Electronic Supplementary Information (ESI) for Soft Matter

Nanoscale structure of surfactant-induced nanoparticle monolayers at the oil/water interface

Davide C. E. Calzolari,^{$a\ddagger$} Diego Pontoni,^{*a} Moshe Deutsch,^b Harald Reichert,^{a,c} and Jean Daillant^d

^a European Synchrotron Radiation Facility, 6 rue Jules Horowitz, BP220, 38043 Grenoble, France. E-mail: pontoni@esrf.fr

^b Physics Department and Institute of Nanotechnology and Advanced Materials, Bar-Ilan University, IL-52900 Ramat Gan, Israel.

^c Max-Planck-Institut für Metallforschung, Heisenbergstr. 3, D-70569 Stuttgart, Germany.

^d CEA, IRAMIS, LIONS, bat. 125 CEA Saclay, F-91191 Gif-sur-Yvette Cedex, France.

‡ Present address: Physics Department, Fribourg University, Ch. du Musée 3, CH-1700 Fribourg, Switzerland.

We report here supplemental material that further highlights two issues: the sensitivity of our approach to the average NP immersion both in the low ϕ_c (Fig.1) and high ϕ_c (Fig.2) systems, and the influence of including the electron density of the CTAB in the model.

The CTAB contribution was assessed for two different physical models for the CTAB: for molecules absorbed at the water/oil interface (silica/CTAB-film model) or at the NP surfaces (silica/CTAB-shell model). The resultant changes in the XRR fits and in the fitted parameter values are shown in Fig.3, Fig.4 and Table 1.

In the first case the flat film of interfacial CTAB molecules is approximated by a box of constant electron density ρ_{ff} , thickness t_{ff} and roughness σ_{ff} placed at the oil side of the interface. This model takes into account the fact that only the water/oil interface not occupied by the spheres is available for interfacial CTAB absorption. In the second model extension, the CTAB molecules adsorbed onto the NP surface are approximated by a spherical shell surrounding the spheres and having electron density ρ_{sh} and thickness t_{sh} . In the case of small separation between neighboring particles, the electron density of the two overlapping shells are added to each other. This is considered as an approximated description of the possible interdigitation between hydrocarbon chains of the CTAB molecules adsorbed onto the surfaces of neighboring particles and it represents an upper limit for the real electron density in the system. As discussed in the main paper, the NPs that segregate to the interface may eventually be covered by an anisotropic distribution of CTAB molecules, which may be described by a combination of the CTAB-film and CTAB-shell models.

While the CTAB modeling above is useful for error estimation, it mainly serves a more important purpose: following the χ^2 variations of the different fits allows drawing important qualitative conclusions regarding the possible arrangement of the interfacial CTAB molecules. The following conclusions emerge from an examination of Table 1:

- The low ϕ_c XRR data are compatible with a flat film of CTAB molecules absorbed at the small fraction of oil/water interface that is not occupied by the spheres
- The low ϕ_c XRR data are not compatible with a complete shell of CTAB molecules surrounding uniformly each interfacial NP
- The high ϕ_c XRR data are not compatible with the presence of CTAB only as a flat film at the NP-free portions of the oil/water interface
- The high ϕ_c XRR data are compatible with a CTAB shell surrounding the NPs, although this shell may not be isotropic as assumed in our model

This journal is © The Royal Society of Chemistry [year]



Fig. 1 Modeling the dilute surfactant XRR data: effect of varying NP immersion. Physical model calculations at various average NP immersion h_{av} . All other parameters are fixed to the best fit values (Table 1 in the main paper) for the ϕ_c =0.05 mM XRR data (\bigcirc). The best fit (h_{av} =0.48 nm) presented in the main paper is intermediate between the red and orange curves. Note that in these close-packed NP monolayers (*s*=0.01 nm; 90.7% NP surface fraction) the height of the $\rho(z)$ profile peak (inset) varies only marginally with immersion.



Fig. 2 Modeling the concentrated surfactant XRR data: effect of varying NP immersion. Physical model calculations at various average NP immersion h_{av} . All other parameters are fixed to the best fit values (Table 1 in the main paper) for the ϕ_c =0.75 mM XRR data (\triangle). The best fit (h_{av} =1.08 nm) presented in the main paper is near to the orange curve. Note that in these non-close-packed NP monolayers (*s*=1.57 nm; 54% NP surface fraction) the height of the $\rho(z)$ profile peak (inset) varies more significantly with immersion than in the close-packed NP monolayer case (Fig.1).

2 | Journal Name, 2010, [vol],1–5



Fig. 3 Including CTAB in the physical model for the dilute surfactant system. The XRR data measured at ϕ_c =0.05 mM (\bigcirc) is plotted together with the best silica-only fit (black line) presented in the main paper. The red lines indicate the best fit for a model including a flat interfacial CTAB film with parameters listed in the second numerical column of Fig.1. The model adds the CTAB electron density only in the interface regions that are not occupied by the NPs. The quality of the silica/CTAB-film fit is only slightly poorer than the silica-only fit, as attested by its χ^2 value. The NP separation is only slightly larger (0.31 nm) than the silica-only model result (0.01 nm). The average immersion decreases from 0.48 nm to 0.38 nm, suggesting a slightly lower binding energy than that found in the silica-only model. However the variation is within the error bar stated in the main paper. The blue lines indicate an example of model fit including a shell around the spheres representing the CTAB molecules adsorbed isotropically on the NP surface. It was not possible to obtain with this model fits of quality comparable to those of the silica-only and silica/CTAB-film best fits.



Fig. 4 Including CTAB in the physical model for the concentrated surfactant system. XRR data measured at ϕ_c =0.75 mM (\triangle) and fits obtained with the silica-only (black lines), silica/CTAB-film (red lines), and silica/CTAB-shell (blue lines) models. In this case the model including only CTAB molecules at the NP-free portion of the water/oil interface (red lines) is not able to reproduce the data correctly. A better agreement with the data is obtained with the silica/CTAB-shell model (blue lines), although the χ^2 value is still larger than that of the silica-only model fit. The silica/CTAB-shell fit would imply a larger NP immersion (1.58 nm) and therefore a larger binding energy than that stated in the main paper. Considering that the real value most probably lies in between those yielded by the silica-only and silica/CTAB-shell models, we increased the binding energy uncertainty in this case to ± 10 kT.

This journal is © The Royal Society of Chemistry [year]

	NO CTAB	CTAB film	CTAB shell	NO CTAB	CTAB film	CTAB shell
	Fig.3	Fig.3	Fig.3	Fig.4	Fig.4	Fig.4
	(black line)	(red line)	(blue line)	(black line)	(red line)	(blue line)
$\phi_c (\mathrm{mM})$	0.05	0.05	0.05	0.75	0.75	0.75
h_{av} (nm)	0.48	0.38	0.82	1.08	1.16	1.58
<i>s</i> (nm)	0.01	0.31	0.74	1.56	1.62	2.07
σ_h (nm)	0.60	0.53	0.61	0.59	0.64	0.65
σ_i (nm)	0.60	0.43	0.60	0.56	0.58	0.55
ρ_{ff} (e ⁻ /nm ³)	/	240	/	/	240	/
t_{ff} (nm)	/	1.56	/	/	1.56	/
$\sigma_{ff}(\text{nm})$	/	0.51	/	/	0.51	/
ρ_{sh} (e ⁻ /nm ³)	/	/	260	/	/	260
t_{sh} (nm)	/	/	1.20	/	/	1.20
χ^2	0.0029	0.0046	0.0228	0.0131	0.0313	0.0251

Table 1 Model parameters for the fits shown in Fig.3 and Fig.4. The particle size parameters were fixed to $r_{av} = 2.67$ nm and $\sigma_r = 0.44$ nm, as inferred from SAXS measurements and XRR fit refinements.



Fig. 5 Comparison of our models with the solution obtained using a model-independent approach. XRR data measured at ϕ_c =0.05 mM (\bigcirc) and fits obtained with the 2-box model (orange lines), physical model (red dashed lines), and the model-independent approach (blue lines) through the StochFit¹ program. The inset shows that the electron density profile given by this stochastic-fitting approach is basically the same we found using our physical model approach, further supporting the validity of our experimental data fitting procedure.

Finally, we include in this supplemental material an additional test, which further supports the validity of the double fitting approach (box and physical models) we have presented in this paper. We have compared the solutions obtained with our models with the solution given by the program *Stochfit*.¹ This program provides a stochastic model-independent (MI) method for analyzing XRR curves of thin films at interfaces. In this MI approach, the solution that best fits the experimental points is obtained without any initial guess of the electron density profile shape: the user only defines some basic boundary conditions, such as the values of water and hexane electron densities and an indicative value for the NPs electron density and the film thickness. The program StochFit then varies stochastically the density of a large number of adjacent thin (~0.5 Å thick) boxes and finds the overall ρ_z profile that best fits the XRR curve.¹

Fig.5 shows the 2-box model (orange lines), the physical model (red dashed lines), and the MI solution (blue lines) for the low CTAB concentration studied. It is clear that the MI solution obtained with Stochfit is basically the same solution we have obtained using our fitting approach. In the frame of the physical model, different NP immersions with respect to the interface yield remarkably different electron density profiles and XRR models, as shown in Fig.1. This means that our physical model approach indeed yielded the best fit, that for the case of ϕ_c =0.05 mM shown in Fig.5 corresponds to a defined particle immersion of 0.45 nm and a defined contact angle of (146±4)°.

References

1 S. M. Danauskas, D. Li, M. Meron, B. Lin and K. Y. C. Lee, J. Appl. Cryst., 2008, 41, 1187–1193.