Surfactant adsorption and aggregate structure at silica nanoparticles: Effect of particle size and surface modification

Bhuvnesh Bharti, Jens Meissner, Urs Gasser and Gerhard H. Findenegg*
*** e-mail: findenegg@chem.tu-berlin.de**

Supplementary Information

1. Characterization of Ludox-TMA nanoparticles

Ludox-TMA was supplied by Sigma-Aldrich as 30 wt-% silica dispersion in water. Aliquots of the sample were diluted and dialyzed for 1 week using membranes with molecular-weight cut-off of 14 kDa. Bigger aggregates were removed from the silica dispersion by filtration through 0.22 µm filters**.**

The sample was characterized by SAXS, nitrogen adsorption and by transmission electron microscopy (TEM), as explained for Lys-Sil particles in the main text. Results of the characterization are displayed in Figure S1 and Table S1.

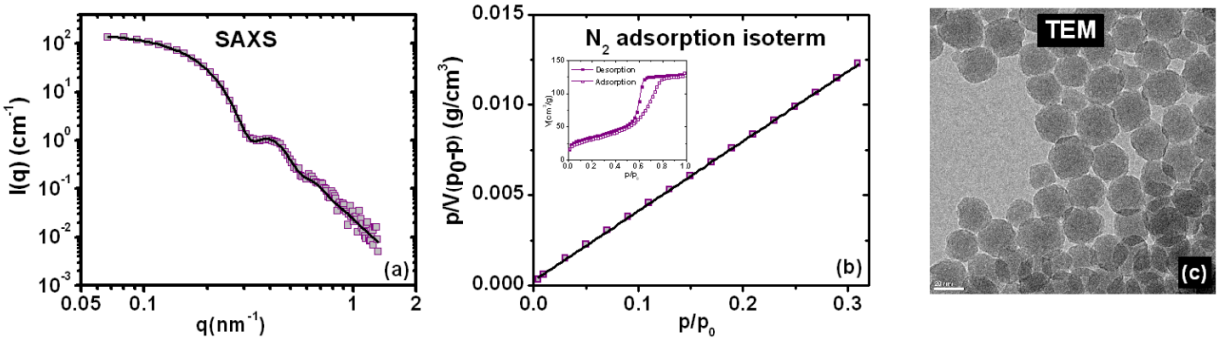

Figure S1. Characterization of Ludox-TMA silica: (a) SAXS intensity profile $I(q)$ of a 1 wt-% dispersion in water and a fit of the data with the form factor model of polydisperse spheres (log-normal size distribution) and a hard sphere structure factor; **(b)** BET plot of the nitrogen adsorption data for reduced vapor pressures p/p_0 up to 0.3; the inset shows the whole isotherm, which exhibits a pronounced hysteresis loop due to the particle clustering during the drying process. This feature is of no relevance for the present study.

Table S1: Important parameters characterizing the Ludox-TMA sample: Mean particle radius R and size polydispersity s as derived from SAXS, and specific surface area a_{BET} of the sols as determined from the nitrogen adsorption measurements

SAXS		**Nitrogen adsorption**
***R* (nm)**	s	a_{BET} (m^2/g)
13.37	0.13	115

2. Analysis of SANS profiles of $C_{12}E_5$ in the absence of silica

The SANS intensity profile of the surfactant $C_{12}E_5$ in D_2O in the absence of silica nanoparticles was measured as a reference for the profiles obtained in the presence of Ludox-TMA at higher lysine concentrations (see Fig. 4 of the article). The model of wormlike micelles (Section 3.3) was used to represent the experimental $I(q)$ data, as described elsewhere[1] the model reproduced both the rigid-rod and random coil limit of the worm like structure. A good fit was obtained as shown in figure S2. The parameters derived from the fit are summarized in Table S2.

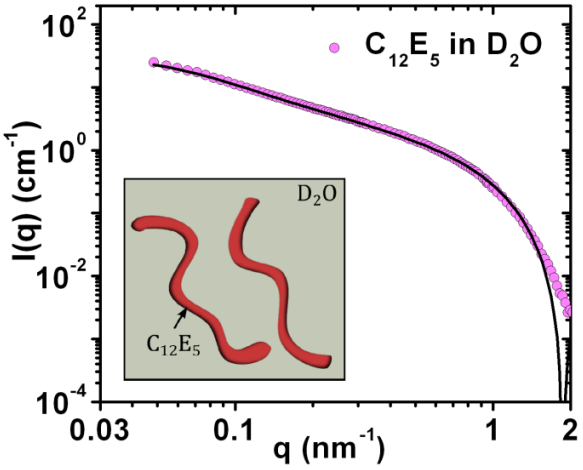

Figure S2. SANS intensity profile for the surfactant $C_{12}E_5$ in D_2O the absence of silica: Experimental data and a fit by the model of wormlike micelles.

Table S2: Fit parameters of the model of wormlike micelles from SANS data of $C_{12}E_5$ in D_2O: cylinder radius R, Kuhn length L_k, and contour length L_c

Cross section radius (nm)	Kuhn length (nm)	Contour length (nm)
2.0	35	114

3. Form Factor Models

3.1 Spherical shell model

The form factor of a spherical shell structure is given by

$$P_{shell}(q) = [\frac{4\pi}{3}(R+\Delta R)^3 J(q(R+\Delta R),1) - \frac{4\pi}{3}R^3 J(qR,1)]^2 \qquad \textbf{(1)}$$

Here, q is the scattering wave vector ($q = (4\pi/\lambda)\sin\theta$), with 2θ the scattering angle and λ the wavelength), ΔR is the thickness of the shell around the core of radius R, and $J(qR, 1)$ is the Bessel function of first kind, which is given by

$$J(qR,1) = 3\frac{\sin(qR) - qR\cos(qR)}{(qR)^3} \quad \textbf{(2)}$$

3.2 Micelle-decorated bead model

$C_{12}E_5$ adsorption on silica nanoparticles was studied by SANS at silica contrast match H_2O/D_2O dispersion. We have analyzed the SANS profiles on the basis of previously developed micelle-decorated silica bead model.[2] This approach explains the structure of the adsorbed layer of surfactant on spherical silica beads ONLY in silica contrast match scenario. Model assumes that there is a discrete and distribution of the spherical (or ellipsoidal) surface micelles of radius R_{mic}.

First step of this model involves the simulating a complete random set of coordinates of the center of each surface micelle lying on the outer surface silica nanoparticles of radius R_{si}. This uniform distribution of spherical micelles was achieved by hypercube rejection method[3] where three numbers (a_1, a_2 and a_3) are generated from a completely random distribution that satisfies the following set of conditions

$$a_4 = a_1^2 + a_2^2 + a_3^2 \quad \textbf{(3)}$$

If $a_1 \neq -1;\ a_2 \neq -1;\ a_3 \neq -1;$ and $a_4 \leq 1$ then the coordinates of the surface micelles is given by

$$x = (R_{si} + R_{mic}) \times (2(a_2a_4 + a_1a_3))/a_4 \quad \textbf{(4)}$$

$$y = (R_{si} + R_{mic}) \times (2(a_2a_4 + a_1a_3))/a_4 \quad \textbf{(5)}$$

$$z = (R_{si} + R_{mic}) \times (2(a_1^2 + a_4^2 - a_2^2 - a_3^2))/a_4 \quad \textbf{(6)}$$

The inter-micellar structure factor $S_{mic}(q)$, arising due to the correlations between the N_{mic} micelles on the surface of the same sphere is generated by Fourier transformation of their real space pair-distribution function. Mathematically, it can be represented as[4]

$$S_{mic}(q) = 1 + \frac{1}{N_{mic}}\sum_{i\neq j}\frac{\sin(q(r_i - r_j))}{q(r_i - r_j)} \quad \textbf{(7)}$$

Here $r_i - r_j$ is the center-to-center distance for the surface micelles sitting on the surface of a single silica particle. To get a statistically averaged $S_{mic}(q)$, the simulation was an average over 1000 iterations. The polydispersity of silica bead as well as for the surface micelles was taken into account by the generating the radii of the silica bead and surface micelle from the log-normal size distribution with corresponding standard deviation.

The form factor of the surface micelles is given by

$$P_{surf-mic}(q) = S_{mic}(q)P_{mic}(q) \quad \textbf{(8)}$$

And hence the overall intensity of the scattering profile in absolute scale is given by the equation which reads as follows

$$I_a(q) = NV^2\Delta\rho^2 P_{mic}(q)S_{mic}(q) \quad \textbf{(9)}$$

Here N is the number density of the surface micelles, $P_{mic}(q)$ is the form factor of surface micelles, V_{mic} is the volume of one surface micelles and $\Delta\rho^2$ is the average contrast of the hydrated surface micelle ($\rho_{C12E5} = 1.18 \times 10^{-4}$ nm^{-2}) against the H_2O/D_2O mixture ($\rho_{si} = 3.54\times10^{-4}$ nm^{-2}).

The complete scattering profile for micelles attached to a spherical bead is given by

$$I(q) = I_a(q)S_{hs}(q). \quad \textbf{(10)}$$

where $S_{hs}(q)$ is the hard-sphere repulsive structure factor accounting for inter-particle (silica bead) correlations.

For spherical surface micelles $P_{mic}(q)$ is given by the form factor of a spheres of radius R_{mic} equal to half the thickness of surfactant shell formed around silica particle

$$P_{mic}(q) = [\frac{4}{3}\pi R_{mic}^3 J(qR,1)]^2 \quad \textbf{(11)}$$

3.3 Worm-like micelle model

Wormlike micelles are modeled by cylinders (radius R_{cyl}) of length L_k (Kuhn length) joined together at arbitrary angles. The maximum stretch length of such a micelle is L_c (contour length). The form factor of wormlike micelle can be factorized as

$$P_{\text{worm}}(q) = P_0(q)P_c(q) \quad \textbf{(12)}$$

where $P_0(q)$ is the form factor given by Kholodenko,[2] which is designed to reproduce rigid –rod limit and random coil limit, where as the cross section form factor is expressed in terms of $P_c(q)$ The former can be expressed in terms of the variable $w=3L_c/L_k$ as

$$P_0(q) = \frac{2}{w}\{I_1(w) - \frac{1}{w}I_2(w)\} \quad \textbf{(13)}$$

$$I_n(w) = \int_0^w f(z) z^{n-1} dz \tag{14}$$

$$f(z) = \begin{cases} \dfrac{\sinh(Ez)}{E\sinh(z)} & q \le \dfrac{3}{L_k} \\ \dfrac{\sinh(Fz)}{F\sinh(z)} & q > \dfrac{3}{L_k} \end{cases} \tag{15}$$

where $E = \sqrt{1 - \left(\frac{L_k q}{3}\right)^2}$ *and* $F = \sqrt{\left(\frac{L_k q}{3}\right)^2 - 1}$

In eq. 12, the factor relating to the cross section of the cylinders is given by

$$P_c = \left(2\frac{J(qR_{cyl}, 1)}{qR}\right)^2 \tag{16}$$

Simulations

Our SANS measurements have established that the surfactant is forming surface micelles adsorbed at the silica nanoparticles, and wormlike micelles in the bulk solution. When the surface energy of the silica particles is lowered by adsorption of lysine, a fraction of the adsorbed surfactant is displaced from the surface and transforms to wormlike micelles in solution. Hence the overall scattering intensity profile of the surfactant can be represented by an incoherent superposition of the two contributions

$$I(q) = (1 - x) I_{surf}(q) + x I_{bulk} I(q) \tag{17}$$

where x is the fractional intensity contribution of non-adsorbed surfactant, (1-x) is the fractional contribution of surfactant adsorbed on silica surface. $I_{\text{surf}}(q)$ is obtained using $P_{surf\text{-}mic}(q)$ (eq. 8) and $I_{\text{bulk}}(q)$ was simulated by $P_{worm}(q)$ (eq 12). In the simulations the size polydispersity of the silica particles as well as a size polydispersity of the surface micelles was taken into account. A log-normal size distribution was assumed in both cases. Results of this simulation are shown in Figure 5 of the paper.

Table S3: Parameters used to simulate the form factors $P_{surf\text{-}mic}(q)$ and $P_{worm}(q)$, and hence $I_{surf}(q)$ and $I_{bulk}(q)$: R_{bead} is the radius of the silica particle, s_{bead} its polydispersity, and s_{mic} is the polydispersity of the surface micelles

$P_{surf\text{-}mic}(q)$					$P_{worm}(q)$		
R_{bead} (nm)	s_{bead}	N_{mic}	R_{mic}	s_{mic}	R_{worm}	L_c	L_k
13.37	0.13	100	2.2	0.1	2.0	142	40.5

Table 3. Fit parameters for surface adsorbed $C_{12}E_5$ in the absence of lysine by micelle-decorated bead model and spherical shell model.

	Γ (μmol/m^2)	R_{bead} (nm)	R_{mic}(nm)	$\Delta\rho$ (× 10^{-4} nm^{-2})	N_{mic}	dR (nm)	x
Surface micelles	3.5	13.37	2.2	2.36	105	----	0.25
Shell	3.5	13.37	----	2.36	----	4.0	----

[a] R_{mic} is the radius of surface micelles and dR is the thickness of shell according to core shell model.

4. Temperature variant Small Angle X-ray Scattering (SAXS)

SAXS measurements for the silica Ludox-TMA dispersion containing equal amount of $C_{12}E_5$ at different temperatures (20-50°C) in the presence and absence of lysine were carried out. In SAXS, because of the low electron density of surfactant, it remains invisible to the incident x-rays in the presence of silica nanoparticles. As can be observed from the Figure S3, the scattering profiles at different temperatures with and without lysine superimpose on each other. The identical nature of the x-ray scattering curves indicate that the increase in turbidity with temperature for dispersion containing lysine (shown in Figure 6 of main paper) is not because of silica aggregation but is resultant of the phase separation of surfactant itself.

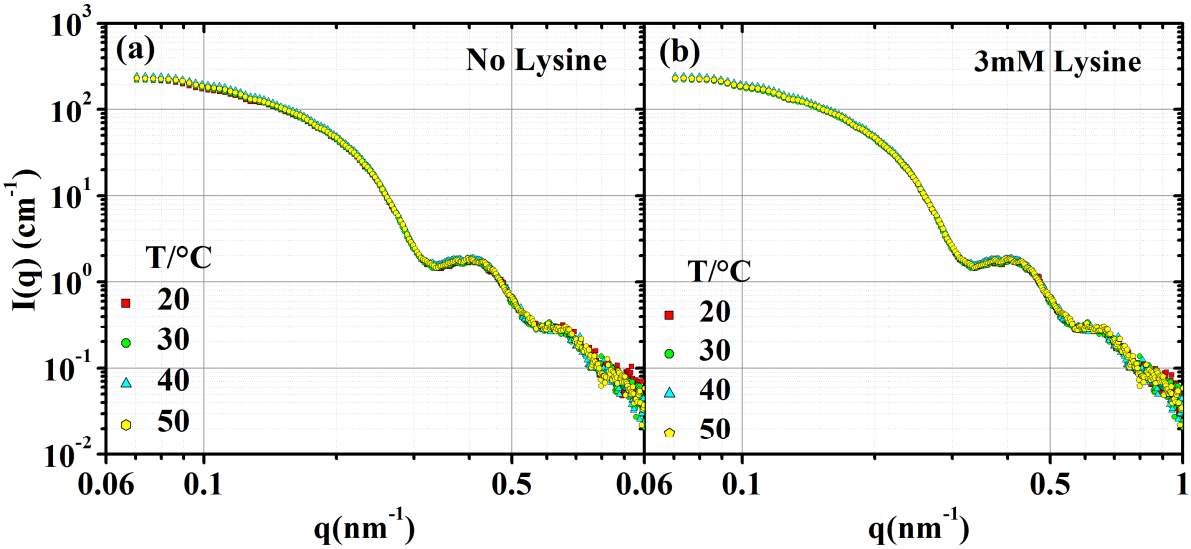

Fig. S3 SAXS profiles for silica dispersion with equal amount of $C_{12}E_5$ (a) without adding any lysine (b) with 3mM of surface modifier lysine.

References

[1] A. L. Kholodenko, *Macromolecules*, 1993, **26**, 4179 .
[2] Oberdisse, J., *Phys. Chem. Chem. Phys.*, **2004**, *6*, 1557.
[3] http://www.math.niu.edu/~rusin/known-math/96/sph.rand
[4] Despert, G., Oberdisse, J., *Langmuir*, **2003**, *19*, 7604.