij 58. C, D) Brij S20. C) shows initial deformations at temp ~ 15 ^{o}C, while D) shows later deformation to swimming shapes, as documented in our recent paper,[3] and Figure S3, at temp ~ 14 ^{o}C.

[1] J. H. Clint, *J. Chem. Soc. Faraday Trans. 1 Phys. Chem. Condens. Phases* **1975**, *71*, 1327.
[2] E. C. Markham, A. F. Benton, *J. Am. Chem. Soc.* **1931**, *53*, 497.
[3] D. Cholakova, M. Lisicki, S. K. Smoukov, S. Tcholakova, E. E. Lin, J. Chen, G. De Canio, E. Lauga, N. Denkov, *Nat. Phys.* **2021**, *17*, 1050.