colloids and interfaces

MDPI

Supporting Information

Structural analysis of a modern o/w-emulsion stabilized by a polyglycerol ester emulsifier and consistency enhancers

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A) DSC

The DSC curves of the pure emulsifier in water in shown in Figure S1 (red); upon addition of consistency enhancer there is an increase in both transition temperature and enthalpy (green). The addition of oil leads to a broadening of the DSC curve, and a reduction in both the transition temperature and the transition enthalpy (purple).

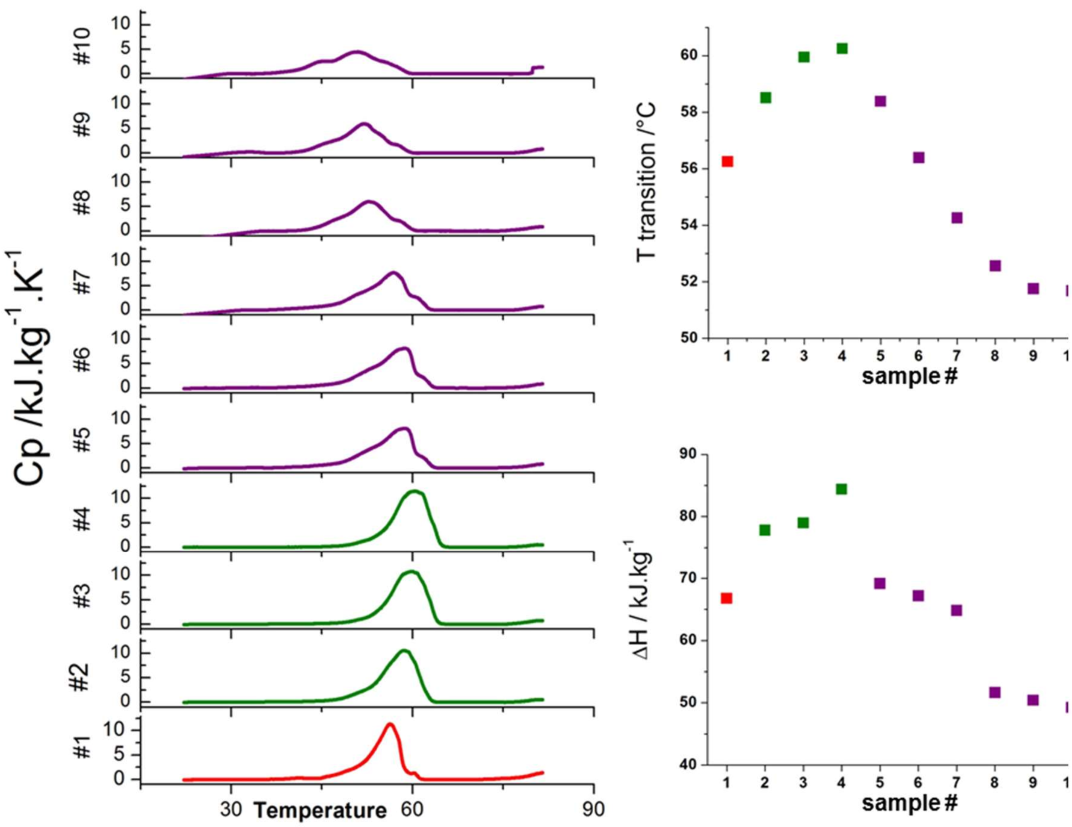

Figure S1. DSC curves of the phase transition region of the emulsifier (sample #1 – red), the mixture of emulsifier and increasing amounts of consistency enhancer (samles #2, #3, #4 – green) and the mixed systems containing emulsifier, consistency enhancers and increasing amount of oil (samples #5, #6, #7, #8, #9, #10 – purple). On the right hand side, the influence of the composition on transition temperature and transition enthalpy ΔH is shown.

B) Rheology

Brookfield viscometry, a method which is still used in most Application Technology laboratories, shows that a significant increase in consistency happens only after addition of sufficient amounts of oil. More detailed rheological studied confirmed this trend: Both the elastic modulus G′ and the viscous modulus G′′ (1h and 48h after sample preparation) increase until they reach a plateau at about 10 parts of oil (sample #8).

Table S1. Brookfield viscosity and rheological data of samples # 1–10 (at 20°C).

	1	**2**	**3**	**4**	**5**	**6**	**7**	**8**	**9**	**10**
Brookfield Viscosity (spindle C/10 rpm) (after 1 day)	-	-	-	-	6	10	35	45	42	56
G′ [Pa] after 1 h (f = 1.5 Hz)	5.3	6.9	9.6	41	78	160	820	1970	1810	2500
G′′ [Pa] after 1 h (f = 1.5 Hz)	-	-	-	-	15	26	115	260	240	340
G′ [Pa] after 48 h (f = 1.5 Hz)	-	-	-	-	400	790	2660	3240	2950	3300
G′′ [Pa] after 48 h (f = 1.5 Hz)	-	-	-	-	64	114	350	400	410	430

C) SANS – Calculation of *R* and a_H from the Porod fit

S/*V*, the surface area per unit volume, is obtained from the Porod model as described by:

$$I(Q) = \frac{2\pi\eta^2}{Q^4}\frac{S}{V} \tag{S1}$$

Assuming that all the mixture emulsifier/consistency enhancer which is not involved in lamellae is now involved in emulsion droplets, the volume fraction φ_s of all emulsion droplets in the sample is now defined by:

$$\phi_s = \phi_{oil} + \phi_{emu} - \phi_{lam} \tag{S2}$$

where φ_s is the spherical droplets volume fraction, φ_{oil} the oil volume fraction, φ_{emu} the total volume fraction of the mixture emulsifier/consistency enhancer and φ_{lam} the volume fraction of emulsifier/consistency enhancers involved in lamellae structures (as presented by the value φ_1 in Table 3 of the paper).
However, in the case of spherical droplets, φ_s can also be written:

$$\phi_s = \frac{n}{V}\frac{4}{3}\pi R^3 \tag{S3}$$

where *n* is the number of droplets, *V* the total volume and *R* the average droplet radius. Similarly, in the case of spherical droplets, the ratio *S*/*V* can be written:

$$\frac{S}{V} = \frac{n 4\pi R^2}{V} \tag{S4}$$

Combining equations S3 and S4, one can also convert this result to an average droplet radius *R*:

$$R = \frac{3\phi_s V}{S} \tag{S5}$$

It is important to keep in mind that this calculation assumes that all the emulsifier which is not involved in lamellae is located at the droplet interface. From the same assumption, one can also calculate the average headgroup area a_H of the mixture emulsifier/consistency enhancers at the droplet interface:

$$a_H = \frac{S}{N_{emu}} \tag{S6}$$

where *S* is the surface area of all droplets (obtained by fitting the data with the Porod law (see eq. S1)) and N_{emu} is the number surfactant molecules involved in droplet structures:

$$N_{emu} = \frac{V.d_{emu}.(\phi_{emu} - \phi_{lam}).N_A}{M_{w.emu}} \quad \text{(S7)}$$

where d_{emu} is the density of the mixture emulsifier/consistency enhancer, N_A is the Avogadro number and $M_{w.emu}$ is the molecular weight of the mixture emulsifier/consistency enhancer.

Calculated values of a_H are given in Table 3 in the paper. These values are very small (<0.1 nm^{-2}) and suggest that the previous assumption is not correct, meaning that a part of the available emulsifier/consistency enhancer mixture is <u>not</u> present at the droplet interface but possibly solubilized in the oil droplets.

D) SANS – Effective structure factor *S*(*Q*) of samples # 1–10

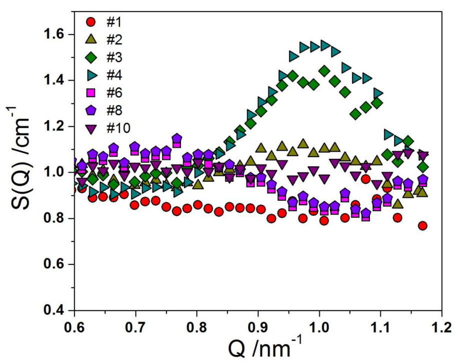

Figure S2. Effective structure factor *S*(*Q*) obtained by dividing the experimental data by the theoretical scattering intensities for the lamellar form factor (obtained with eq. 2).

E) NMR

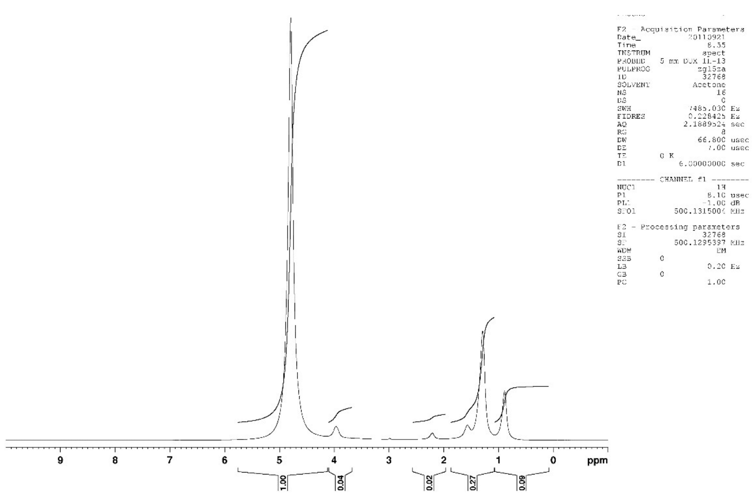

Figure S3. ^{1}H-NMR spectrum of sample #10.

The NMR spectrum of the corresponding silicone oil emulsion reveals that the components containing alkyl chains, which are forming solid bilayers (emulsifier, consistency enhancers), are hardly contributing to the signals in the alkyl region (Figure S4).

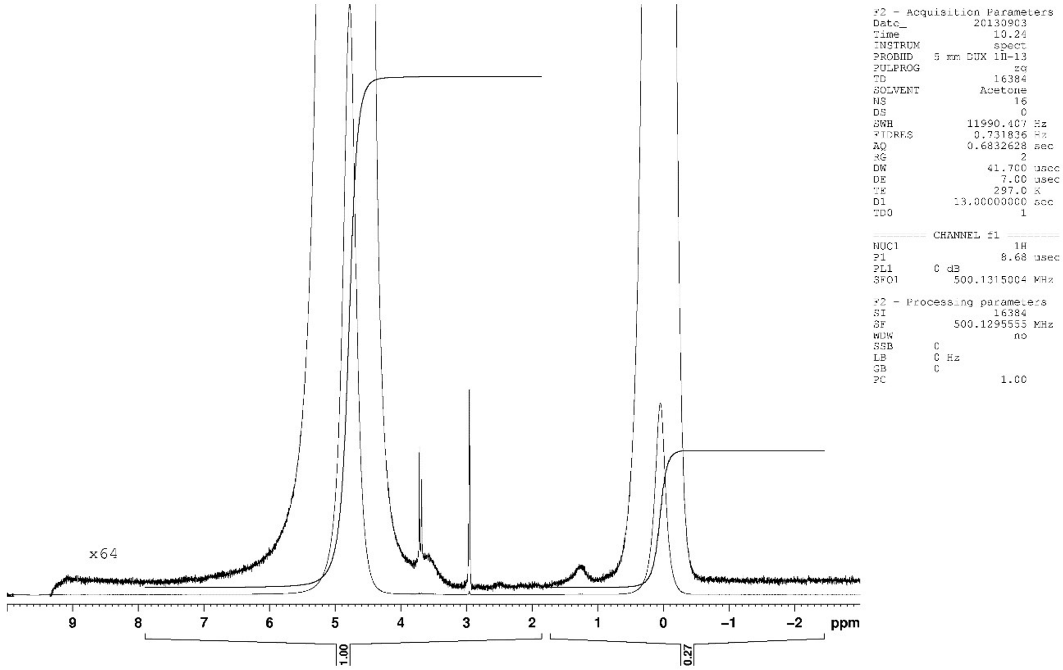

Figure S4. ^{1}H-NMR spectrum of an emulsion according to composition #10 but silicone oil (350 mPas) instead of the ester oils.

F) Droplet Size Distribution in Sample #10:

Several electron microscopy images of sample #10 have been analyzed to determine the size distribution of the vesicles. The vertical bars in the histogram (Figure S5) represent the distribution of normalized values of the frequency of measured diameters. To calculate the normalized spline function (solid line in Figure S5) superimposing the vertical bars, a two parameter unimodal Schultz distribution has been applied, following an analytical expression given in: Aragón, S.R.; Pecora, R.J. Theory of dynamic light scattering from polydisperse systems. *J. Chem. Phys.* **1976**, *64*, 2395-2404, DOI 10.1063/1.432528.

$$f_z(d) = \frac{1}{z!}[(z+1)/\overline{d}]^{z+1} d^z \exp[-(z+1)d/\overline{d}] \tag{S8}$$

and $$\overline{(\Delta d)^2} = \overline{d}^2/(z+1) \tag{S9}$$

where $\overline{d}$ is the number average diameter of the vesicles, $\overline{(\Delta d)^2}$ denotes the mean square deviation of the obtained diameter values, and z is a parameter that measures the width of the distribution. Using equation (S9), the parameter z was first calculated to a value of $z = 3$ and then applied to equation (S8) to generate data values for Schultz distribution, which after normalisation has been superimposed to the data in Figure S5.

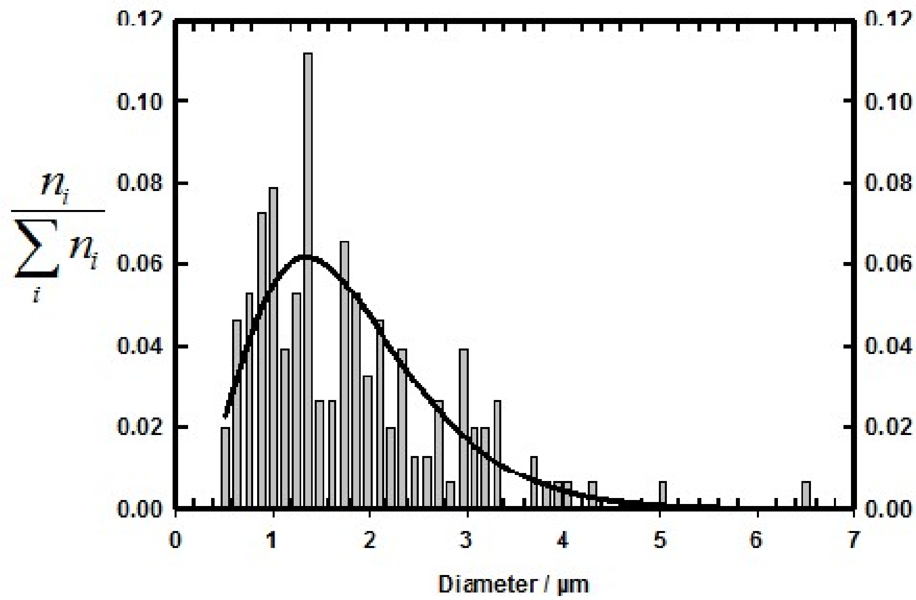

Figure S5. Normalized histogram of particle sizes of sample #10 from FF-TEM images; black line = normalized Schulz distribution.

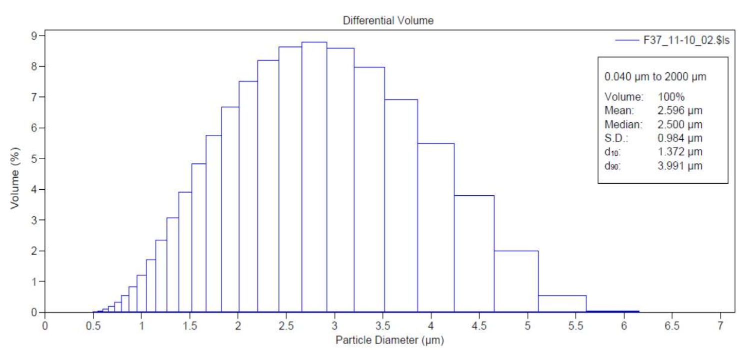

Figure S6. Droplet sizes in sample #10 as determined by Static Light Scattering.