Supporting Information for:

Analytical Expressions for Proton Transfer Voltammetry: Analogy to Surface Redox Voltammetry with Frumkin Interactions

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1. General Solution for the Voltammetric Response

We consider a modified electrode with two populations of acid groups (Figure 1), one located at plane $a$ inside the monolayer with a surface concentration $\Gamma^a_T = \Gamma^a_{ROH} + \Gamma^a_{RO^-}$, and the other located at the boundary of the diffuse layer (plane $d$) with a surface concentration $\Gamma^d_T = \Gamma^d_{ROH} + \Gamma^d_{RO^-}$. For the sake of generality, we shall consider that the degree of ionization of both populations can be varied potentiostatically, although later on it will be demonstrated that the ionization state of the external population remains almost invariant along the potential window where full ionization of the internal population occurs.

The fractions of the neutral (ROH) and ionized (RO-) forms of the acid groups at planes $a$ and $d$ are given by:

\[
\theta^{a}_{ROH} = \frac{a_{H^+}}{a_{H^+} + K_a z^{a}} ; \quad \theta^{a}_{RO^-} = \frac{K_a z^{a}}{a_{H^+} + K_a z^{a}} \quad (S-1)
\]

\[
\theta^{d}_{ROH} = \frac{a_{H^+}}{a_{H^+} + K_d z^{d}} ; \quad \theta^{d}_{RO^-} = \frac{K_d z^{d}}{a_{H^+} + K_d z^{d}} \quad (S-2)
\]

where $\theta^k_i = \Gamma^k_i / \Gamma^k_T$ (with $k = a, d$), $K_a$ is the acid dissociation constant, $a_{H^+}$ is the hydronium ion bulk activity, and the potential-dependent factors $z^{a}$ and $z^{d}$ are defined as:

\[
z^{a} = \exp\left(\frac{F \phi^{a}}{RT}\right) ; \quad z^{d} = \exp\left(\frac{F \phi^{d}}{RT}\right) \quad (S-3)
\]

where $\phi^{a}$ and $\phi^{d}$ are the mean-field potentials at the planes $a$ and $d$, respectively.

1.1. Mean-Field Potential at the Dissociation Planes

Let $\delta_{md}$ and $\varepsilon_m$ be the thickness and relative permittivity of the adsorbed film, respectively; and $\delta_{ma}$ and $\delta_{ad}$ be the thicknesses of the two monolayer slabs at both sides of the internal ionization plane (plane $a$). Let $K_{md}$, $K_{ma}$ and $K_{ad}$ be the corresponding integral capacitances of the film and of its two dielectric slabs, respectively:
\[ K_{md} = \frac{\varepsilon_m}{\delta_{md}} \], \quad K_{ma} = \frac{\varepsilon_m}{\delta_{ma}} \], \quad K_{ad} = \frac{\varepsilon_m}{\delta_{ad}} \] (S-4)

Assuming that electrolyte ions do not permeate the film, Poisson’s equation reduces to:

\[ \frac{d^2\phi}{dx^2} = 0 \] (S-5)

within the monolayer. This differential equation is subjected to the following boundary conditions at the metal plane \((x = 0)\):

\[ \phi(x = 0) = \phi^m \], \quad \left( \frac{d\phi}{dx} \right)_{x=0} = -\frac{\sigma^m}{\varepsilon_m} \] (S-6)

and at the internal ionization plane \((x = \delta_{ma})\):

\[ \phi(x = \delta_{ma}) = \phi^a \], \quad \left( \frac{d\phi}{dx} \right)_{x=\delta_{ma}} - \left( \frac{d\phi}{dx} \right)_{x=\delta_{ma}} = \frac{\sigma^a}{\varepsilon_m} \] (S-7)

where \(\sigma^m\) is the surface charge density at the metal, and \(\sigma^a\) is the surface charge density at the internal ionization plane, which is related to \(\theta_{RO^-}^a\) by:

\[ \sigma^a = -F \Gamma_i^{a} \theta_{RO^-}^{a} \] (S-8)

Double integration of eq S-5 in the \(0 \leq x \leq \delta_{ma}\) and \(\delta_{ma} \leq x \leq \delta_{md}\) spatial regions, with the corresponding boundary conditions, eqs S-6 and S-7, leads to:

\[ \phi(x) = \phi^m - \frac{\sigma^m}{\varepsilon_m} x \] for \(0 \leq x \leq \delta_{ma}\) \] (S-9)

\[ \phi(x) = \phi^a - \frac{(\sigma^m + \sigma^a)}{\varepsilon_m} (x - \delta_{ma}) \] for \(\delta_{ma} \leq x \leq \delta_{md}\) \] (S-10)
By substituting \( x = \delta_{\text{ma}} \), \( \phi(x) = \phi^m \) and \( x = \delta_{\text{md}} \), \( \phi(x) = \phi^d \) into eqs S-9 and S-10, respectively; defining \( \omega_a = K_{\text{md}} / K_{\text{ad}} \) and taking into account that \( K^{-1}_{\text{md}} = K^{-1}_{\text{ma}} + K^{-1}_{\text{ad}} \), we obtain:

\[
\phi^d = \omega_a \phi^m + (1 - \omega_a) \phi^d - \frac{\omega_a (1 - \omega_a) F \Gamma^a_{\text{md}}}{K_{\text{md}}} \Theta^a_{\text{RO}}
\]  
(S-11)

where \( \phi^d \) is the potential at plane \( d \).

According to the Gouy-Chapman theory for a 1:1 electrolyte, \( \phi^d \) is given by:

\[
\phi^d = \frac{2RT}{F} \ln \left( \frac{-\sigma^{\text{diff}}}{2A_{\text{GC}}} + \sqrt{\left( \frac{-\sigma^{\text{diff}}}{2A_{\text{GC}}} \right)^2 + 1} \right)
\]  
(S-12)

where \( A_{\text{GC}} = (2RT \epsilon \sigma \varepsilon \varepsilon_{\text{ele}})^{1/2} \) and \( -\sigma^{\text{diff}} = \sigma^m + \sigma^a + \sigma^d \), with \( \sigma^d \) being the surface charge density at plane \( d \):

\[
\sigma^d = -F \Gamma^d \Theta^d_{\text{RO}}
\]  
(S-13)

and \( \sigma^m \) can be expressed in terms of \( \phi^m - \phi^d \) by substituting \( x = \delta_{\text{ma}} \) and \( \phi(x) = \phi^m \) in eq S-9, and taking into account that \( K_{\text{ma}} = K_{\text{md}} / (1 - \omega_a) \):

\[
\sigma^m = \frac{K_{\text{md}}}{1 - \omega_a} (\phi^m - \phi^d)
\]  
(S-14)

### 1.2. Voltammetric Response

Due to the nonfaradaic nature of the protonation/deprotonation process, the voltammetric current density is given by:

\[
i = v \frac{d\sigma^m}{d\phi^m}
\]  
(S-15)

where \( v \) is potential scan rate.

By combining eq S-15 with eqs S-14 and S-11, it is obtained:
\[ i = vK_{md} \left( 1 - \frac{d\phi^d}{d\phi^m} \right) + \omega a F v \Gamma_T^a \frac{d\theta_{RO}^a}{d\phi^m} \]  
(S-16)

where the first term on the RHS represents the capacitative baseline \((i_{bi})\) and the second term accounts for the acid/base conversion \((i_{cor})\), which is analogous to a surface redox conversion except for the parameter \(\omega a\) replacing the number of electrons \(n\). Integration of the baseline-corrected voltammogram (i.e. of the second term in eq S-16), leads to:

\[ \left| \int i_{cor} d\phi^m \right| = \omega a F v \Gamma_T^a \]  
(S-17)

which opens the way to calculate \(\Gamma_T^a\) provided the value of \(\omega a\) is known.

The presence of \(\phi^d\) in the relevant equations for the potential profile precludes the formulation of explicit analytical expressions for the voltammetric current, which must be calculated numerically. For a given set of values of the system parameters, and distinct values of \(\phi^m\), eqs S-11 and S-12 were solved numerically for the unknowns \(\phi^a\) and \(\phi^d\), by using eqs S-8, S-13, S-14, S-1, S-2 and S-3 to calculate the values of \(\sigma^a\), \(\sigma^d\) and \(\sigma^m\) required in each iteration. The voltammetric current was then calculated from eq S-15 by numerically differentiating \(\sigma^m\) with respect to \(\phi^m\).

2. Applicability of Relevant Approximations

2.1. Invariance of the External Ionization with the Applied Potential

Figure S-1 depicts the variation of the ionized fraction of the external (upper panel) and internal (lower panel) acid populations with the applied potential for a range of values of \(pH\) and \(K_{md}\). As can be seen, for typical values of the integral capacitance of thiol self-assembled monolayers \((K_{md} < 10 \, \mu F \, cm^{-2})\), \(\theta_{RO}^d\) varies by less than 0.15 in a potential window as wide as 2 V. Accordingly to the lower panel of Figure S-1, this variation can be
safely neglected in the narrower potential intervals where full ionization of the internal population occurs. Throughout the present work, we make use of this approximation by keeping the surface concentration of ionized external groups $\Gamma_{RO}^{d}$ invariant with the applied potential, so that $\sigma^{d} = -F\Gamma_{RO}^{d}$ remains constant in the calculation of $\phi^{d}$ (eq S-12).

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**Figure S-1.** Variation of the ionized fraction of the external (upper panel) and internal (lower panel) acid populations of an ionizable SAM with the applied electrode potential for the indicated values of the solution pH and the integral capacitance of the film. Other parameter values: $\Gamma_{F}^{d} = 10$ pmol cm$^{-2}$, $\Gamma_{f}^{d} = 800$ pmol cm$^{-2}$, $pK_{a} = 5.0$, $\omega_{a} = 0.7$, $c_{ele} = 5$ mM, $\epsilon_{a} = 78.5$ and T = 298 K.
2.2. Invariance of the Diffuse Layer Potential

The applicability of the *invariant diffuse layer scenario* requires that the diffuse layer potential $\phi^d$ remains invariant along the voltammetric wave, and that its value approaches the potential of zero charge of the modified electrode in the absence of internal ionization $\phi_{pc.0}^m$. Figures S-2 and S-3 illustrate how the $\phi^d - \phi_{pc.0}^m$ difference, computed at the peak potential, varies with the relevant system parameters ( $\Gamma_{RO}^d$, $c_{ele}$, $\omega_a$ and pH) for a typical modified electrode with $K_{md} = 3 \mu$F cm$^{-2}$. In general, $\phi^d_p - \phi_{pc.0}^m$ decreases upon increasing $\Gamma_{RO}^d$, $c_{ele}$ and $\omega_a$, and whenever the solution pH approaches the $pK_a$ value. These results reveal that it suffices that $\Gamma_{RO}^d \geq 100$ pmol cm$^{-2}$ or $c_{ele} \geq 0.5$ M for such a difference to be within ±15 mV.

![Figure S-2](image.png)

**Figure S-2.** Difference between the diffuse layer potential at the voltammetric peak potential, $\phi^d_p$, and the potential of zero charge in the absence of internal ionization, $\phi_{pc.0}^m$, as a function of the amount of ionized external groups for the indicated values of $c_{ele}$, pH and $\omega_a$. Other parameter values: $\Gamma_T = 10$ pmol cm$^{-2}$, $pK_a = 5.0$, $K_{md} = 3 \mu$F cm$^{-2}$, $\varepsilon_a = 78.5$, and $T = 298$ K.
Figure S-3. Difference between the diffuse layer potential at the voltammetric peak potential, $\phi^d_p$, and the potential of zero charge in the absence of internal ionization, $\phi^m_{pzc,0}$, as a function of the amount of ionized external groups for the indicated values of pH and $\omega_a$. Other parameter values: $\Gamma^d_T = 10$ pmol cm$^{-2}$, $pK_a = 5.0$, $K_{md} = 3$ µF cm$^{-2}$, $c_{ele} = 5$ mM, $\varepsilon_a = 78.5$, and $T = 298$ K.

The error in the estimate of $pK_a$ from the $\phi^m_p$ values by using the approximation $\phi^d_p \approx \phi^m_{pzc,0}$ in eq 13 is given by:

$$\Delta pK_a = \frac{(1-\omega_a)F}{2.3RT} (\phi^d_p - \phi^m_{pzc,0})$$  \hspace{1cm} (S-18)

According to the variation of the $\phi^d_p - \phi^m_{pzc,0}$ difference with the relevant system parameters (Figures S-2 and S-3), it suffices that $\Gamma^d_{RQ} \geq 100$ pmol cm$^{-2}$ or $c_{ele} \geq 0.5$ M for the error in $pK_a$ to be less than $\pm 0.25(1-\omega_a)$ at 298 K.
3. Voltammetric Peak Parameters for the Invariant Diffuse Layer Scenario

For the invariant diffuse layer scenario \((i.d.l.s.)\), the baseline-corrected voltammetric wave is given by eq 4 and the second term on the RHS of eq 6:

\[
\phi^m = \phi^m_{1/2,0} + \frac{RT}{\omega_a F} \left\{ \ln \left( \frac{\theta_R^a}{1 - \theta_R^a} \right) + g \Gamma_T^a \omega_a \theta_R^a \right\}
\]  
(S-19)

\[
i_{cor} = \frac{\omega_a^2 F^2 v \Gamma_T^a}{RT} \frac{\theta_R^a (1 - \theta_R^a)}{1 + g \Gamma_T^a \omega_a \theta_R^a (1 - \theta_R^a)}
\]  
(S-20)

where the parameters \(g\) and \(\phi^m_{1/2,0}\) are defined by:

\[
g = \frac{(1 - \omega_a) F^2}{K_{md} RT}
\]  
(S-21)

\[
\phi^m_{1/2,0} = \frac{2.3RT}{\omega_a F} (pK_a - pH) - \frac{1 - \omega_a}{\omega_a} \phi^m_{cor,0}
\]  
(S-22)

Analytical expressions for the peak potential \(\phi^m_p\), peak current density \(i_{cor,p}\), and full width at half maximum \((fwhm)\) of the baseline-corrected voltammetric wave for the \(i.d.l.s.\) case can be derived from eqs S-19 and S-20. At the peak potential, \(\theta_R^a = 1/2\), so that by introducing this condition in eqs S-19 and S-20 one obtains:

\[
\phi^m_p = \phi^m_{1/2,0} + \frac{(1 - \omega_a) F}{2K_{md} \Gamma_T^a}
\]  
(S-23)

\[
i_{cor,p} = \frac{\omega_a^2 F^2 v \Gamma_T^a}{RT(4 + g \Gamma_T^a \omega_a)}
\]  
(S-24)

At the \(fwhm\), \(i_{cor} = i_{cor,p} / 2\), so that by introducing this condition in eq S-20 and combining it with eq S-24, the following expression is obtained for \(\theta_R^a\) at the two potentials that define the \(fwhm\):

\[
\theta_R^a = \frac{1 \pm \Psi}{2}
\]  
(S-25)
where

$$\Psi = \left( \frac{4 + g \omega_a \Gamma_T^a}{8 + g \omega_a \Gamma_T^a} \right)^{1/2}$$  \hspace{1cm} (S-26)

By substituting eq S-25 into eq S-19, the following expression is obtained for the fwhm:

$$fwhm = \frac{RT}{\omega_a F} \left\{ 2 \ln \left( \frac{1 + \Psi}{1 - \Psi} \right) + g \omega_a \Psi \Gamma_T^a \right\}$$  \hspace{1cm} (S-27)