

Electronic Supplementary Information

Interfacial properties of lipid sponge-like nanoparticles and the role of stabilizer on particle structure and surface interactions

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SANS modelling:

The core-shell sphere model is described as follows (from SASView models):

\[
p(q) = \frac{\text{scale}}{V_s} \left[ 2V_c(\rho_c - \rho_s) \frac{\sin(qr_c) - qr_c \cos(qr_c)}{(qr_c)^3} + 3V_c(\rho_c - \rho_{\text{solv}}) \frac{\sin(qr_c) - qr_c \cos(qr_c)}{(qr_c)^3} \right]^2 + \text{background}
\]

where scale is a scale factor, \( V_s \) is the volume of the outer shell, \( V_c \) is the volume of the core, \( r_s \) is the radius of the shell, \( r_c \) is the radius of the core, \( \rho_c \) is the scattering length density of the core, \( \rho_s \) is the scattering length density of the shell and \( \rho_{\text{solv}} \) is the scattering length density of the solvent.

SANS results: Table S1 shows the estimated solvent fractions and SLD corrected by the solvent values of the core and the shell of L3-NP, obtained by comparing two isotopic solvent contrasts.

<table>
<thead>
<tr>
<th>Estimated values of</th>
<th>dP80</th>
<th>hP80</th>
</tr>
</thead>
<tbody>
<tr>
<td>Hydration Core (%)</td>
<td>55.7</td>
<td>55.5</td>
</tr>
<tr>
<td>Hydration Shell (%)</td>
<td>90.7</td>
<td>90.8</td>
</tr>
<tr>
<td>SLD Core (Å⁻²) lipid/P80 mixture</td>
<td>1.04</td>
<td>1.03</td>
</tr>
<tr>
<td>SLD Shell (Å⁻²) lipid/P80 mixture</td>
<td>3.38</td>
<td>3.43</td>
</tr>
</tbody>
</table>

If we assume that SLDcore and volume fraction of the solvent (x) is equal for both solvent contrast (1 and 2):

\[
x = \frac{\text{SLDcore-Fitting1} - \text{SLDcore-Fitting2}}{\text{SLDsolvent1} - \text{SLDsolvent2}}
\]
QCM-D theory

Voigt viscoelastic model:

This model takes into account the effects of coupled water or solvent used and the adsorbed film is represented by a complex shear modulus according to:

\[ G = G'_f + iG''_f = \mu_f + i2\pi f \eta_f = \mu_f (1 + i2\pi f \tau_f) \]

where \( \mu_f \) is the elastic shear modulus, \( \eta_f \) the shear viscosity, \( f \) the oscillation frequency, and \( \tau_f \) the characteristic relaxation time of the film. The frequency and dissipation changes are then correlated to the viscoelastic properties of the film as

\[ \Delta f = \frac{\text{Im}(\beta)}{2\pi \tau_f \rho_q} \]

and

\[ \Delta D = -\frac{\text{Re}(\beta)}{\pi f \tau_q \rho_q} \]

where \( \beta \) relies on the thickness (\( t \)) and density (\( \rho = 0.984 \text{ g cm}^{-3} \)) of the film, and on the bulk-liquid density (\( 0.997 \text{ g cm}^{-3} \)) and viscosity (0.9 mPa·s).

\( \beta \) expression for QCM-D data analysis:

\[ \beta = \frac{2\pi f \eta_f - i\mu_f}{2\pi f \eta_f - i\mu_f} + 1 \]

\[ \alpha = \frac{2\pi f \eta_f - i\mu_f}{2\pi f \eta_f - i\mu_f} \]

\[ \xi_1 = \frac{2\pi f \rho_f}{\mu_f - (2\pi f \eta_f) \xi_2} \]

\[ \xi_2 = \frac{2\pi f \rho_f}{\eta_f} \]

where \( f \) is the oscillation frequency, \( \eta \) is the shear viscosity, \( \mu \) is the elastic shear modulus and \( \rho \) the density.

QCM results

QCM fitting: Figure S1 depicts the viscosity and shear values obtained from fitting the QCM-D data in Figure 3 to the Voigt viscoelastic model.

Figure S1. Viscosity and shear values obtained from the Voigt viscoelastic model fit. Arrows indicate addition of L3-NPs and rinsing processes.
Neutron reflectometry results: 5-layer model

Neutron reflectometry data was also fitted using a 5-layer model (Figure S3 and Table S2). This model consists of the same 4-layers described on the paper with the addition of a solvent layer between the silica surface and the lipid film. As a result of adding this extra layer, the head group thickness is reduced and it is closer to the head group size expected for DGMO and GMO-50 rather than the one from P80. In addition, the head group layer became much less hydrated. This can be explained because some of the solvent in the head group layer from the 4-layer model is now found in the solvent layer and hence, the head group hydration is diminished. It can be noticed that the SLD value of the head group is lower, while the SLD value of the hydrocarbon tail is higher than the 4-layer model. The resulting reflectivity curve could be averaging these two values and that is why one compensates the other. It should be although noted that the highly hydrated head group film in the 4-layer model makes this layer very little sensible to changes in head group SLD. The rest of the parameters are quite similar to the ones obtained with the 4-layer model and the total adsorbed mass was calculated to be very close as well (340 ng/cm²). Therefore, most of the discussion regarding the 4-layer model can be also applied here, although the $\chi^2$ values very slightly better for the other model.

Figure S2. Adsorption of 0.1mg/ml of L-3-NPs on bare hydrophilic silica a) In water with no salt, b) 10mM citrate buffer pH=4 and no salt, c) 10mM citrate buffer pH=5.5 and no salt and d) 10mM citrate buffer pH=5.5 and 150mM NaCl. Number 1 and 2 indicate injection of sample and rinsing with corresponding solvent, respectively. Asterisk display when the pump was stopped. Experimental is depicted for four different overtones.
Table S2. Parameters used to fit the neutron reflectometry data displayed on Figure S3 with a 5-layer model.

<table>
<thead>
<tr>
<th></th>
<th>Thickness (Å)</th>
<th>SLD ($10^{-6}$ Å$^{-2}$)</th>
<th>Solvent (vol%)</th>
<th>Roughness (Å)</th>
</tr>
</thead>
<tbody>
<tr>
<td>1.SiO$_2$</td>
<td>6 ± 1</td>
<td>3.41</td>
<td>1.4 ± 4.5</td>
<td>0.9 ± 3.2</td>
</tr>
<tr>
<td>2.Solvent layer</td>
<td>9.7 ± 2.7</td>
<td>same as solvent</td>
<td>100</td>
<td>3.9 ± 3.1</td>
</tr>
<tr>
<td>3.Lipid head</td>
<td>8.3 ± 3.3</td>
<td>0.8 ± 0.3</td>
<td>38 ± 10</td>
<td>6.2 ± 2</td>
</tr>
<tr>
<td>4.Lipid tail</td>
<td>28.1 ± 3.4</td>
<td>-0.13 ± 0.09</td>
<td>0.004 ± 4</td>
<td>0.06 ± 5</td>
</tr>
<tr>
<td>5.Lipid head</td>
<td>8.3 ± 3.3</td>
<td>0.8 ± 0.3</td>
<td>38 ± 10</td>
<td>6.2 ± 2</td>
</tr>
</tbody>
</table>

References