CORRELATION BETWEEN GEOMETRICAL SHAPE AND GROWTH BEHAVIOUR OF SURFACTANT MICELLES INVESTIGATED WITH SMALL-ANGLE NEUTRON SCATTERING

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Models employed in the least-square fitting data analysis

The scattering cross section per unit mass of solute as a function of scattering vector $q$ for a sample of coexisting free surfactant monomers and monodisperse micelles can be written as follows

$$\frac{d\sigma_m(q)}{d\Omega} = \Delta\rho_m^2 M_w P(q) [1 + \beta(q)(S(q) - 1)] \quad (S1)$$

$P(q) \equiv \langle F^2(q) \rangle_0$ is the orientational averaged form factor for ellipsoidal micelles taking into account the geometrical shape of the micelles and $F(q)$ is the amplitude. The inter-micellar interactions were found be weak in presence of large amounts of salt and the quality of the model fits could never be improved by introducing a structure factor $S(q)$ which was simply set to unity.

Rather small and compact micelles were best fitted using a model for triaxial ellipsoids with half axis $a$, $b$ and $c$. The orientational averaged form factor for ellipsoids equals

$$\langle F^2(q) \rangle_0 = \frac{2}{\pi} \int_0^{\pi/2} \int_0^{\pi/2} F^2(q, r(a, b, c, \phi, \theta)) \sin \phi d\phi d\theta \quad (S2)$$

where $F(q, r) = 3[\sin(qr) - qrcos(qr)]/(qr)^3$ and

$$r(a, b, c, \phi, \theta) = \sqrt{(a^2 \sin^2 \theta + b^2 \cos^2 \theta) \sin^2 \phi + c^2 \cos^2 \phi}.$$  

The following scattering cross-section was used for polydisperse rodlike micelles$^2$

$$I_{agg}(q) = \Delta\rho_m^2 P_{cs}(q) P_r(q) \langle M_w \rangle \quad (S3)$$

where $\langle M_w \rangle$ is the weight-average molar mass. The form factor $P_{cs}(q)$ for an elliptical cross-section with half axes $a$ and $b$, respectively, is given by
\[ P_{cs}(q, a, b) = \frac{2}{\pi} \int_{0}^{\pi/2} \left( \frac{2B_1(qr(a, b, \phi))}{qr(a, b, \phi)} \right)^2 d\phi \]  

(S4)

where

\[ r(a, b, \phi) = \sqrt{a^2 \sin^2 \phi + b^2 \cos^2 \phi} \]  

(S5)

and \( B_1(x) \) is the Bessel function of first order.

The scattering function for polydisperse rigid rods can be written as follows

\[ P_r(q) = \frac{\int N_{rod}(L) L^2 S_{rod}(q, L) dL}{\int N_{rod}(L) L^2 dL} \]  

(S6)

where \( N_{rod}(L) \) is the number distribution of micelles with respect to their length \( L \) and the form factor for an infinitely thin rod is given by

\[ S_{rod}(q, L) = 2\text{Si}(qL) - 4 \sin^2(qL/2) / (qL)^2 \]  

(S7)

where

\[ \text{Si}(x) = \int_{0}^{x} \frac{\sin t}{t} dt \]  

(S8)

For one sample in presence of [NaBr] = 0.3 M, the model fits could be significantly improved using a model for flexible wormlike micelles, \textit{i.e.} eqn S3 with the following expression for \( P_r \)
\[ P_r(q) = \frac{\int N_{\text{worm}}(L)L^2 S_{KP}(q, L, l_p) dL}{\int N_{\text{worm}}(L)L^2 dL} \]  

(S9)

Eqn S9 is valid for polydisperse self-avoiding Kratky-Porod worm-like chains with a contour length \( L \), persistence length \( l_p \). We have employed the expressions for the scattering function \( S_{KP}(q, L, l_p) \) given by Pedersen and Schurtenberger.\(^4\)

In our data analysis we have assumed the number density of lengths of rigid and flexible rodlike micelles to follow a Schultz distribution in the entire range of aggregation numbers \( 0 < N < \infty \) , i.e.

\[ N_{\text{rod/worm}}(L) = \frac{L^z}{z!} \left( \frac{z+1}{\langle L \rangle_N} \right)^{z+1} e^{-L(z+1)/\langle L \rangle_N} \]  

(S10)

where \( \langle L \rangle_N \) is the number-weighted average length of the micelles. Below we have presented our results in terms of the volume-weighted average length \( \langle L \rangle = (z+2)/(z+1) \times \langle L \rangle_N \) i.e. the mean value as calculated from the probability distribution of finding an aggregated surfactant in a micelle of length \( L \), and the corresponding relative standard deviation \( \sigma_L / \langle L \rangle = 1 / \sqrt{z+2} \).

The number of fit parameters, including residual incoherent background scattering, is \( M = 7-8 \) and always much smaller than the number of data points \( N = 150-220 \). We have aimed at keeping our models as simple as possible and always been careful not to introduce any additional fitting parameters unless they give rise to a significantly improved quality of the model fit.

Both micelles and bilayer aggregates were fitted with a homogeneous one-shell model and the quality of the fits could not be improved using a core-and-shell model or a model taking into account internal differences in scattering length densities in the micelle core. This is not surprising considering that the head group of SOS has a similar scattering length density as deuterium oxide and is invisible in a SANS experiment\(^5\) whereas CTAB has almost identical scattering...
length densities as the surfactant tails and that the head groups only protrude a few angstroms outside the core.

Throughout the data analyses corrections were made for instrumental smearing. For each instrumental setting the ideal model scattering curves were smeared by the appropriate resolution function when the model scattering intensity was compared with the measured one by means of least-squares methods. The parameters in the model were optimized by means of conventional least-squares analysis and their errors were calculated with conventional methods. The quality of the fits were measured in terms of the reduced chi-squared parameter defined as

$$\chi^2 = \frac{1}{N-M} \sum_{i=1}^{N} \left( \frac{I_{\text{exp}}(q_i) - I_{\text{mod}}(q_i)}{\sigma_i} \right)^2$$  \hspace{1cm} (S11)

where $I_{\text{exp}}(q_i)$ and $I_{\text{mod}}(q_i)$ are the experimental and model intensities, respectively, at a scattering vector modulus $q_i$, $\sigma_i$ is the statistical uncertainties on the data points, $N$ is the total number of data points and $M$ is the number of parameters optimized in the model fit.
Figure S1. Normalized scattering cross section as a function of the scattering vector \( q \) for CTAB in deuterium oxide. The surfactant concentrations of the samples are [CTAB] = 40 mM (squares), 20 mM (circles) and 10 mM (triangles). Symbols represent SANS data and the solid lines represent the best available fits with a model for general ellipsoids. The results of the fits are given in Table 1. The quality of the fits as measured by \( \chi^2 \) is 14.0 (squares), 4.3 (circles) and 2.7 (triangles).
Figure S2. Normalized scattering cross section as a function of the scattering vector $q$ for mixtures of CTAB and SOS in deuterium oxide for a given mole fraction of SOS in solution $y = 0.05$. The overall surfactant concentrations of the samples are $[\text{SOS}] + [\text{CTAB}] = 40 \text{ mM}$ (squares), $20 \text{ mM}$ (circles) and $10 \text{ mM}$ (triangles). Symbols represent SANS data and the solid lines represent the best available fits with a model for general ellipsoids. The results of the fits are given in Table 1. The quality of the fits as measured by $\chi^2$ is 7.8 (squares), 3.2 (circles) and 3.1 (triangles).
Figure S3. Normalized scattering cross section as a function of the scattering vector $q$ for mixtures of CTAB and SOS in deuterium oxide for a given mole fraction of SOS in solution $y = 0.15$. The overall surfactant concentrations of the samples are $[\text{SOS}] + [\text{CTAB}] = 40$ mM (squares), 20 mM (circles) and 10 mM (triangles). Symbols represent SANS data and the solid lines represent the best available fits with a model for general ellipsoids (circles and triangles) or polydisperse rodlike micelles with an elliptical cross-section (squares). The results of the fits are given in Table 1. The quality of the fits as measured by $\chi^2$ is 2.5 (squares), 2.3 (circles) and 3.6 (triangles).
Figure S4. Normalized scattering cross section as a function of the scattering vector $q$ for mixtures of CTAB and SOS in deuterium oxide for a given mole fraction of SOS in solution $y = 0.25$. The overall surfactant concentrations of the samples are $[\text{SOS}] + [\text{CTAB}] = 40$ mM (squares), 20 mM (circles) and 10 mM (triangles). Symbols represent SANS data and the solid lines represent the best available fits with a model for polydisperse rodlike micelles with an elliptical cross-section. The results of the fits are given in Table 1. The quality of the fits as measured by $\chi^2$ is 5.0 (squares), 2.0 (circles) and 1.7 (triangles).
Figure S5. Normalized scattering cross section as a function of the scattering vector $q$ for mixtures of CTAB and SOS in deuterium oxide for a given mole fraction of SOS in solution $\gamma = 0.30$. The overall surfactant concentrations of the samples are $[\text{SOS}] + [\text{CTAB}] = 40$ mM (squares), 20 mM (circles) and 10 mM (triangles). Symbols represent SANS data and the solid lines represent the best available fits with a model for polydisperse rodlike (circles and triangles) or wormlike (squares) micelles with an elliptical cross-section. The results of the fits are given in Table 1. The quality of the fits as measured by $\chi^2$ is 9.8 (squares), 3.6 (circles) and 1.9 (triangles).
The general micelle model

The geometrical shape of tablet-shaped micelles considered in the general micelle model is given in Fig. S6.

Figure S6. Schematic illustration of a tablet-shaped micelle modelled as consisting of a central rectangular bilayer of thickness $2\xi$, width $2R$ and length $L$ with two half-circular ends with radius $R$. The bilayer part is surrounded by two straight half cylindrical rims of length $L$ and radius $\xi$ along its long sides and two semitoroidal rim parts of radius $\xi$ along the half circular ends of the micelle.

The free energy of a self-assembled interface as a function of mean and Gaussian curvature ($H$ and $K$, respectively) may be obtained from the Helfrich-expression as\textsuperscript{10}

$$E = \gamma_0 A + 2k_c \int (H - H_0)^2 dA + \bar{k}_c \int KdA$$ \hspace{1cm} (S12)

The first term on the right-hand side in eqn S12 ($= \gamma_0 A$) represents the free energy of stretching a self-assembled interface with area $A$ and interfacial tension $\gamma_0$. The second and third terms take into account effects due to the dependence of free energy on the local curvature of the self-assembled interface, usually referred as to the bending free energy. According to the Gauss-Bonnet theorem, the last term in eqn S12 equals $4\pi\bar{k}_c$ for a geometrically closed interface and does not depend on the size of the self-assembled interfacial aggregate.

From eqn S12 it is possible to derive an expression of the free energy $E$ of the tablet-shaped micelle shown in Fig. S1 as a function of the dimensionless length $l \equiv L/\xi$ and dimensionless half width $r \equiv R/\xi$, i.e.\textsuperscript{11}
\[
\frac{E(r,l)}{kT} = \alpha + \delta \psi(r) \beta (\pi r + l) + 2r(\pi r + 2l)\lambda
\]  

(S13)

where \( \lambda \equiv \xi^2 \gamma_p/kT \) is the reduced and \( \gamma_p \) the real planar interfacial tension of the self-assembled interface. \( \alpha \equiv 2\pi(3k_c + 2\bar{k}_c - 8\xi k_c H_0)/kT + 4\pi \lambda \), \( \beta \equiv \pi k_c (1 - 4\xi H_0)/kT + 2\pi \lambda \) and \( \delta \equiv 2\pi k_c/kT \) are three dimensionless parameters taking into account the bending free energy. The \( \psi \)-function \((0 < \psi < 1)\) equals unity in the limit \( r \to 0 \) and zero as \( r \to \infty \).\(^{11,12} \)

By means of taking into account the entropy of self-assembling surfactant molecules to form a dispersion of tablet-shaped micelles gives the following relation between the volume fraction of micelles \( \phi_{mic} \) and bending elasticity constants,

\[
\phi_{mic} = \frac{\pi \xi^6}{\nu^2} \int_0^\infty \frac{8r^2 + 6\pi r + \pi^2}{\beta + 4\lambda r} e^{-\delta \psi(r) - \pi \beta r - 2\pi \lambda r^2} \, dr
\]  

(S14)

From the length and width distribution function given in eqn S14 it is straightforward to calculate the average width \( \langle \Omega \rangle = 2(\langle R \rangle + \xi) \) and length \( \langle \Lambda \rangle = \langle L \rangle + \langle \Omega \rangle \), in a dispersed phase of tablet-shaped micelles, as functions of the different bending elasticity constants. Similarly, it is possible to estimate the bending elasticity constants from experimentally obtained values of micelle width and length.
Calculation of maximum aggregation number of strictly spherical micelles

The volume in Å$^3$ of a linear aliphatic alkyl chains with $n$ carbons is given by

\[ v = 27.4 + 26.9n \]  \hspace{1cm} (S15)

Likewise, the length in Å of the fully stretched out chain is given by

\[ l_c = 1.5 + 1.265n \]  \hspace{1cm} (S16)

As a result, the maximum volume of a spherical micelle is set by $V_{max} = \frac{4\pi l_c^3}{3}$ and the corresponding aggregation number $N_{max} = \frac{V_{max}}{v} = \frac{4\pi l_c^3}{3v}$. For $n = 8$ this gives $N_{max} = 27$ whereas $N_{max} = 95$ for $n = 16$. For a mixed SOS/CTAB micelle, the maximum radius is set by the longer chain, i.e. $l_c = 21.7$ for CTAB whereas the average molecular volume is given by the linear relation $v = x v_8 + (1 - x) v_{16}$. As a result, $N_{max} = 101$ for $x = 0.15$ and $N_{max} = 103$ for $x = 0.20$. 
Derivation of relation between growth behavior and polydispersity for self-assembled aggregates

The following derivation was first carried out by Hall and Pethica in 1967. Here we have considered the distributions as continuous and used integral approximations, which gives an identical result as in ref 14.

The average aggregation number in a size distribution \( \phi(N) \) is defined as

\[
\langle N \rangle = \frac{\int N \phi(N) dN}{\int \phi(N) dN}
\]  \hspace{1cm} (S17)

Likewise, the average of the aggregation number squared equals

\[
\langle N^2 \rangle = \frac{\int N^2 \phi(N) dN}{\int \phi(N) dN}
\]  \hspace{1cm} (S18)

The total volume fraction of aggregated surfactant equals

\[
\phi_t = \int \phi(N) dN
\]  \hspace{1cm} (S19)

Taking the logarithm of eqn (S17) and combining with eqn (S19) gives

\[
\ln \langle N \rangle = \ln \int N \phi(N) dN - \ln \phi_t
\]  \hspace{1cm} (S20)

and the derivative with respect to \( \ln \phi_t \)

\[
\frac{d \ln \langle N \rangle}{d \ln \phi_t} = \frac{d \ln \int N \phi(N) dN}{d \ln \phi_t} - 1
\]  \hspace{1cm} (S21)

Using the following expression

\[
\phi(N) = e^{-N(\Delta \mu_{mic} - kT \ln \phi_{free})/kT} = e^{-N\Delta \mu_{mic}/kT} e^{N \ln \phi_{free}}
\]  \hspace{1cm} (S22)

we obtain

\[
\frac{d \ln \int N \phi(N) dN}{d \ln \phi_{free}} = \frac{1}{\int \phi(N) dN} \int \frac{d}{d \ln \phi_{free}} e^{-N\Delta \mu_{mic}/kT} e^{N \ln \phi_{free}} dN
\]  \hspace{1cm} (S23)

where
\[
\frac{d \int N \phi(N) dN}{d \ln \phi_{\text{free}}} = \frac{d \int N e^{-N \Delta \mu_{\text{mic}} / kT} e^{N \ln \phi_{\text{free}}} dN}{d \ln \phi_{\text{free}}} = \int N^2 e^{-N \Delta \mu_{\text{mic}} / kT} e^{N \ln \phi_{\text{free}}} dN = \int N^2 \phi(N) dN
\]  
(S24)

Combining eqns (S23) and (S24) consequently gives

\[
\frac{d \ln \int N \phi(N) dN}{d \ln \phi_{\text{free}}} = \frac{\int N^2 \phi(N) dN}{\int \phi(N) dN} = \frac{\langle N^2 \rangle}{\langle N \rangle}
\]  
(S25)

Likewise, in a similar manner it follows that

\[
\frac{d \ln \frac{\phi_t}{\phi_{\text{free}}}}{d \ln \phi_{\text{free}}} = \frac{d \ln \int \phi(N) dN}{d \ln \phi_{\text{free}}} = \frac{\int N \phi(N) dN}{\int \phi(N) dN} = \langle N \rangle
\]  
(S26)

and combining eqns (S25) and (S26) gives

\[
\frac{d \ln \int N \phi(N) dN}{d \ln \phi_t} = \left( \frac{d \ln \frac{\phi_t}{\phi_{\text{free}}}}{d \ln \phi_{\text{free}}} \right)^{-1} = \frac{\langle N^2 \rangle}{\langle N \rangle^2}
\]  
(S27)

Eqns (S20) and (S27) gives

\[
\frac{d \ln \langle N \rangle}{d \ln \phi_t} = \frac{d \ln \int N \phi(N) dN - d \ln \phi_t}{d \ln \phi_t} = \frac{\langle N^2 \rangle}{\langle N \rangle^2} - 1
\]  
(S28)

The relative standard deviation \(\sigma_N / \langle N \rangle\) is defined by the relation

\[
\left( \frac{\sigma_N}{\langle N \rangle} \right)^2 = \frac{(\langle N^2 \rangle - \langle N \rangle^2)}{(\langle N \rangle^2)} = \frac{(\langle N^2 \rangle)}{(\langle N \rangle)^2} - 1
\]  
(S29)

Combining eqns (S28) and (S29) finally gives

\[
\left( \frac{\sigma_N}{\langle N \rangle} \right) = \sqrt{\frac{d \ln \langle N \rangle}{d \ln \phi_t}}
\]  
(1)
Derivation of relation between relative standard deviations with respect to aggregation number and radius for spherical micelles

The relative standard deviation with respect to aggregation number $N$ is defined as

$$\frac{\sigma_N}{\langle N \rangle} = \sqrt{1 - \frac{\langle N^2 \rangle}{\langle N \rangle^2}} \tag{S30}$$

and with respect to radius $R$

$$\frac{\sigma_R}{\langle R \rangle} = \sqrt{1 - \frac{\langle R^2 \rangle}{\langle R \rangle^2}} \tag{S31}$$

Since $N \propto R^3$ for spherical geometry we obtain the following relation

$$\frac{\langle N^2 \rangle}{\langle N \rangle^2} = \frac{\langle R^6 \rangle}{\langle R \rangle^6} \tag{S32}$$

From eqns S30 and S31 it follows

$$\frac{\langle R^6 \rangle}{\langle R \rangle^6} = \left(1 - \left(\frac{\sigma_R}{\langle R \rangle} \right)^2\right)^3 \tag{S33}$$

Combining eqns S27, S28 and S30 gives

$$\frac{\sigma_N}{\langle N \rangle} = \sqrt{1 - \left(1 - \left(\frac{\sigma_R}{\langle R \rangle} \right)^2\right)^3} \tag{S34}$$

which may be evaluated as

$$\frac{\sigma_N}{\langle N \rangle} = 3 \frac{\sigma_R}{\langle R \rangle} - 3 \left(\frac{\sigma_R}{\langle R \rangle} \right)^2 + \left(\frac{\sigma_R}{\langle R \rangle} \right)^3 \tag{S35}$$

According to eqn S35, $\sigma_R/\langle R \rangle = 0.20$ corresponds to $\sigma_N/\langle N \rangle = 0.70$ and $\sigma_R/\langle R \rangle = 0.25$ corresponds to $\sigma_N/\langle N \rangle = 0.75$. 

16
Calculations of the Surfactant Mole Fraction in Micelles

The free surfactant concentration above cmc is expected to depend only on the composition in the aggregates, in so far inter-aggregate interactions are negligible. Accordingly, the concentration of free SOS (Surfactant 1) and CTAB (Surfactant 2), respectively, may be calculated by setting $c_1^{\text{free}} = \gamma_1 x_{\text{cmc}} c_1$ and $c_2^{\text{free}} = \gamma_2 (1 - x) c_{\text{cmc}}$. As a result, the concentration of surfactant present in self-assembled interfacial aggregates ($c_{\text{agg}}$), as well as the aggregate mole fraction of SOS ($x$), may be calculated for a given total surfactant concentration $c_t = c_{\text{agg}} + c_1^{\text{free}} + c_2^{\text{free}}$ and overall mole fraction of SOS $y = (c_1^{\text{free}} + xc_{\text{agg}})/c_t$ from given expressions for the activity coefficients as functions of $x$. The activity coefficients $\gamma_1$ and $\gamma_2$ were calculated from expressions derived in \textsuperscript{15}, i.e.

$$\gamma_1 = \left( s + \sqrt{s^2 + 1} \right)^{-2|2x - 1|/(2x - 1)} \left( \frac{2q}{s} \right)^{2j} \exp \left[ -2|2x - 1|q - \frac{\mu_1}{kT} - 4pq \frac{1 - x}{2x - 1} \right] \quad (S36)$$

$$\gamma_2 = \left( s + \sqrt{s^2 + 1} \right)^{-2|2x - 1|/(2x - 1)} \left( \frac{2q}{s} \right)^{2j} \exp \left[ -2|2x - 1|q - \frac{\mu_2}{kT} + 4pq \frac{1 - x}{2x - 1} \right] \quad (S37)$$

where

$$s \equiv |2x - 1| \frac{2\pi l_B}{ak} \quad (S38)$$

is the reduced charge density and

$$p \equiv \frac{s}{\sqrt{s^2 + 1}} \quad (S39)$$

$$q \equiv \frac{s}{\sqrt{s^2 + 1 + 1}} \quad (S40)$$
$\mu_1 \equiv \mu(x = 1)$ and $\mu_2 \equiv \mu(x = 0)$ are the molecular electrostatic free energies in pure solutions of Surfactant 1 (SOS) and Surfactant 2 (CTAB), respectively. The area per aggregated surfactant was set to $a = 40 \, \text{Å}^2$ and the Bjerrum length $l_B$ equals about 7.15 Å and the Debye screening length $\kappa^{-1} = 3.04/\sqrt{c_{el}} \, \text{Å}$ for a 1:1 electrolyte in an aqueous medium at 25 °C. $J \equiv aH/\pi l_B$ is the dimensionless curvature and the mean curvature was roughly set to $H = 0.05 \, \text{Å}^{-1}$ for samples with micelles. The choice of $J$ is found to have a small and almost negligible influence on the calculated aggregate compositions $x$.

The critical micelle concentration of SOS is $cmc_1 = 133 \, \text{mM}$ and the critical micelle concentration of CTAB is $cmc_2 = 0.92 \, \text{mM}$. Results from the calculations for investigated samples are tabulated below.

<table>
<thead>
<tr>
<th>$y$</th>
<th>$c_t/\text{mM}$</th>
<th>$x$</th>
<th>$c_{agg}/\text{mM}$</th>
<th>$c_{1\text{free}}/\text{mM}$</th>
<th>$c_{2\text{free}}/\text{mM}$</th>
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<td>$9.6 \cdot 10^{-6}$</td>
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As a result of the low free monomer concentrations, we may conclude that the composition in the micelles $x$ is fairly constant in the range of measured samples above $c_t = 10 \, \text{mM}$.
References