Supporting Information: Interfacial properties and iron binding to bacterial proteins that promote the growth of magnetite nano-crystals: X-ray reflectivity and surface spectroscopy studies

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Analysis of X-ray reflectivity

X-ray reflectivity is commonly used to deduce the electron density (ED) profile $\rho(z)$ with z-axis normal to the air-liquid surface,[1] and it is then related to the density profile of the film. In the

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kinematical approximation, the reflectivity $R(Q_z)$, $(Q_z = 4\pi \sin\alpha_i / \lambda)$ is given by

$$R(Q_z) = R_F \left| \frac{1}{\rho_{sub}} \int \frac{d\rho(z)}{dz} \exp(iQ_z z) dz \right|^2 \qquad (1)$$

where R_F is the calculated reflectivity from an ideally sharp, flat interface separating the liquid (ED ρ_{sub}) and the vapor (ED $\rho_v = 0$). The reflectivity can also be calculated by using a recursive dynamical method[2] as we do in this study. The interpretation of reflectivity data was based on the effective-density model,[3] which has been successfully used to study iron nanoparticles and proteins adsorption at the air/water interface.[4–6] The ED profile $\rho(z)$ is constructed by piling up N layers along the surface normal (z-direction), each of which with an electron number density (ρ_j) and a thickness (d_j). Subscripts $j = 0$ and $j = N+1$ represent the subphase and the vapor phase, respectively. The effective-density model assumes uncorrelated roughnesses among interfaces, such that the ED profile is obtained as follows:[3]

$$\rho(z) = \left(\sum_{j=0}^{N} \rho_j w_j(z) \right) / \left(\sum_{j=0}^{N} w_j(z) \right) \qquad (2)$$

where, the weighting function $w_j(z)$ is defined as

$$w_j(z) = \begin{cases} \frac{1}{2}\left\{ 1 + \mathrm{erf}\left[(z - z_j)/\sqrt{2}\sigma_j \right] \right\} & z \leq \zeta_j, \\ \frac{1}{2}\left\{ 1 - \mathrm{erf}\left[(z - z_j)/\sqrt{2}\sigma_j \right] \right\} & z > \zeta_j, \end{cases} \qquad (3)$$

The coordinate $\zeta_j = (\sigma_j z_{j-1} + \sigma_{j-1} z_j)/(\sigma_j + \sigma_{j-1})$. $\sigma_j, j = 0, 1, 2, ..., N$, represents the roughness between $(j-1)$-th and j-th layers. The continuous ED profile obtained using Eq. (2) is sliced into a histogram of M slabs of constant thickness and ED (determined by Eq. (2) evaluated at the midpoint of each slab). The reflectivity is then calculated by the Parratt formalism with $M \sim 100$ and a uniform slab thickness ~ 1 Å.

In accordance with the assumption that the adsorbed layer(s) consists of Mms6, subphase solutions and iron, ρ_j $(j = 1, 2, ..., N)$ is set to be larger than ρ_{sub}, i.e. $\rho_j > 0.334$ e/Å^3. ρ_0 and ρ_{N+1} are

set as constants 0.334 e/Å^3 and 0, respectively. In this study, it is found that $N = 2$ (in the absence of iron constituents) and $N = 3$ (in the presence of iron constituents) are sufficient to fit the R/R_F from adsorbed Mms6 layer(s) well. Further increase in N does not improve χ^2 significantly.

The multi-dimensional parameter space spanned by parameter set (ρ_j, d_j and σ_j) are sampled through Monte-Carlo method as follows:

(1) The initial values of parameter set are generated randomly (within physically meaningful boundaries) and undergo optimization iterations until reaching a local minimum of χ^2, denoted as $\chi^2_{\text{local min}}$.

(2) The refined parameters and the corresponding $\chi^2_{\text{local min}}$ are registered.

(3) Repeat (1) and (2) for a sufficiently large number of times (10^3-10^4 times, in this case).

(4) The global minimum of χ^2, denoted as $\chi^2_{\text{global min}}$, is the minimum of all $\chi^2_{\text{local min}}$. Its corresponding parameters are considered as the best parameter set.

(5) A hyper-surface in parameter space is such that it encloses all the registered parameter sets whose $\chi^2_{\text{local min}}$ values differ from $\chi^2_{\text{global min}}$ by no more than a desired amount. These parameter sets are selected to construct ED profiles.

(6) The volume fraction profiles and Mms6 adsorption can be calculated based on parameters selected through (5). Their variation range can be determined thereafter.

An example is shown in Figure 1. In (a), the R/R_F data (symbols) correspond to 47 μg Mms6 deposited and compressed on the buffer surface area $\sim$ 105 cm^2. The overlay of solid lines are calculated reflectivities corresponding to χ^2 changing from $\chi^2_{\text{global min}}$ by 100%. In (b), the ED profiles are given in three special cases. The black one corresponds to $\chi^2_{\text{global min}}$. The other two solid lines correspond to $\chi^2_{\text{global min}} \times 200\%$. In (c), their corresponding volume fraction profiles are given. The numerical values are summarized in Table 1.

Table 1: Structure Parameters for adsorbed Mms6 on aqueous surface characterized by XR data in Figure 1 (a).[a]

ρ_1 (e/Å^3)	ρ_2 (e/Å^3)	Total layer thickness ξ (Å)	Mms6 adsorption Γ_s ($\times 10^{-4}$ mg/cm^2)
0.393 ± 0.013	0.426 ± 0.015	30.6 ± 1.2	2.70 ± 0.10

[a] The upper and lower bound of each parameters correspond to an increase in $\chi^2_{\text{global min}}$ by 100%.
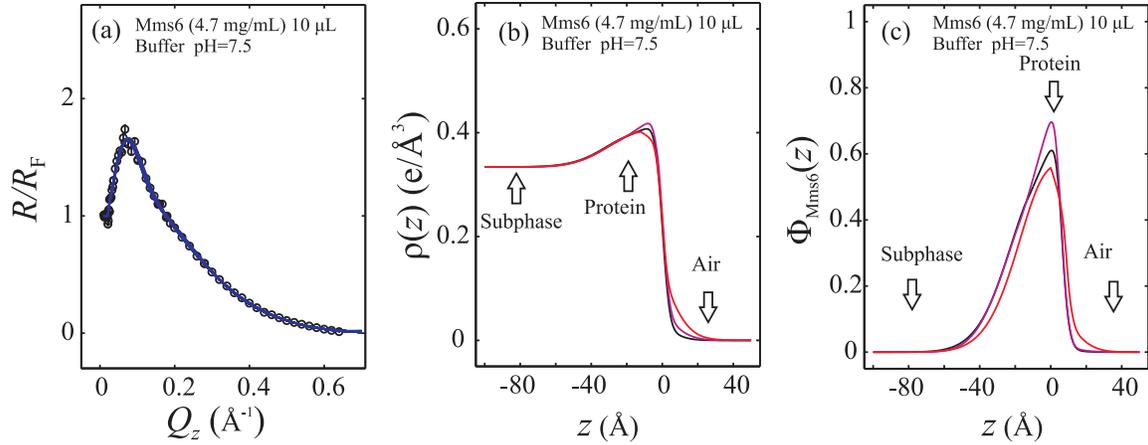
Figure 1: (a) Measured reflectivity data (symbols) of Mms6 on aqueous surfaces. The solid lines are an overlay of 150 calculated reflectivities corresponding to χ^2 changing from $\chi^2_{\text{global min}}$ by 100%. (b) ED profiles generated by three parameter sets. The black line corresponds to $\chi^2_{\text{global min}}$. The other two solid lines correspond to $\chi^2_{\text{global min}} \times 200\%$. (c) Volume fraction profiles corresponding to (b).

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