Supporting Information for: Iron near edge X-ray spectroscopy at aqueous-membrane interfaces

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1 Reflectivity Data Analysis

The R/R_F data were analyzed in terms of the effective-density model, which is capable of taking into account the large and uncorrelated interfacial roughness.[1] The electron density (ED) profile across the interfaces along the surface normal, $\rho(z)$, is constructed as follows:

$$\rho(z) = \left(\sum_{j=1}^{N+1} \rho_j w_j(z)\right) / \left(\sum_{j=1}^{N+1} w_j(z)\right) \qquad \text{(S1)}$$

where, the weighting function $w_j(z)$ is defined as follows.[1]

$$w_j(z) = \begin{cases} \frac{1}{2}\left\{1+\mathrm{erf}\left[(z-z_j)/\sqrt{2}\sigma_j\right]\right\} & z \le \zeta_j, \\ \frac{1}{2}\left\{1-\mathrm{erf}\left[(z-z_{j-1})/\sqrt{2}\sigma_{j-1}\right]\right\} & z > \zeta_j, \end{cases} \qquad \text{(S2)}$$

The coordinate $\zeta_j = (\sigma_j z_{j-1} + \sigma_{j-1} z_j)/(\sigma_j + \sigma_{j-1})$. $\sigma_j, j = 1,1,2,...,N,N+1$, represents the roughness between $(j-1)$-th and j-th layers. The continuous ED profile obtained using Eqn. (S1) is sliced into a stack of M slabs of constant thickness (≈ 1 Å) and uniform ED (determined by Eqn. (S1) evaluated at the midpoint of each slab). The reflectivity is then evaluated by the Parratt formalism[2,3] with $M \sim 100$.

The construction of the ED profile via the effective-density model is shown in Fig. S1 for the case of $N = 2$, i.e. the surface monolayer is parsed into two layers (head group and tail group of known EDs). From left to right in Fig. S1 (a), the electron density changes gradually from that of an aqueous subphase, a monolayer (consisting of a headgroup and a tail group), and to air. The transition between media of different ED is approximated with an error function (erf). The thickness of the transition regime is measured by the roughness σ_j between medium j and $j+1$, as shown in Fig. S1(b).

In practice, the effective-density model is mostly applied to the thin films consisting of single-layer or multi-layer in which the ED of j-th layer (ρ_j) is known while thickness (d_j, $d_j = |z_j - z_{j-1}|$) and interfacial roughness σ_i is to be determined from the reflectivity data.[1] If the interfacial roughness is small compared to the layer thickness, the effective-density

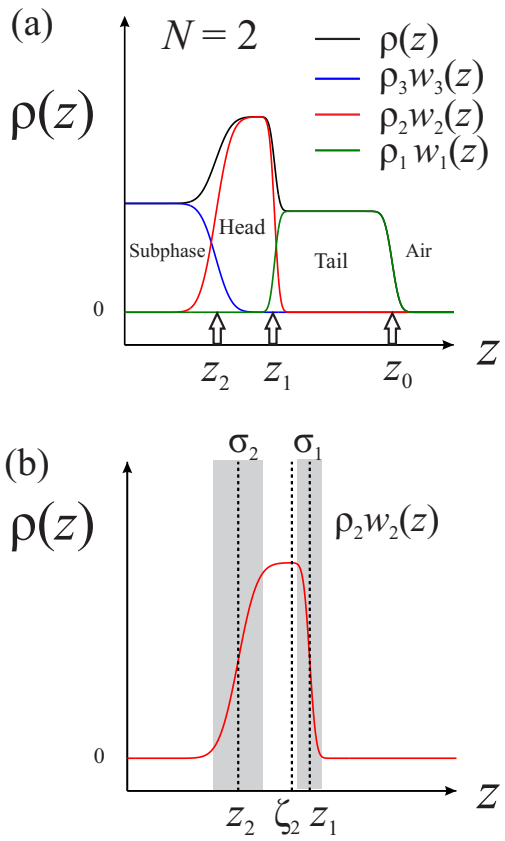

Fig. S1 Example of the construction of the ED profile in terms of the effective-density model for $N = 2$.[1] In (a), the black line represents the *effective* electron density profile along the surface normal. The blue line ($\rho_3 \cdot w_3(z)$) represents the subphase ED. The red line ($\rho_2 \cdot w_2(z)$) and green line ($\rho_1 \cdot w_1(z)$) represent a monolayer that is parsed into head and tail with known ED and thickness. In (b), the head group constituent ($\rho_2 \cdot w_2(t)$) in (a) is singled out. The head group moiety is confined between two interfaces (gray bands) approximated with two error functions, each of which has a width measured as σ_2 and σ_1. The position z_1 and z_2 (dashed vertical lines) correspond to the reflection points (slope maxima) in the error functions. They are used to define the interface positions when the two interfaces are well-separated, i.e.$|z_2 - z_1| \gg (\sigma_1 + \sigma_2)$.

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Sample	AA/$FeCl_3$	AA/$FeCl_2$	DHDP/$FeCl_3$	DHDP/$FeCl_2$
$z_1 - z_2$ (Å)	0.4 ± 1.2	3.7 ± 1.5	5.7 ± 1.7	4.0 ± 0.6
ρ_2 (e/Å^3)	0.73 ± 0.05	0.54 ± 0.04	0.52 ± 0.04	0.58 ± 0.04
σ_2 (Å)	7.7 ± 0.3	3.6 ± 0.8	4.0 ± 0.7	4.1 ± 0.3
$z_0 - z_1$ (Å)	21.1 ± 0.2	23.0 ± 0.5	17.4 ± 0.8	19.0 ± 0.3
ρ_1 (e/Å^3)	0.33 ± 0.01	0.32 ± 0.01	0.31 ± 0.01	0.31 ± 0.01
σ_1 (Å)	1.5 ± 0.2	4.7 ± 1.1	3.3 ± 0.5	4.2 ± 0.3
σ_0 (Å)	4.8 ± 0.1	3.1 ± 0.3	3.2 ± 0.3	3.1 ± 0.1
χ_v^2	~ 5.6	~ 1.2	~ 1.5	~ 1.1

Table S1 Best-fit parameters and associated uncertainties based on the effective-density model that are used to profile-fit the R/R_F data.

model is reduced to the multi-box model commonly used in the liquid surface reflectivity data analysis,[4] in which the ED, thickness and roughness can all be determined, given the physically meaningful confinements. In cases where the interfacial roughnesses are large and uncorrelated, and the EDs of the constituent layers are unknown, the effective-density model still provides an avenue to build an ED profile, similar to those free-form ED profiles.[5,6]

In this study, it is found that the effective-density model gives satisfactory R/R_F profile-fitting (reduced χ^2, $\chi_v^2 \sim 1-5$ for best-profile-fitting) and only $N = 2$ is required, which corresponds to a two-layer surface structure, reminiscent of a typical monolayer consisting of hydrophilic head groups immersed in the aqueous subphase and hydrophobic, hydrocarbon chains (tail groups). Table S1 lists the parameters (and associated uncertainties) used to profile-fit the R/R_F data and generate the corresponding ED profiles shown in the main text.

2 Surface binding scenario

Under the chosen subphase pH and concentration conditions, the surface monolayer charge (deprotonation) density can be qualitatively estimated for a hypothetically "classic" metal ions M of valence $n+$ (denoted as M^{n+}).[7,8] Figure S2 (a) shows the estimated charge conditions for AA and DHDP monolayer on a subphase of 1 mM "classical", free, and trivalent metal ions such as La^{3+} or divalent metal ions, such as Ca^{2+}. Figure S2 (b) shows the likely binding scenario for symmetry breaking that accounts for the pre-edge structure in XANES.

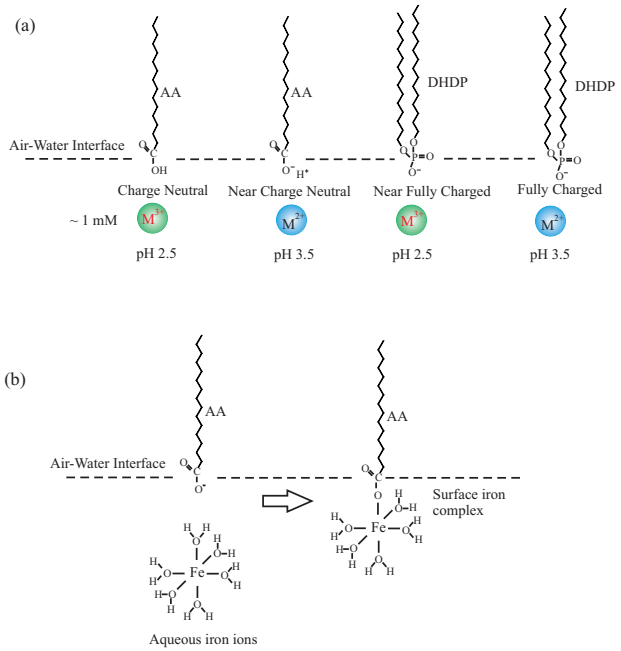

Fig. S2 (a) Qualitative estimate of surface charge conditions on a subphase trivalent metal ions (M^{3+}) or divalent metal ions (M^{2+}). The "near charge neutral" and "near fully charged" conditions refer to the cases when the fraction of charged surface is below 50% and above 50%, respectively. (b) A likely scenario for the aqueous iron ions to approach and bind to the surface monolayer. The aqueous iron ions are likely to be enclosed by hydration shell symmetrically. The H_2O molecules in the hydration shell can be replaced with hydroxyl group(s). This symmetry may be broken upon surface binding.

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