Supporting information

On the behaviour of nanoparticles in oil-in-water emulsions with different surfactants

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SAXS analysis

Scattering experiments were performed on gold nanoparticles suspended in hexane. We used the SAXSutilities software of ESRF to obtain radius and polydispersity of the nanoparticles. Supplementary Figure S1 shows the fit of the reference scattering data with the solid sphere model implemented in the program.

This data was then used to calculate a Form Factor $F(q)$ of the nanoparticles and to obtain the Structure Factor $S(q)$ from the scattering intensity $I(q)$ of measurements by dividing $S(q) = \frac{I(q)}{F(q)}$.

The hard-sphere model also implemented in SAXSutilities[1] assumes attractive particles and

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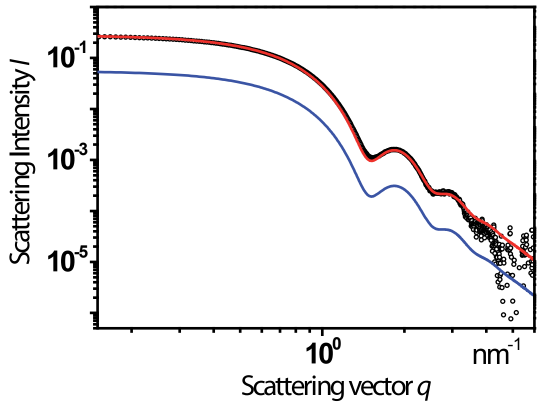

Figure S1: Hard-sphere model fits of free gold nanoparticles dispersed in hexane. The results of this fit (red continuous line) were used to calculate form factors (blue continuous line) for the analysis of SAXS data from emulsions.

predicts additional scattering $S_c(q)$ to occur when the particles interact and form clusters,

$$S_c(q) = \frac{I_M}{(1+q^2\xi^2)^p}, \tag{1}$$

depending on the average mass and characteristic size of the formed clusters that are proportional to I_M and ξ, respectively, and their fractal dimension p.

The fit correctly indicates a steadily decreasing correlation length ξ for emulsion containing SDS and Tween 85 and an a increasing correlation length ξ during the first 150 min following a decrease for emulsion containing Span 20. It also provide volumes fraction of nanoparticles that corresponds to that obtained for the particles in the droplets.

Evaporation time t	Volume fraction ϕ	Correlation length ξ	Fractal dimension p
0 min	0.13	890 nm	1.73
50	0.17	537	1.77
210	0.36	171	1.73

Figure S2: Cluster-model fits of SAXS from evaporating emulsions containing SDS.

Evaporation time t	Volume fraction ϕ	Correlation length ξ	Fractal dimension p
0 min	0.08	1004 nm	1.73
30	0.08	794	1.69
90	0.01	795	1.74
150	0.10	545	1.63
180	0.13	345	1.62
210	0.19	327	1.65
240	0.29	218	1.58
270	0.33	101	1.58

Figure S3: Cluster-model fits of SAXS from evaporating emulsions containing Tween.

Evaporation time t	Volume fraction ϕ	Correlation length ξ	Fractal dimension p
0 min	0.15	83 nm	2.01
30	0.17	100	1.99
90	0.20	132	1.95
120	0.23	138	1.92
150	0.20	145	1.87
180	0.28	134	1.81
210	0.26	127	1.80
270	0.35	121	1.71

Figure S4: Cluster-model fits of SAXS from evaporating emulsions containing Span 20

References

(1) Sztucki, M.; Narayanan, T. *J. App. Crystallogr.* **2007**, *40*, S459.