The Effect of the Interfacial Potential Distribution on the Measurement of the Rate Constant for Electron Transfer between Electrodes and Redox Adsorbates

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Abstract

The effects of the interfacial potential distribution on cyclic voltammetry (CV) of adsorbed redox molecules exhibiting slow (quasi-reversible and irreversible) electron transfer is considered in a theoretical model. Results of numerical simulations based on this model are presented and compared to CVs and measurements in the absence of double layer effects. The slopes of plots of peak potential versus Log sweep rate are the same, i.e. $RT/anF$ and $RT/(1 - \alpha)nF$ for the cathodic and anodic reactions respectively, as predicted in the absence of double layer effects. The calculation of the rate constant can be greatly influenced by the double layer effects.
Introduction

The recent publication of a paper by Smith and White\textsuperscript{1} on the effects of the interfacial potential distribution (IPD) on the reversible voltammetric response of adsorbates has stimulated a lot of interest in this area of research mainly in the context of possible effects on the cyclic voltammetry of self assembled monolayers (SAMs). Recent theoretical work has focused on the effects of ionizeable acid-bases groups located at the monolayer solution interface\textsuperscript{2-4}, ion pairing\textsuperscript{5-7} and discreteness of charge effects\textsuperscript{6,8} on the voltammetric response and the effect of the IPD on potential step chronoamperometry (PSCA) of reversible reactions\textsuperscript{9}. Application of these models is not limited to SAMs. Smith and Whites model has also recently been applied to the study of the reduction of methylene blue to explain the non ideal peak shape and the shift in peak potential with increasing coverage\textsuperscript{10}. Many of these recent developments, in the context of their application to the study of self assembled monolayers (SAMs), have been reviewed recently by Finklea\textsuperscript{11}.

The determination of the rate constant for electron transfer between an immobilised redox molecule and the electrode is frequently done by PSCA\textsuperscript{12} or cyclic voltammetry (CV). Laviron\textsuperscript{13} has published a frequently cited method of determining the rate constant via cyclic voltammograms which is based on Butler-Volmer kinetics. Plots of $(E_p - E')$ versus log $\nu$ are expected to be linear in when the reaction is irreversible and the rate constant can be calculated from the peak separation relative to the reversible peak potentials. In the quasi-reversible region the rate constant can be calculated from a working curve. At high overpotentials the reaction is likely to be influenced by effects described by Marcus\textsuperscript{14}. Qualitatively one expects that in this region plots of $(E_p - E')$ versus log $\nu$ will no longer be linear but will display curvature toward the $y$ axis. At still higher overpotentials the rate constant is predicted to become independent of potential suggesting that CVs should in fact be flat. Importantly the point at which a departure from
the model based on Butler-Volmer kinetics is to be expected will depend on the reorganisation energy. Systems with larger reorganisation energies will display Butler-Volmer like kinetics at larger overpotentials than systems with smaller reorganisation energies.

Another recent development in the study of the linear sweep and cyclic voltammetry of adsorbates has been an attempt to include Marcus theory into models of the irreversible voltammetric response of redox adsorbates\textsuperscript{15-17}. Nahir et al.\textsuperscript{15} used their model to explain the experimental CV for cytochrome c adsorbed on a carboxyalkanethiol monolayer. Weber and Creager\textsuperscript{16} and Tender et al.\textsuperscript{17} considered the problem more generally and provided tables\textsuperscript{17} from which the experimentalist maybe able to estimate both the rate constant and reorganisation energy. The reader is reminded that a significant potential region is available from which to determine the rate constant from within a Butler-Volmer framework. Even when rate constants have been used in Marcus theory simulations their seems to be little difference between the values used for curves of best fit and those determined by Lavirons formalism at moderate overpotentials\textsuperscript{12}.

It is often reported that PSCA results of redox SAMs are non-linear at short times and that CVs are typically broader than predicted for ideal adsorbates. Kinetic and formal potential dispersion is often cited as a potential cause for this peak broadening\textsuperscript{18} although IPD effects may also lead to CV peak broadening\textsuperscript{1} and non-linear PSCA semi-log plots of reversible reactions\textsuperscript{9}. One aspect that has yet to be considered is how the IPD effects the LSV and CV peak shape and measurement of the rate constant when the sweep rate is sufficiently rapid for the electron transfer to no longer be reversible. For example it is not known whether the influence of the IPD may induce peak distortion and how that may impact on the determination of the rate constant.
The IPD models that have been developed cannot be directly used for calculations on quasi-reversible and irreversible systems because Nernstian behaviour is a fundamental assumption underpinning the method of calculation of the charge on the electrode surface, $\sigma_M$, and the charge at the plane were the redox groups are located, $\sigma_P$. The behaviour of $\sigma_M$ and $\sigma_P$ as the potential is swept for an irreversible system, for example, will be different to that for a reversible system and it follows that calculation of $\phi$ will also be quite different. In this paper the effects of the IPD on the quasi-reversible and irreversible CVs of redox adsorbates are reported. While the stimulation for this work has been due to the interest in the study of redox SAMs the theory and results below apply equally to physically adsorbed molecules.

**Theory**

We will consider the reduction of an adsorbate, $O$, with charge $z_O$

$$O^{z_o} + ne^- \rightleftharpoons R^{z_R} \quad \quad E_c^f \quad \quad \quad \quad \ldots(1)$$

and the subsequent oxidation of $R$ on the reverse sweep

$$R^{z_R} \rightleftharpoons O^{z_o} + ne^- \quad \quad E_a^f \quad \quad \quad \quad \ldots(2)$$

$E_c^f$ and $E_a^f$ are the reversible peak potentials. Subscripts $c$ and $a$ refer to cathodic and anodic processes respectively through this paper. The reversible region is defined as the region, bounded on one side by $\nu \rightarrow 0$, in which the peak potentials are constant with increasing sweep rates. The point at which the peak potential changes with increasing
sweep rate represents the onset of quasi-reversibility. $E'_c$ and $E'_a$ are listed as separate values since it is frequently observed that even under reversible conditions the cathodic and anodic peaks are separated ($\Delta E_p \neq 0$).

In order to derive the equations for the LSV of adsorbates the following assumptions are made:

(i) The redox couple is not present in the bulk phase or is present in such low concentrations that the contribution to the current from electron transfer reactions of molecules diffusing to the electrode is negligible. Adsorption is considered to be so strong that in the timescale of the experiment desorption is negligible. The total adsorbate concentration is therefore constant during the experiment

$$\Gamma_O(t) + \Gamma_R(t) = \Gamma_T$$  \hfill (3)

where $\Gamma_O(t)$ and $\Gamma_R(t)$ are the surface excess of $O$ and $R$, and $\Gamma_T$ is the total (oxidized plus reduced) surface excess; (ii) All the adsorption sites are equivalent (homogeneous surface); (iii) The area occupied by the oxidized and reduced adsorbate are equivalent; (iv) Adsorption is rapid and therefore does not control the kinetics of the reaction; (v) Faradaic and capacitative currents can be separated; (vi) In the case of physical adsorption a Langmuir isotherm is assumed in which the adsorption coefficients and the maximum surface coverage are independent of potential; (vii) The surface concentration is equivalent to the surface activity.

To allow for the effect of the IPD on the adsorbates the additional assumptions are that

(viii) The redox centers of the adsorbate are all located in a plane, referred to as the plane of electron transfer (PET), at a finite distance, $d$, from the electrode (figure 1); (ix) That electrolyte ions from the solvent do not penetrate into the film; (x) The diffuse capacitance is described by Gouy-Chapman theory; (xi) The charge due to the redox centers is distributed homogeneously in the PET; (xii) The dielectric constant of the
adsorbed layer is constant; (xiii) The potential drop across the adsorbate monolayer is linear.

For the reaction of a surface confined molecule the current is defined as

\[ i = -nFA \frac{d\Gamma_R}{dt} \]  \hspace{1cm} ...(4)

In a cyclic voltammetric experiment the potential at any time, \( t \), is \( E = E_i + \nu t \), where \( E_i \) is the initial potential and \( \nu \) is the sweep rate which is negative for a cathodic sweep and positive for an anodic sweep. Dividing Eq. (3) by \( \Gamma_T \) gives \( x_R + x_O = 1 \) where \( x_R = \frac{\Gamma_R}{\Gamma_T} \) and \( x_O = \frac{\Gamma_O}{\Gamma_T} \), are the mole fractions of \( R \) and \( O \). It is convenient to express the current in terms of a dimensionless function therefore we substitute

\[ d\Gamma_R / dt = \Gamma_T \left( dE / dt \right) (dx_R / dE), \]  and \( dE / dt = \nu \), and into Eq. (4) to give

\[ i = nF\Gamma_T \nu \left( \frac{nF}{RT} \right) \psi \]  \hspace{1cm} ...(5)

where \( \psi \) is the dimensionless current which is defined as

\[ \psi = \frac{RT}{nF} \frac{dx_R}{dE} \]  \hspace{1cm} ...(6)

In order to include the effects of the IPD a modified form of the Butler-Volmer equation is used\(^{19}\)

\[ i_a = nFAk_s \left\{ \Gamma_R^{1-\alpha} - \Gamma_O^{-\alpha} \right\} \]  \hspace{1cm} ...(7a)
\[ i_c = nF k_s \left\{ \Gamma_R \xi_{c}^{1-a} - \Gamma_O \xi_{c}^{-a} \right\} \]  

...(7b)

where \( k_s \) is the heterogeneous rate constant (s\(^{-1}\)), \( \xi_{a,c} = \exp\left[ nF \eta_{a,c} / RT \right] \), and \( \eta_{a,c} \) is the (anodic or cathodic) overpotential which we define as \( \eta_a = E - \phi - E^c_a \) and \( \eta_c = E - \phi - E^c_c \). The potential at the PET, \( \phi \), is defined as

\[ \phi = \left( \frac{2RT}{zF} \right) \sinh^{-1} \left( \frac{\sigma_M + \sigma_P}{2A} \right) \]  

...(8)

where

\[ A = \left( 2000c_s \varepsilon_0 \varepsilon_3 RT \right)^{\frac{1}{2}} \]  

...(9)

\[ \sigma_P = FT_R \left[ z_0 \left( 1 - x_R \right) + z_R x_R \right] \]  

...(10)

\[ \sigma_M = \varepsilon_0 \varepsilon_1 \left( E - E_{pzc} - \phi \right) d \]  

...(11)

\( c_s \) is the molar concentration of the \( z : z \) supporting electrolyte, \( \varepsilon_0 \) is the permittivity of free space, \( \varepsilon_i \) is the dielectric constant of the monolayer, \( \varepsilon_j \) is the dielectric constant of the solute, \( \sigma_p \) is the charge density of the PET, \( \sigma_M \) is the charge density on the electrode, \( d \) is the thickness of the monolayer, and \( E_{pzc} \) is the potential of zero charge of the bare electrode. In the derivation by Smith and White the term \( E_{pzc} \) was in fact used as a replacement term for the potential difference between the solution and the reference metal electrode (eg. Hg, Ag). While the \( E_{pzc} \) of the electrode shifts in the presence of adsorption the potential difference between the solution and the reference electrode remains unchanged therefore the \( E_{pzc} \) of the bare electrode (i.e. no adsorption) is used in these calculations.

Combining Eqs. (3), (4), (6), (7) gives
\[ \frac{dx_R}{dE} = -\frac{k_s}{v} \left\{ x_R \xi_{a,c}^{1-\alpha} - (1 - x_R) \xi_{a,c}^{-\alpha} \right\} \quad \ldots(12) \]

and the equation for the dimensionless current

\[ \psi = m \left\{ x_R \xi_{a,c}^{1-\alpha} - (1 - x_R) \xi_{a,c}^{-\alpha} \right\} \quad \ldots(13) \]

where \( m \) is the dimensionless rate constant given by

\[ m = \left( \frac{RT}{nF} \right) \left( \frac{k_s}{v} \right) \quad \ldots(14) \]

It is not possible to solve Eqs. (12) and (13) analytically but CVs calculated from numerical solutions to Eqs. (12) and (13) are presented below. As \( m \to 0 \) the reaction becomes totally irreversible and for the cathodic curve \( \eta_c^{1-\alpha} \ll \eta_c^{-\alpha} \) and \( \eta_c \ll 1 \) and for the anodic curve \( \eta_c^{-\alpha} \ll \eta_a^{1-\alpha} \) and \( \eta_a \gg 1 \) therefore

\[ \psi_c = -m(1 - x_R)\xi_c^{-\alpha} \quad \ldots(15) \]

\[ \psi_a = mx_R\xi_a^{1-\alpha} \quad \ldots(16) \]

To arrive at an expression for the total dimensionless current we define the dimensionless capacitative current as

\[ \psi_{cap} = \pm C_T \left( \frac{n^2 F^2}{RT} \right) \Gamma_T \quad \ldots(17) \]

where the double layer capacitance, \( C_T \), is
\[
\frac{1}{C_T} = \frac{d}{\varepsilon_1 \varepsilon_0} + \frac{1}{\varepsilon_3 \varepsilon_0 \kappa \cosh(zF\phi/2RT)} \quad \ldots(18)
\]

and \( \kappa = zF(2000c_s/\varepsilon_0 \varepsilon_3 RT)^{1/2} \). The total dimensionless current, \( \psi_T \), is the sum of the faradaic (Eq. 13) and capacitative (Eq. 17) dimensionless currents.

Taking the derivatives of Eq. (15) with respect to \( E \) the peak potentials occur when

\[
\left( \frac{dx_R}{dE} \right)_p = -(1 - x_R)_p \frac{a n F}{R T} \left( 1 - \frac{d \phi}{dE} \right)_p \quad (19)
\]

\[
\left( \frac{dx_R}{dE} \right)_a = -(x_R)_a \frac{(1 - \alpha)n F}{R T} \left( 1 - \frac{d \phi}{dE} \right)_a \quad (20)
\]

where the subscript \( p \) refers to the value of the particular identity at the peak potential.

Equating Eqs. (19) and (20) with Eq. (12) for \( m \to 0 \) gives the irreversible cathodic and anodic peak potentials

\[
E_{p_c} = Ec_r + \phi_{p_c} - \left( RT/a n F \right) \ln \left[ (\alpha/m)(1 - d \phi/dE)_p \right] \quad (21)
\]

\[
E_{p_a} = Ea_r + \phi_{p_a} - \left( RT/(1 - \alpha)n F \right) \ln \left[ (1 - \alpha)(1 - d \phi/dE)_a / m \right] \quad (22)
\]

The rate constant for the reaction can be determined from the peak separation by subtracting Eq. (21) from (22) and rearranging to give

\[
\ln k_s = \alpha \ln(1 - \alpha) + (1 - \alpha) \ln \alpha - \ln \left( RT/nF |v| \right) - \left[ \alpha(1 - \alpha)nF \Delta E_p / RT \right] + H \quad (23)
\]

where \( H \) is a collection of additional terms.
\[ H = \alpha(1 - \alpha) \left( nF/RT \right) \left( \phi_{pa} - \phi_{pc} \right) + \alpha \ln \left[ 1 - (d\phi/dE)_{pa} \right] + (1 - \alpha) \ln \left[ 1 - (d\phi/dE)_{pc} \right] \]

(24)

and \( \Delta E_p = \left( E_{pc} - E_{c}^r \right) - \left( E_{pa} - E_{a}^r \right) \) i.e. the peak separation from the reversible peak potentials rather than the absolute peak separation.

The first four terms on the right hand side of Eq. (23) are the same as those given by Laviron in Eq. (22) of ref. 13. Laviron considered only the case in which the formal potentials of both the oxidation and reduction were equivalent. It is straightforward to show that if two different formal potentials are substituted into Eqs (20) and (21) of ref. 13 the same results for \( \log k_s \) is obtained as for Eq. (23) of this paper if the collection of additional terms, \( H \), which are due to the double layer effects, are set to zero.

In an experiment where a peak separation occurs under reversible conditions then if the absolute peak separation was used in calculations, even in the absence of double layer effects, the magnitude of the error induced is

\[ \delta(\ln k) = -\alpha(1 - \alpha) nF \Delta E^r / RT \]

...(25)

where \( \Delta E^r \) is the reversible peak separation.

Unfortunately it is relatively common for formal potentials to be reported as the mid-point between two reversible adsorbate voltammetric peaks in the same manner that the mid-point between peaks of a diffusional CV is taken as the formal potential. This is the reason that the use of the term “reversible potentials” rather than “formal potentials” has been used in this derivation. Peak separation is expected for ideal diffusional CVs, but not for “ideal” adsorbates. Peak separation of “real” reversible adsorbate CVs may be due
to many things of non-kinetic origin, for example differences in solvation between the oxidized and reduced adsorbates may lead to differences in peak potentials. Also for physically adsorbed molecules differences in the adsorption coefficients between oxidized and reduced molecules lead to differences in the respective formal potentials. By definition if a peak separation occurs under reversible conditions it cannot be of kinetic origin. Taking the mid point of the peak separation and defining it as a “formal potential” and substituting it into Laviron’s equation to determine the rate constant$^{21}$ immediately implies that the reversible peak separation that exists is due to slow kinetics!

It is this contradiction that is the qualitative reason why the peak separation that occurs when the sweep rate is increased must be taken from the reversible peak potentials and not their mid-point. Of course quantitatively the derivation of both the equations presented here and in Laviron’s model requires it.

**Experimental**

Equations (8) and (12) were solved numerically using programs written in Mathematica 3.0 (Wolfram Research, Champaign, Il) and run on an Apple Power Macintosh 9500/150 computer. The Mathematica notebooks are available electronically from the author$^{22}$ or in printed form as supplementary material. The method of solution was as follows:

1. Initially Eq. (12) was solved over the desired working potential range in 1 mV steps after making the initial approximation that $\phi = 0$.
2. An interpolated function of $x_R$ as a function of $E$ was substituted into Eq. (8) and $\phi$ calculated in 1 mV steps by Newton’s method.
3. An interpolated function of $\phi$ as a function of $E$ was then substituted into Eq. (12).
4. Eq. (12) was solved over the desired working potential range in 1 mV steps and a new interpolated function of $x_R$ as a function of $E$ was calculated.

After completion of the iteration the calculated value of $\phi$ was substituted into Eq. (13) and the CV was simulated.
MATHEMATICA uses as defaults Lagrange or Hermite polynomials for interpolation, Adams or Gear method for solving differential equations (Eq. 12), and Gauss-Kronrod method for numerical integration. Detailed descriptions of all these numerical methods are available elsewhere.

Steps (2), (3) and (4) were looped until the peak potential remained constant to within 0.1 mV and the integrated peak area agreed with \( nF\Gamma_r \) to within 1%. Using the experimental variables given in the results section steps (2), (3) and (4) were repeated a 6 to 8 times to achieve the desired precision. The values of \( x_\phi \) and \( \phi \) were then substituted into Eq. (13) to calculate \( \psi \). This was then added to \( \psi_{cap} \) to give \( \psi_T \).

**Results and Discussion**

Given the number of variables in Eqs. (7) and (8) it is not practical to present working curves which can be used to quantify the effects of the IPD on the LSV and CV response. In order to illustrate the IPD effects CVs were simulated for conditions which are commonly encountered in SAM studies. CVs were simulated of a reduction and subsequent oxidation of a univalent oxidant present with a surface excess of 0.15 and 1.5 \( \times \) 10\(^{-11} \) mol cm\(^{-2} \), in 1:1 0.1 M and 1.0 M supporting electrolyte solutions. Other values of variables used in the calculations were \( E_{pce} = \pm 200 \) mV vs. \( E^\circ \), \( \varepsilon_1 = 2.6 \), \( \varepsilon_3 = 78.5 \), \( d = 20 \) Å, \( T = 298K \), \( \alpha = 0.5 \).

Figure 2 shows plots of peak potential, \( E_p \), versus Log(\( k/|v|/ \)). The dotted line corresponds to predictions based on Laviron’s model\(^{13} \). The lines of best fit (not shown) intersect at the reversible peak potential. In these examples the reversible cathodic and anodic peak potentials are equivalent but differ from the formal potential due to the influence of the
IPD\textsuperscript{1}. The figure shows that under all of the experimental conditions considered the slopes of the plots are the same as that expected in the absence of double layer effects, i.e. $RT\ln F$ and $RT(1 - \alpha)nF$ for the cathodic and anodic reactions respectively, in agreement with the predictions of Eqs. (21) and (22). It follows from the derivation of Eqs. (21) and (22), that a linear slope is always to be expected unless the transfer coefficient exhibits some potential dependency.

The additional terms, $H$, present in Eq. (23) give a means of estimating the error induced by discounting the double layer effects and determining $k_s$ from the Laviron model. The equation derived by Laviron for CV in the absence of IPD effects is the same as Eq. (23) when $H = 0$ therefore

$$k_{s,Lav} = k_{s,true} \exp(-H) \quad \text{...(26)}$$

where $k_{s,Lav}$ and $k_{s,true}$ are the rate constant determined by ignoring IPD effects and the true rate constant respectively. At the lower coverage the additional terms are $\sim$ zero in 1.0 M solution and in 0.1M solution the value of $k_s$ is $\sim$ 7% higher than the experimental value when calculated from Lavirons equation (i.e. Eq. (23) with $H = 0$). At the higher coverage, even with the very low value of the monolayer capacitance used in these calculations, the effects on the calculation of the rate constant are more noticeable. In 0.1M solution the value of $k_s$ is $\sim$ 45% higher when calculated from Lavirons equation and even in 1.0 M solution the calculated value of $k_s$ is $\sim$28% above the value used experimentally.

Simulated voltammograms are shown in figures 3 and 4. In the presence of IPD effects the reversible peak potential is predicted to shift from the formal potential of the redox couple with varying surface coverage and electrolyte concentration. More detailed discussion about this can be found in Smith and Whites paper\textsuperscript{1}. To allow comparison of several CVs the potential is shown relative to the formal potential of the system. At low
coverages (figures 3 A and C) the peaks, though smaller and broader than in the absence of double layer effects, remain asymmetric. At higher coverages (figures B and D) however the peaks are significantly smaller, broader and the cathodic peak is near symmetrical. These effects are due to the increase in the charge in the PET with increasing coverage. This is quite interesting and may provide a qualitative diagnosis of double layer effects since asymmetrical peaks of constant shape and height are predicted by Laviron's model\textsuperscript{13}. The shape and position of the CVs seems relatively insensitive to the value of the $E_{pzc}$ used in these calculations.

The predictions of this theory can be tested by comparison to literature data. In figure 5a figure 6 from Tender et al.\textsuperscript{17} is reproduced. The voltammograms shown in this figure in fact originate from C.E.D. Chidsey. Tender et al. used the data provided to them to test a model which attempted to combine Marcus theory with cyclic voltammetry. It is for this reason that this data has been chosen to test the irreversible IPD model. Figure 5b illustrates that non-Marcus type effects can give rise to cyclic voltammograms quite unlike those predicted by the traditional Butler-Volmer theory for “ideal” adsorbates. In this particular example the reversible peaks were calculated to have shifted approximately 58 mV from the formal potential (indicated by the dotted line) due to IPD effects. Figure 5b was simulated by taking the value for the surface coverage, sweep rate, electrolyte concentration and temperature given in the figure caption to fig.6 of ref. 17 and inserting these into the model presented in this paper along with estimates of the dielectric constant of the monolayer and the monolayer thickness based on literature values. The potential of zero charge of the gold electrode was estimated to be – 500 mV versus the formal potential of the adsorbed ferrocene/ferrocinium couple. With these values in place the CV was simulated by adjusting the rate constant to give a peak potential of – 210 mV\textsuperscript{25}. The simulation therefore contained one adjustable parameter, the rate constant.

The simulations based on the irreversible IPD model, while being slightly smaller and broader can nonetheless be considered in excellent agreement with the experimental results.
The ideal Butler-Volmer peak was simulated using the same values used by Tender et al in fig. 6 of ref. 17. The values of \( k_s = 0.06 \text{ s}^{-1} \), for the ideal peak and \( k_s = 0.05 \text{ s}^{-1} \) for the IPD peak were used in the simulations. The ratio of these rate constants is consistent with the proposition discussed above that the rate constant calculated by assuming ideality will tend to overstate the true value by a small amount, in this case \( \sim 20\% \), when an adsorbed redox system is influenced by IPD effects.

**Conclusion**

A model has been presented to describe the effects of the IPD on the peak shape and position and measurement of the rate constant for adsorbed redox systems undergoing irreversible electron transfer. Simulations show that predicted peak shapes may vary considerably from the ideal Butler-Volmer case. For systems under the effects of the IPD rate constants that have been calculated from the model of Laviron for ideal adsorbates will tend to overestimate the true rate constant.
References and Notes

(19) The equations for both the anodic and cathodic currents have been given separately to highlight that the reversible peak potentials for the cathodic and anodic reactions need not be the same, and therefore the overpotentials need not be the same for sweeps in both
directions. In other words the anodic and cathodic currents are not necessarily mirrors of each other.

(20) Strictly speaking the definition of $m$ should include the sign on $v$. However by the definition of $\psi$ given in Eq. (6) the dimensionless current must have the same sign for both the anodic and cathodic sweeps. Taking only the magnitude of $v$ allows the sign of $\psi$ to be the same as the current in both directions. This also allows $m$ to always be positive.

(21) Either Eq. (22) of ref. 13 or for $\eta_{\Delta E_p} < 200$ mV the working curve constructed from Table 1 in ref. 13.

(22) According to Wolfram Research the MATHEMATICA notebooks are cross platform so while these calculations were performed on a Power Macintosh computer the notebooks should be able to be used on other platforms without modification or conversion.


(25) The reader should note when comparing the IPD simulation with the original Marcus theory simulation of fig. 6 of ref. 17 that several typographical errors appear in relation to fig. 6. The surface coverage listed in the text differs from the value given in the figure caption. The peak potential of the 250 mV s$^{-1}$ peak listed in the text ($\sim 238$ mV) is quite different to the peak potential of the CVs in fig. 6 ($\sim 210$ mV), which is the value calculated for $\log [v/k^o] = \log[0.25/0.06] = 0.62$ at 273K for the Butler-Volmer peak. It seems from the text that the authors were unsure what temperature they were working at. The scale on the $y$ axis of fig. 6 is incorrect but fortunately the normalised ideal Butler-Volmer peak (which has a constant shape and height) allows figures 5A (fig. 6 of ref. 17) and B to be compared.

x
Figure Captions

**Figure 1.** Drawing of a redox adsorbate showing the redox centers located at the plane of electron transfer (at $d$) in contact with the solution. The potential profile in the region $0 \leq x \leq d$ which has a dielectric constant of $\varepsilon_j$ and capacitance $C_j$ is assumed to be linear. The potential profile in solution is non-linear and described by the Gouy-Chapman theory.

**Figure 2.** Plot of peak potential, $E_p$, versus $\log(k_f/\nu)$ for (a) 1:1 0.1M supporting electrolyte and (b) 1:1 1.0M supporting electrolyte. $E_{pzc} = +0.2$ V, $\Gamma_r = 15$ pmol cm$^{-2}$; $E_{pzc} = -0.2$ V, $\Gamma_r = 15$ pmol cm$^{-2}$; $E_{pzc} = +0.2$ V, $\Gamma_r = 1.5$ pmol cm$^{-2}$; $E_{pzc} = -0.2$ V, $\Gamma_r = 1.5$ pmol cm$^{-2}$.

**Figure 3.** Simulated CVs for $\log(k_f/\nu) = 0, -2.0, \text{ and } -4.0$ in 1:1 0.1 M supporting electrolyte. Vertical dotted line indicates the $E_{pzc}$ (w.r.t. $E_o'$) used in calculations. Dotted line CV is a CV in the absence of double layer effects ($\phi = 0$). Solid line CVs include the effects of the IPD and are calculated as described in the text. A and C, $\Gamma_r = 1.5$ pmol cm$^{-2}$; B and D, $\Gamma_r = 15$ pmol cm$^{-2}$.

**Figure 4.** Simulated CVs for $\log(k_f/\nu) = 0, -2.0, \text{ and } -4.0$ in 1:1 1.0 M supporting electrolyte. Vertical dotted line indicates the $E_{pzc}$ (w.r.t. $E_o'$) used in calculations. Dotted line CV is a CV in the absence of double layer effects ($\phi = 0$). Solid line CVs include the effects of the IPD and are calculated as described in the text. A $\Gamma_r = 15$ pmol cm$^{-2}$; B $\Gamma_r = 15$ pmol cm$^{-2}$.

**Figure 5.** a) Figure 6 from ref. 17. Top panel contains experimental voltammograms for CpFeCpCO$_2$(CH$_2$)$_{18}$SH SAM ($\Gamma = 9.3 \pm 0.2 \times 10^{-11}$ mol cm$^{-2}$) cochemisorbed with CH$_3$(CH$_2$)$_{17}$SH on Au(111). Other experimental conditions: 0.1 M HClO$_4$, T = 273K, $\nu$
= 100 mV s\(^{-1}\) (left hand peak) and 250 mV s\(^{-1}\) (right hand peak). Bottom panel is a comparison between the 250 mV s\(^{-1}\) peak from the top panel and a simulated ideal Butler-Volmer peak for \(k_s = 0.06\) s\(^{-1}\), \(\alpha = 0.5\), \(T = 273\). See original reference for more details\(^{25}\).

b) Simulation using the irreversible IPD model using the same data. Additional parameters used in calculations were \(k_s = 0.05\) s\(^{-1}\), \(\varepsilon = 2.6\), \(d = 24\) Å, \(E_{pce} = -500\) mV, \(\alpha = 0.5\).
Figure 1b
Figure 2a
Figure 2b
Figure 3
Figure 4
Figure 5