Supplementary Information

Title

Surface charge of acidic sophorolipids micelles: effect of base and time

Authors

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Analytical expression for the structure factor.

We use here an analytical expression of the structure factor *S(q)* for the interaction potential $U(r)$, that is obtained in the Mean Spherical Approximation (MSA)[1], assuming that the Yukawa potential is a weak repulsive tail:

$$S_{Yukawa}(q) = \frac{1}{1 + nc_{HS}(q) + nc_{Yukawa}(q)} \quad \text{Eq 1}$$

where *n* has been defined before as the number of micelles per unit volume. The term $c_{HS}(q)$ is the direct correlation function for a simple hard-sphere interaction, where the hard-sphere volume fraction is ϕ_{HS}

$$nc_{HS}(q) = 24\phi_{HS}A(qD_{HS})/(qD_{HS})^6 \quad \text{Eq 2}$$

with

$$A(x) = 24\gamma_{HS} - 2\beta_{HS}x^2 - \cos(x)\left(24\gamma_{HS} - 2(\beta_{HS} + 6\gamma_{HS})x^2 + (\alpha_{HS} + \beta_{HS} + \gamma_{HS})x^4\right) + x\sin(x)\left(-24\gamma_{HS} + (\alpha_{HS} + 2\beta_{HS} + 4\gamma_{HS})x^2\right) \quad \text{Eq 3}$$

$$\alpha_{HS} = \frac{(1+2\phi_{HS})^2}{(1-\phi_{HS})^4} \quad \beta_{HS} = -\phi_{HS}\frac{3}{2}\frac{(2+\phi_{HS})^2}{(1-\phi_{HS})^4} \quad \gamma_{HS} = \frac{\alpha_{HS}\phi_{HS}}{2} \quad \text{Eq 4}$$

and :

$$nc_{Yukawa}(q) = -24\frac{\phi_{HS}U_0}{D_{HS}^2 q\left(\kappa^2 + q^2\right)}\left(q\cos(qD_{HS}) + \kappa\sin(qD_{HS})\right) \quad \text{Eq 5}$$

Finally, the low-q portion (q< 0.01 Å^{-1}) of the spectra has been fitted by adding a power-law term, $q^{-\beta}$, where $1 < \beta < 2$, to the expression of I(q). All data have been treated using a least-square fitting procedure.[2]

The fitting model.

As it was proposed before,[3] and considering the molecular structure of sophorolipids, it is reasonable to use a core-shell model: the sophorose group identifies the hydrophilic shell while the oleic acid moiety is associated with the hydrophobic core. R_h and R_c refer, respectively, to the shell and core sizes, whereas (R_c+R_h) represents the overall cross-micellar radius. For the specific case of lactonic sophorolipids, Penfold et al.[3] also proposed a vesicle shape with a double surfactant layer and an inner water-rich core. This choice is in agreement with the molecular structure of sophorolipids and it raises important, unsolved, questions even for the acidic form of the compound. In fact, tentatives to describe the local conformation of the oleic acid chain and the exact positioning of the COOH group have been done for acidic sophorolipids[4] and similar bolaform systems,[5] but a clear answer is not yet found.

In terms of the type of shape, three simple forms can be employed: sphere, ellipsoid and cylinder. The choice is relatively easy when no intermicellar interactions are present, that is for unitary values of the structure factor, S(q), which occur in the regime 1 for the SL-COOH system. In regime 2, where S(q)≠ 1, spherical/elliptical objects are rather observed. For this reason, we tested a sphere and ellipsoid of revolution form factors to fit SANS spectra presented here. In particular, as argumented in the following, the two-axis core-shell ellipsoid of revolution (R_c= inner core cross-radius; R_h= width of the corona; L= ellipsoid half length; See Figure 2 in the main text) is actually preferred over the sphere.

Beyond the shape, the model also takes into account the core (ρ_{core}), shell (ρ_{shell}) and solvent densities (ρ_0), which are summarized in the α parameter, α= (ρ_{shell}-ρ_0)/(ρ_{core}-ρ_0). Experiments have been run in D_2O, for which the neutron Scattering Length Density (SLD) is known to be ρ_0= $6.36 \cdot 10^{-6}$ Å^{-2}. Estimating the SLD for sophorolipids in water, and in particular the core and shell components is more delicate. To do so, we used the NIST database calculator[6] in which we separately calculated the sophorose ($C_{12}H_{21}O_{10}$) and oleic acid ($C_{18}H_{35}O_3$) contributions, nevertheless taking the sophorolipids density (1.097 g·cm^{-3}). The theoretical α value from the known SLD of D_2O (ρ_0), core (ρ_{core}) and shell (ρ_{shell}) for sophorolipids is 0.83 and a preliminary set of fits was done (results not shown) keeping this parameter constant. Then, α was set as a free variable. In this case, the fit was controlled by assuming that the effective micellar shell density (ρ_{shell}) should always be contained between the solvent (ρ_0) and the theoretical SLD of the sophorose layer, ρ_{shell}(sophorose)= $1.20 \cdot 10^{-6}$ Å^{-2}. Finally, the structure factor is characterized by four parameters: the volume fraction, ϕ, the hard-sphere radius, R_{HS}, the potential strength (in K_bT units), U_0/K_bT and the screening

parameter, κ (refer to Eq.2-5 in the main text and Eq.2 and Eq. 10 in the SI). The most important parameters in the fit, their value and units are summarized in Table 1 in the main text.

References

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