## Formation of Surfactant-Stabilised Silica Organosols -Supporting Information

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## Scattering laws used to analyse SANS.

The absolute scattering intensity, I(Q), for polydisperse, homogeneous hard-spheres can be written as,

$$I(Q) = N_P[P(Q, R)p(R)]S(Q)$$
(S1)

where  $N_P$  is the particle number density, P(Q) is the single particle form factor, p(R) is a normalized distribution function, and S(Q) is the interparticle structure factor, which accounts for interactions. When dealing with spherical core-shell particles, the general form factor, P(Q, r), is given as:<sup>1</sup>

$$P(Q, r) = \frac{16\pi^2}{9} \left[ (\rho_{shell} - \rho_{solvent}) 3r_d^3 \left( \frac{\sin Qr_d - Qr_d \cos Qr_d}{(Qr_d)^3} \right) - 3r_c^3 \left( \frac{\sin Qr_c - Qr_c \cos Qr_c}{(Qr_c)^3} \right) \right]^2 + \left[ (\rho_{core} - \rho_{solvent}) 3r_c^3 \left( \frac{\sin Qr_c - Qr_c \cos Qr_c}{(Qr_c)^3} \right) \right]^2$$
(S2)

where  $r_d$  is the particle (core+shell) radius,  $r_c$  the core radius,  $\rho_{shell}$ ,  $\rho_{solvent}$  and  $\rho_{core}$  the scattering length density of the shell, solvent and core respectively. The shell (layer) thickness ( $\tau$  in the main text) can be determined as  $r_d - r_c$ .

In the silica and surfactant systems studied here, there was very little effect of a structure factor, S(Q), probably due to a combination of the low particle volume fraction and their low

surface charge.

The polydispersity in the system was given by a Schultz distribution function, described by an average particle radius and root mean square deviation:<sup>2</sup>

$$\sigma = \frac{R^{av}}{(Z+1)^{1/2}}$$
(S3)

where  $R^{av}$  is the average particle radius, and Z is a width parameter.

Under the limiting conditions  $\rho_{shell} = \rho_{core}$  then Equation S2 reverts to the form factor for a homogenous spheres,<sup>1,2</sup> called equation S2'. And then the scattering law formulated from equations S1, S2' and S3 can be used to describe SANS from homogeneous spherical micelles, obeying a Schulz polydispersity. This approach was used in the paper to fit the equilibrium reversed micellar components found for the AOT and DDAB-stabilized systems. Figure 5, described in the main paper, shows simulations using this composite scattering law for core-shell silica colloids (Equation S1, S2 and S3) in equilibrium with homogeneous spherical reversed micelles (Equations S1, S2' and S3). Figure 4 in the main paper shows fits to real data using these two scattering laws.

The approach is outlined in the main manuscript Results and discussion: Structure and interactions; "The effect of these two populations and their composite scattering is shown in Figure 5. Scattering from the shell and micelles were calculated separately, as simultaneous fitting of both laws (i.e. core-shell silicas with Equations S1, S2 and S3 with also homogeneous spherical micelles with S1, S2' and S3) resulted in too many floating parameters to achieve reliable fits. The generated fits for the micellar and shell regions were then added in a weighted summation to provide the final model fit."

Model fits were generated using the least squares fitting program FISH.<sup>3</sup>

## References

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