Internal Structure of Nanometer-Sized Droplets Prepared by Antisolvent Precipitation

SUPPORTING INFORMATION

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SI 1. SANS exposure times

Table SI 1. SANS Exposure Times at Different Instrumental Setups (Collimation Length/ Sample-Detector-Distance) and Temperature during the Measurement.

sample name	T [°C]	t [min] at 20 m/19.7 m | 8 m/7.7 m | 8 m/1.2 m
CV-H1	15	15|10|3
CV-D	15	15|10|3
CV-H2	15	18|15|3
CV-H3	15	25|18|3
CV-H4	15	30|25|3

SI 2. Headspace gas chromatography

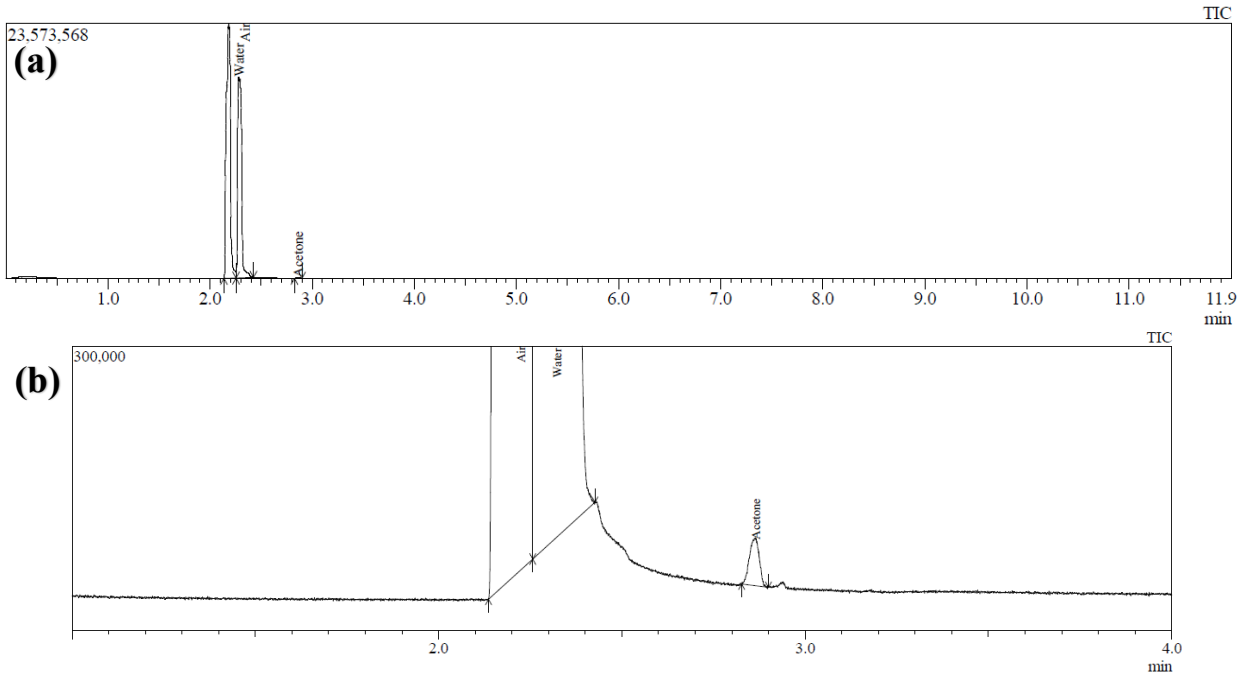

Figure SI 1. a) Exemplary HS-GC measurement of a 0.16 wt % concentrated sample (CV-H1) and b) a zoomed-in magnification of the signal (bottom).

SI 3. Excluded SAXS SANS fit models

The nanoparticles appear to be spherical as can be derived from CryoTEM images (cf. Figure 5). However, two spherical models were excluded, here demonstrated for sample with protonated SDS (CV-H1) for the model without shell and for CV-H1 and the sample with deuterated SDS (CV-D) for the model with one shell:

1) Sphere without shell: A simple sphere form factor could be excluded as it was not possible to fit SAXS and SANS of CV-H1 simultaneously with a global particle number and size. Fitting the data with individual parameters revealed a significant difference in fitted particle number N and size (cf. Table SI **2**). The total mean diameter $\bar{d}_{tot}$ obtained from the SANS fit is 17.7 nm, while the SAXS fit yielded a $\bar{d}_{tot}$ of 6.5 nm (cf. Figure SI 2a). Consequently, there had to be a further contribution.

2) Sphere with one shell: A core-shell model with one shell was able to fit the SAXS and SANS of CV-H1 simultaneously with a reasonable $\bar{d}_{tot}$ of 19.4 nm for SAXS and SANS data, with a volume-weighted mean diameter $\bar{d}_{vol}$ = 14.6 nm core diameter and a 2.38 nm shell thickness (cf. Figure SI 2b and Table SI 2), whereby N, the size parameter μ and the width parameter σ of the particle size distribution were set global. The simultaneous SAXS and SANS fits of CV-D lead to a comparable $\bar{d}_{tot}$ of 19.4 nm. However, the fits to both SAXS curves and to the SANS curve of CV-D do not agree very well with the data in the Q-range of 0.7 -2 nm^{-1}. Further, the SLDs for the shells are non-physical as such relatively high values for the XSLD would suggest that this relatively thick shell would mainly consist of the small electron-dense headgroups or of SDS only (XSLD = $11.02 \cdot 10^{10}$ cm^{-2}, cf. Table 3), because the XSLD of Q10 ($9.32 \cdot 10^{10}$ cm^{-2}) is comparably low. This can be ruled out, because the volume of the shell is too large for the available SDS in the sample (for calculation cf. SI7), and because of the NLSD of the shell of CV-D is too low for such a high content of deuterated SDS, whose NSLD = $6.92 \cdot 10^{10}$ cm^{-2}.

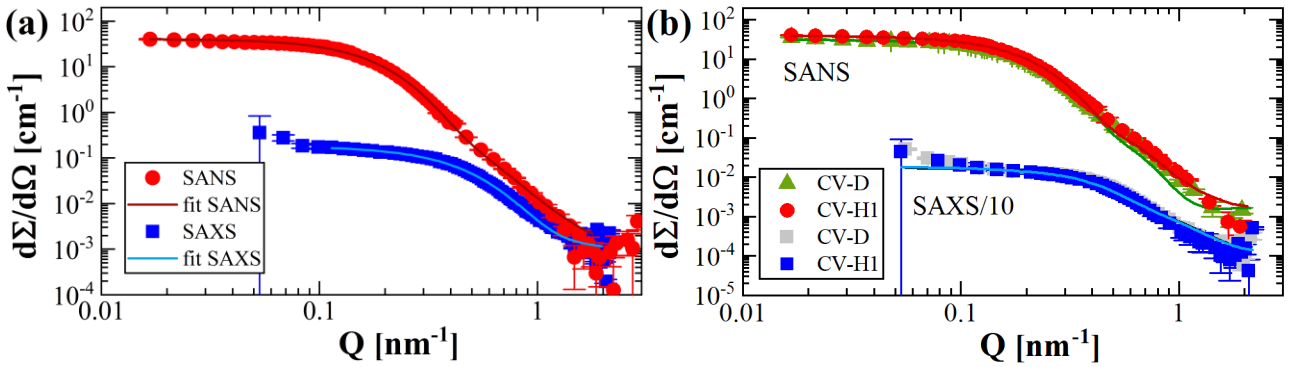

Figure SI 2. SAXS (blue squares) and SANS (red circles) data with the respective fits: a) no shell for CV-H1 and b) one shell model for CV-H1 and CV-D (SAXS: grey circles; SANS: green triangles). The respective fits are plotted as solid line. The intensity values of the SAXS curves in b) are divided by 10 to make the curves and fits more apparent. The parameters of the respective model can be found in Table SI2.

Table SI 2. SAXS SANS Parameters of the Excluded Models.

model	sample		N [cm^{-3}]	$\bar{d}_{vol}$ [nm]	σ	R_{shell} [nm]	$\bar{d}_{tot}$ [nm]	SLD [10^{10} cm^{-2}]		
								core	shell	medium
no shell	CV-H1	SANS	$6.08 \cdot 10^{14}$	17.7	0.30	-	17.7	0.45	-	6.37
		SAXS	$1.01 \cdot 10^{16}$	6.5	0.32	-	6.5	7.6	-	9.40
one shell	CV-H1	SANS	$5.48 \cdot 10^{14}$	14.6	0.32	2.38	19.4	0.45	1.21	6.37
		SAXS	$5.48 \cdot 10^{14}$	14.6	0.32	2.38	19.4	7.6	11.08	9.40
	CV-D	SANS	$5.64 \cdot 10^{14}$	14.8	0.31	2.38	19.5	0.45	2.72	6.37
		SAXS	$5.64 \cdot 10^{14}$	14.8	0.31	2.38	19.5	7.6	11.08	9.40

SI 4. SAXS SANS model: fit parameters

Table SI 3. SAXS SANS Fit Parameters.

sample	N [cm^{-3}]	$\bar{d}_{vol}$ [nm]	σ	R_{shi} [nm]	R_{sho} [nm]	$\bar{d}_{tot}$ [nm]	NSLD [10^{10} cm^{-2}]				XSLD [10^{10} cm^{-2}]			
							core	sh_i	sh_o	med	core	sh_i	sh_o	med
CV-H1	$5.41 \cdot 10^{14}$	12.7	0.38	2.5	1.1	19.9	0.45	0.24	3.15	6.37	7.61	9.10	12.10	9.40
CV-H2	$4.33 \cdot 10^{14}$	12.7	0.38	2.5	1.1	19.9	0.45	0.24	2.76	4.98	-	-	-	-
CV-H3	$3.24 \cdot 10^{14}$	12.7	0.38	2.5	1.1	19.9	0.45	0.24	2.38	3.6	-	-	-	-
CV-H4	$2.16 \cdot 10^{14}$	12.7	0.38	2.5	1.1	19.9	0.45	0.24	2.24	2.21	-	-	-	-
CV-D	$5.75 \cdot 10^{14}$	12.7	0.37	2.5	1.1	19.9	0.45	1.18	4.19	6.37	7.61	9.10	12.10	9.40

R_{shi}: thickness of the inner shell; **R_{sho}**: thickness of the outer shell; **sh_i**: inner shell**; sh_o**: outer shell; **med:** dispersion medium.

SI 5. SAXS SANS model: sphere with two shells – SAXS of SDS-d25-stabilized NPs (CV-D)

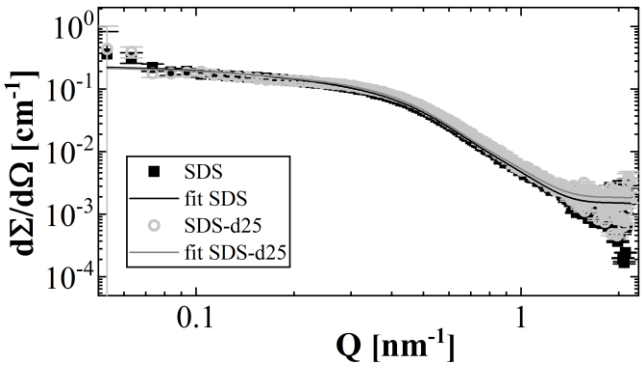

Figure SI 3. SAXS curve (VAXSTER, ICSP) of Q10 NPs stabilized with protonated (black squares, sample CV-H1) and deuterated SDS (grey circles, sample CV-D). The simultaneous fits are indicated as solid lines, the parameters can be found in Table SI3.

SI 6. SAXS SANS model: SDS calculations

The concentration of SDS molecules in the sample $C_m(SDS)$ is calculated as follows (here demonstrated for sample CV-H1)*:*

$$C_m(SDS) = \frac{C(SDS)\cdot N_A}{M_{SDS}} = 1.80 \cdot 10^{18}\ mL^{-1}, \quad (1)$$

with the SDS concentration due to sample preparation $C(SDS)$ = 0.864 mg/mL (cf. Table 1), the molar mass of SDS M_{SDS} = 288.38 g/mol and the Avogadro constant $N_A = 6.022 \cdot 10^{23}$ mol^{-1}. The volume of the total shell V_{shell} is

$$V_{shell} = V_{tot} - V_{core} = \frac{4}{3}\pi(r_{tot}^3 - r_{core}^3) = 3054\ nm^3, \quad (2)$$

with the mean total volume of a particle V_{tot}, the volume of the core V_{core}, the total radius $r_{tot} = \bar{d}_{tot}/2$ and the radius of the core $r_{core} = \bar{d}_{vol}/2$ (cf. Table SI3). The SDS molecule concentration required to fill V_{shell} is

$$C_{req}(SDS) = \frac{N\cdot V_{shell}}{V_{molecular}(SDS)} = 4.14 \cdot 10^{18}\ mL^{-1}, \quad (3)$$

with the particle concentration $N = 5.41 \cdot 10^{14}$ cm^{-3} derived by the SAXS SANS analysis (cf. Table SI3) and the assumed molecular volume of SDS $V_{molecule(SDS)}$ = 0.399 nm³ for the SDS bulk density of 1.2 g/cm³ (cf. Table SI3). Given that $C_{req(SDS)} > C_{m(SDS)}$, we assume that the shell cannot be filled with SDS only. The same assumption is made in case of the excluded model with one shell (cf. SI3): $C_{req(SDS)} = 3.01 \cdot 10^{18}$ mL^{-1} > $C_{m(SDS)}$, with $N = 5.48 \cdot 10^{14}$ cm^{-3} and V_{shell} = 2193 nm^3 (cf. Table SI2).