Raspberry Model Sensitivity

The Raspberry Model for small angle scattering data is useful for quantifying the adsorption of particles at emulsion interfaces. Because there are so many fit parameters in this model, it is critical to constrain as many of them as possible with known values from independent experiments. Here we examine the sensitivity of this model to the oil droplet radius and the percentage of oil-water interface that is covered with particles. In Figure S1, the scattering curve of a 1.0 vol% hexadecane in water emulsion stabilized by 0.024 vol% 6.11nm amphiphilic gold particles that are functionalize with 0.8 PEG chains/nm²Au and butane-thiol is compared to the Raspberry Model for three different oil droplet radii. The model is relatively insensitive to this parameter. Therefore, the average oil droplet radius (~500 nm) had to be independently measured with Dynamic Light Scattering for confirmation. Figure S2 shows the differences in the scattering curve that result from different percentages of oil-water interface covered with particles. The model is quite sensitive to this parameter with a deviation of 2%. The best fit for this sample is 88% of the oil-water interface covered with nanoparticles.
Figure S1. Desmeared SAXS data for a 1.0 vol% hexadecane in water emulsion stabilized by 0.024 vol% 6.11nm amphiphilic gold particles that are functionalize with 0.8 PEG chains/nm² Au and butane-thiol. The Raspberry Model fits are compared for three different oil droplet radii where the remaining parameters of the model are an oil droplet polydispersity index of 0.1 (Gaussian distribution), $R_o = 6.11$ nm, $\delta = 0$, $\phi_o = 0.00998$, $\phi_p^T = 0.00024$, $\rho_w = 9.46 \times 10^{-6}$ Å⁻², $\rho_o = 7.52 \times 10^{-6}$ Å⁻², $\rho_p = 1.25 \times 10^{-4}$ Å⁻², 88.0% interface coverage.

Figure S2. Desmeared SAXS data for a 1.0 vol% hexadecane in water emulsion stabilized by 0.024 vol% 6.11nm amphiphilic gold particles that are functionalize with 0.8 PEG chains/nm² Au and butane-thiol. The Raspberry Model fits are compared for five different percentages of oil-water interface covered with particles. The remaining parameters of the model are $R_o = 494$ nm with a polydispersity index of 0.1 (Gaussian distribution), $R_p = 6.11$ nm, $\delta = 0$, $\phi_o = 0.00998$, $\phi_p^T = 0.00024$, $\rho_w = 9.46 \times 10^{-6}$ Å⁻², $\rho_o = 7.52 \times 10^{-6}$ Å⁻², $\rho_p = 1.25 \times 10^{-4}$ Å⁻².
Nanoparticle Surfactant Clusters

The amphiphilic gold nanoparticle surfactants form clusters in water prior to emulsification. The aggregation number, or number of particles in each cluster, can be quantified using Transmission Electron Microscopy. Here, the clusters are freeze-dried on a TEM grid to prevent clusters from aggregating during solvent evaporation. The TEM images show that there is a distribution of cluster sizes in this sample. However, the average cluster size is 5 particles per cluster. Figure S3 shows several examples of TEM images that were obtained for gold particles functionalized with 0.8 PEG chains/nm²Au and butane-thiol. The bottom right graph is the resulting histogram that is generated from the TEM images. This histogram is then used to model the SAXS data using the Debye equation.¹

Figure S3. Example TEM micrographs of nanoparticle surfactant clusters of 0.8 PEG chains/nm²Au and butane-thiol. The bottom right graph is the distribution of cluster sizes for the sample.
The particle clusters also have unique optical properties due to the plasmon resonance of gold. Individual gold particles have an absorbance peak at 520 nm. That absorbance peak is red-shifted to higher wavelengths when clusters containing several particles spaced closely together are formed. However, this shift is much smaller than that which is observed upon emulsification of oil in the presence of nanoparticle surfactants. In Figure S4a we show the spectra for particles functionalized with 0.6 PEG chains/nm$^2$Au and different alkane-thiols. The butane-thiol particles are more red-shifted than the rest because this is the shortest alkane-thiol and the inter-particle spacing is also small. Clearly, the shift in absorbance peak is not nearly as pronounced compared to that observed when these same particles are emulsified in oil (Figure 5). Furthermore, there are also no significant changes in absorbance in the near-IR region. Figure S4b shows the absorbance peak for all of the clusters examined in this study prior to emulsification.

Figure S4. a) UVVis spectra of nanoparticle surfactant clusters with 0.6 PEG chains/nm$^2$Au and different alkane-thiols. The curves are normalized by the total particle concentration in each sample. b) Absorbance peak plotted as a function of PEG-thiol concentration for butane-thiol (circles), octane-thiol (triangles) and dodecane-thiol (squares) where the dotted line is the absorbance for bare gold particles.
References