Asymmetric Marcus–Hush model of electron transfer kinetics: Application to the voltammetry of surface-bound redox systems

Martin C. Henstridge, Eduardo Laborda, Richard G. Compton

Department of Chemistry, Physical & Theoretical Chemistry Laboratory, Oxford University, South Parks Road, Oxford OX1 3QZ, United Kingdom

A R T I C L E   I N F O

Article history:
Received 16 February 2012
Received in revised form 4 April 2012
Accepted 6 April 2012
Available online 18 April 2012

Keywords:
Asymmetric Marcus–Hush model
Surface-bound redox system
Asymmetric Tafel plots
Butler–Volmer model

A B S T R A C T

The asymmetric Marcus–Hush model (MH) is applied to the study of the voltammetric response of electroactive monolayers. While the well-documented symmetric MH model has been successful in modelling many aspects of surface-bound redox systems, it cannot account for the asymmetry evident in the Tafel plots for many experimental systems.

The asymmetric model has previously been used to explain deviations from the symmetric MH model observed for solution-phase redox systems [E. Laborda, M.C. Henstridge, R.G. Compton, J. Electroanal. Chem. 667 (2012) 48–53] by taking into account inner-shell differences between the oxidised and reduced species. We extend the theory to the description of electron transfer reactions of surface-bound species and examine several experimental features for both cyclic and square wave voltammetry, as well as Tafel plots, using both symmetric and asymmetric Marcus–Hush models and the phenomenological Butler–Volmer model.

The asymmetric MH model is seen to outperform the other models in terms of the quantitative description of the full voltammetric waveshape and is able to reproduce all of the experimental trends examined, as such its use for the analysis of surface-bound redox couples is highly recommended.

© 2012 Elsevier B.V. All rights reserved.

1. Introduction

The Marcus theory of electron transfer [1–7] is ubiquitous in homogeneous electron transfer reactions [8] and has increasingly been used to describe electrochemical reactions occurring at electrodes in an attempt to gain greater physical insight than is available from the semi-empirical Butler–Volmer model. This has largely been via the so-called Marcus–Hush model [9–12] which applies the symmetric form of Marcus theory to the continuum of energy levels in the electrode using Fermi–Dirac statistics. This approach has been particularly successful in modelling surface-bound redox couples due to the ability of the model to reproduce the curved Tafel plots which have often been observed experimentally [10,13,14].

Despite its successes the symmetric Marcus–Hush model has its failings. It has been shown to be markedly less able to parameterise experimental solution-phase voltammetry than the phenomenological Butler–Volmer model [15–20], despite the simplicity of the latter. More recently, the asymmetric formulation of Marcus theory has been applied to the voltammetry of solution-phase redox systems with promising results [21]. When applied to parameterising the experimental voltammetry (cyclic, square wave and differential multipulse) of several solution-phase redox systems, the so-called asymmetric Marcus–Hush model has been shown to permit accurate fitting on par with the Butler–Volmer model [22]. Indeed, it is only in the limits of very small reorganisation energy and very sluggish electrode kinetics that the two models are expected to differ significantly. Thus, for solution-phase redox couples, the use of the simpler Butler–Volmer model has been recommended for the fitting of experimental data, complemented with the physical insights derived from the asymmetric Marcus model [22].

Within the field of electroactive monolayers there are also documented examples of experimental systems (deviating from symmetric MH) which exhibit curved Tafel plots whose anodic and cathodic branches have differing slopes in the vicinity of the formal potential [23–31]. This cannot be accounted for either by the symmetric MH model, for which a Tafel plot is always symmetrical about the formal potential, or by the BV model which cannot reproduce the curvature of such plots. Some researchers have treated the anodic and cathodic branches entirely separately using the symmetric MH model with two different values for the standard rate constant and reorganisation energy [26–28,31], but this approach is not consistent with the Nernst equation.

A “through-space” tunnelling model has been proposed as a possible justification for the asymmetric Tafel plots observed for surface-bound systems [32]. This introduces an additional
potential-dependent term which quantifies the probability of an electron tunnelling through an energy barrier. The inclusion of this term permits asymmetric Tafel plots, but this method always yields a greater slope for the cathodic branch than for the anodic. However there have been systems reported, both surface-bound and solution-phase, for which the opposite trend is observed [22,27,28].

In this paper we consider the application of the asymmetric Marcus–Hush theory to the study of surface-bound redox couples. The qualitative effects of the reorganisation energy ($\lambda$) and the asymmetry parameter ($\beta/\lambda$) on Tafel plots and both cyclic and square wave voltammetries are examined, as well as their effect on observable voltammetric features such as peak potential and peak current. Results show that the asymmetric model accounts for the asymmetric, curved Tafel plots reported in the literature [23,24,26–31]. Moreover it is consistent with the experimentally observed behaviour of voltammetric peak currents and potentials.

2. Theory

2.1. Surface-bound reaction model

For the one-electron reaction

$$A \mp e^- \rightleftharpoons B$$

(1)

in which both A and B are irreversibly bound to the electrode surface, the current is given by the following:

$$I = \mp F A \frac{d\Gamma_A}{dt}$$

(2)

$$\frac{d\Gamma_A}{dt} = -k_{ox}\Gamma_A + k_{red}\Gamma_B$$

(3)

where $F$ is the Faraday constant, $A$ is the electrode area, $\Gamma_A$ is surface coverage of A and $t$ is time. The values $k_{ox}$ and $k_{red}$ are the rate constants for oxidation and reduction respectively and have a potential-dependent form which varies between different kinetic models as described below. Where two signs are given in an equation, the upper sign refers to oxidation, the lower sign to reduction.

2.2. Kinetic models

The most widespread model of electrode kinetics is the Butler–Volmer model, for which

$$k_{ox}^{BV} = k_0 \exp[(1 - \alpha)\theta]$$

(4)

$$k_{red}^{BV} = k_0 \exp[-\alpha\theta]$$

(5)

where $k_0$ is the standard electrochemical rate constant, $\alpha$ is the transfer coefficient and $\theta$ is a dimensionless overpotential, defined thus:

$$\theta = \frac{F}{RT}(E - E^0)$$

(6)

where $R$ is the gas constant, $T$ is the absolute temperature, $E$ is potential and $E^0$ is the formal potential.

The asymmetric Marcus–Hush model has the general form [21]:

$$k_{ox}^{MH} = k_0 \frac{S_{ox}(\lambda^*, \theta)}{S_{ox}(\lambda^*, 0)}$$

(7)

$$k_{red}^{MH} = k_0 \frac{S_{red}(\lambda^*, \theta)}{S_{red}(\lambda^*, 0)}$$

(8)

where $\lambda^*$ is the dimensionless analogue of reorganisation energy, $\lambda$ (eV), defined as:

$$\lambda^* = \frac{F}{RT} \lambda$$

(9)

The function $S_{ox(red)}(\lambda^*, \theta)$ is given by

$$S_{ox(red)}(\lambda^*, \theta) = \int_{-\infty}^{\infty} \frac{-\Delta G'_{ox(red)}(\epsilon)}{1 + \exp(\pm \epsilon)} \, d\epsilon$$

(10)

in which $\epsilon$ is an integration variable and

$$\Delta G'_{ox(red)}(\epsilon) = \frac{\lambda^*}{4} \left( \frac{\theta + \epsilon}{\lambda} \right)^2 + \beta^* \frac{(\theta + \epsilon)^2}{4\lambda^*} \left( 1 - \left( \frac{\theta + \epsilon}{\lambda} \right)^2 \right)$$

(11)

where $\beta^*$ is the dimensionless analogue of $\beta$, which parameterises the asymmetry between the oxidation and reduction reactions, given by

$$\beta^* = \frac{F}{RT} \beta$$

(12)

A full discussion of this parameter has been presented previously [21], but in summary it is a function of the inner-sphere reorganisation energy and force constants of the vibrational modes of the oxidised and reduced species. Note that in this work $\beta$ does not refer to the tunnelling attenuation parameter. For the case of equal force constants for the oxidised and reduced species the asymmetry parameter ($\beta$) is zero and the model reduces to its symmetric counterpart. When the force constants for the oxidised species are larger than for the reduced species $\beta > 0$, while the opposite is true $\beta < 0$. The limits in which this model is accurate are discussed in a previous publication [21].

The ratio $\beta/\lambda$ affects the potential-dependence of rate constants in a manner qualitatively similar to the Butler–Volmer transfer coefficient [22]. Indeed, in the limit of very large reorganisation energy the asymmetric Marcus–Hush model reduces to the Butler–Volmer model with a transfer coefficient given by

$$\alpha = \frac{1}{2} + \frac{1}{4} \frac{\beta}{\lambda}$$

(13)

The integrand in Eq. (10) is roughly Gaussian in shape, the integral is therefore evaluated using the trapezium rule over the range $\epsilon_{peak} \pm 50$ with a step size of 0.01. These values were chosen following a convergence study. Eqs. (2) and (3) are solved for both cyclic and square wave voltammetric waveforms via the implicit finite difference method using programs made in-house and run on desktop computers. Typical simulation times were of the order of a few seconds.

3. Results

3.1. Asymmetric Tafel plots

Among the most distinctive features of the Marcus–Hush model [9–12], both symmetric and asymmetric, is the contrast between its prediction of curved Tafel plots compared to the linear plots predicted by the Butler–Volmer model. While the latter predicts rate constants which increase exponentially with overpotential ad infinitum, the Marcus–Hush model predicts that rate constants begin to level off at large overpotential and tend towards limiting values. Early work by Chidsey [10] using ferrocene tethered to a gold electrode yielded a markedly curved, yet symmetric Tafel plot.

However, there have since been several reported instances of experimental systems [23,24,26–31] for which the anodic and cathodic branches are curved, but not symmetric. Neither the Butler–Volmer nor symmetric Marcus–Hush model can account for both of these observations simultaneously: the symmetric MH model produces curved Tafel plots, but it cannot account for the any asymmetry between anodic and cathodic branches. The
overpotentials. While the symmetric MH model describes the Volmer data, as the rate constants begin to level off at large applied potentials, especially when compared with the corresponding Butler–Volmer model (anodic values of both reorganisation energy and standard rate constant are higher). Haddox and Finklea fitted the anodic and cathodic branches show definite curvature and the asymmetry parameter on Tafel plots is shown in Fig. 1. The curvature of the plots is more pronounced as the asymmetry parameter increases in magnitude, so does the difference between the anodic and cathodic slopes.

Further the monolayer is assumed kinetically homogeneous. Low pH this value ought to remain approximately constant during measurements. While the kinetics of this redox process will be a function of the local proton concentration, at very high and very low pH this value ought to remain approximately constant during the reaction and the electron transfer kinetics will not be obscured. Haddox and Finklea’s Osmium system has been demonstrated experimentally [26–28,37]. As an illustrative example the forward (oxidative) peak current for Haddox and Finklea’s Osmium system discussed in the previous section is presented in Fig. 2.

We have tested the asymmetric model against experimental data published by Haddox and Finklea [27]. They studied the proton-coupled oxidation of a surface-bound osmium complex at a gold electrode. While the kinetics of this redox process will be a function of the local proton concentration, at very high and very low pH this value ought to remain approximately constant during the reaction and the electron transfer kinetics will not be obscured. The electrode area is 0.1 cm², the surface coverage is 10⁻¹⁰ mol cm⁻², and the rate constant for a range of k values. The deviations from linearity are marked:

Fig. 1. Simulated Tafel plots for a redox couple obeying asymmetric MH kinetics. In each case $\lambda = 1$ eV, $\beta/\lambda = -0.3$ (black), -0.3 (white) and 0 (grey). The dotted line shows the corresponding data calculated using the Butler–Volmer model (with $\alpha = 0.5$) for comparison.

Fig. 2. Plot of rate constant vs. overpotential for a surface-bound Osmium aquo complex. Experimental data (squares) are taken from Ref. [27], as is the theoretical fit using symmetric MH theory (dotted) which uses two values of $k_0$ and $\lambda$. The theoretical fit using asymmetric MH theory (solid) was calculated using $k_0 = 21$ s⁻¹, $\lambda = 0.85$ eV and $\beta/\lambda = -0.18$.

3.2. Voltammetric peak current

When studying surface-bound redox couples using cyclic voltammetry (CV), assuming irreversible Butler–Volmer kinetics, the peak current is predicted to scale linearly with scan rate [33]. If Marcus–Hush kinetics operate, however, plotting peak current against scan rate yields a curve with the peak current smaller than expected from classical theory at high scan rates [34–36], as has been demonstrated experimentally [26–28,37]. As an illustrative example the forward (oxidative) peak current for Haddox and Finklea’s Osmium system discussed in the previous section is predicted to be only approximately 70% that expected from the classical Butler–Volmer treatment for a scan rate of 1000 V s⁻¹.

This feature is common to both symmetric and asymmetric formulations of the Marcus–Hush model as illustrated in Fig. 3, which shows the theoretical scan rate dependence of both oxidative and reductive peak currents for a system with $k_0 = 10$ s⁻¹ and $\lambda = 1$ eV for a range of $\beta/\lambda$ values. The deviations from linearity are marked:

Fig. 3. Variation of peak current with scan rate for a surface-bound redox couple. The electrode area is 0.1 cm², the surface coverage is 10⁻¹⁰ mol cm⁻², $\lambda = 1$ eV and $\beta/\lambda = -0.3$ (black), -0.3 (white) and 0 (grey). The linear relationship expected from Butler–Volmer kinetics is shown for comparison.
all values of $\beta/\lambda$ yield a curve; including $\beta/\lambda = 0$, which corresponds to the symmetric MH model. Positive values of this parameter yield larger reductive peak currents than the symmetric model and smaller oxidative peaks, negative values yield smaller reductive peak currents.

The Butler–Volmer model predicts an analogous trend for square wave voltammograms (SWV): for a totally irreversible system the peak current is proportional to the pulse frequency. The variation of the peak current with the dimensionless heterogeneous rate constant $k_0/f$ is plotted in Fig. 4 for a reduction for both BV and MH kinetic models. In the reversible and quasi-reversible regions ($\beta > 0.1$) only small differences are observed between the models since the peaks occur at small overpotentials where the values for the rate constants are very similar. Both models predict the so-called “quasi-reversible maximum” [38,39] at $\alpha = 0.5$. When considering more irreversible systems, however, the differences between the models become more apparent. While peak current scales linearly with frequency for the Butler–Volmer model, at high frequencies the peak height is smaller than predicted by classical theory. The trends regarding the value of $\beta/\lambda$ are the same as those observed for CV.

Working surfaces detailing the variation of anodic and cathodic peak currents with $\lambda$ and $\beta$ are provided in Supporting information.

3.2.1. Peak split

A further characteristic of electroactive monolayers, unique to SWV, is the splitting of the peak for fast electron transfers when large pulse amplitudes are employed [39]. The separation between the two resulting peaks increases with increasing pulse amplitude. As can be seen in Fig. 5, this behaviour is successfully reproduced by both BV and MH kinetic models. This phenomenon has been observed for several redox systems by employing the appropriate frequency value and both have been used to characterise the kinetics of the electron transfer [39].

While the frequency of the quasi-reversible maximum permits estimation of the $k_0$ value, the ratio of the two resulting peak currents is characteristic of the transfer coefficient as can be inferred from Fig. 5. Within the Butler–Volmer model the peak currents are predicted to be equal for $\alpha = 0.5$, the anodic peak is larger for $\alpha < 0.5$ and the cathodic peak is larger for $\alpha > 0.5$. Similarly, this ratio relates to the asymmetry parameter in the Marcus–Hush model: a larger cathodic peak indicates a positive $\beta/\lambda$ value (i.e. the force constants of the oxidised species are greater on average than those of the reduced species). The opposite applies when the anodic peak is larger. Thus studying the symmetry of the two peaks under suitable conditions enables simple detection and quantification of asymmetry effects.

![Fig. 4. Variation of the dimensionless reductive peak current of square wave voltammograms with the dimensionless heterogeneous rate constant $k_0/f$. Frequency = 100 Hz, pulse amplitude = 50 mV, step potential = 5 mV. $\psi = \frac{I}{nFAT'}f$.](attachment:fig4.png)

![Fig. 5. Split of the SWV peak for fast electron transfers at large pulse amplitudes predicted by the MH (square points) and BV (solid line) models. Different values for the transfer coefficient are considered: (a) $\alpha = 0.5$, $\beta/\lambda = 0$ (grey), variable pulse amplitude; (b) $\alpha = 0.6$, $\beta/\lambda = 0$ (grey) and +0.45 (black), pulse amplitude = 75 mV. In both cases $k_0/f = 3$, $\lambda = 1$ eV, step potential = 10 mV. $\psi = \frac{I}{nFAT'}f$.](attachment:fig5.png)
3.3. Voltammetric peak potential

Due to the difficulty in correctly subtracting non-Faradaic background current from experimental cyclic voltammetry, peak potentials have sometimes been preferred for extracting quantitative data [34]. According to the work of Laviron, for a kinetically irreversible system (with peak splitting > 200 mV) the peak potential should scale linearly with the logarithm of scan rate [33]. Under Marcus–Hush kinetics, however, peak potential deviates from this relationship—increasing at a greater rate than log scan rate, as shown in Fig. 6. Symmetric MH predicts that oxidative and reductive peaks should occur equally separated from the formal potential, whereas within the asymmetric model the two peaks may occur at different overpotentials. This feature of the asymmetric model, specifically, has been observed experimentally in the Osmium system described in Ref. [27].

As is the case for peak current, there is an analogous theoretical relationship for SWV assuming BV kinetics: peak potential scales linearly with log frequency [38]. The Marcus–Hush model, however, does not follow this prediction, as shown in Fig. 7.

![Fig. 6. Plot of peak potential vs. log scan rate for a surface-bound redox couple. The electrode area is 0.1 cm², the surface coverage is 10⁻¹⁰ mol cm⁻², k₀ = 10 s⁻¹, λ = 1 eV and β/λ = 0 (black), 0.3 (white) and 0 (grey). The relationship expected from Butler–Volmer kinetics is shown for comparison.](image1)

![Fig. 7. Variation of the dimensionless reductive peak current (A) and peak potential (B) of square wave voltammograms with the dimensionless heterogeneous rate constant k⁰/β. Frequency = 100 Hz, pulse amplitude = 25 mV, step potential = 10 mV, ψ = 0.01.](image2)

3.4. Voltammetric waveshape

The authors have, in the context of solution-phase voltammetry, previously drawn comparison between the Butler–Volmer transfer coefficient (z) and the asymmetry parameter β/λ [22]. Figs. 8 and 10 show cyclic and square wave voltammograms respectively for a range of β/λ values. The results are indeed qualitatively akin to those expected from varying z: when β/λ = 0 (roughly equivalent to α = 0.5) the forward and back peaks are the same height and occur at the same magnitude of overpotential. If β/λ deviates from 0 then one peak becomes sharper and taller, occurring at lower overpotential and the other becomes broader, shorter and moves away from the formal potential.

When comparing the asymmetric MH model with the BV model quantitatively, however, the equivalence no longer holds for the smaller values of reorganisation energy (~1 eV) typical for surface-bound systems. Figs. 9 and 11 show voltammetry simulated for both cyclic and square wave voltammetry using asymmetric MH kinetics (λ = 1 eV, β/λ = +0.45, a = 0.01 and b = 0.01 respectively) and the closest fits of the reductive peak possible using the BV model (while keeping k₀ fixed). In both cases it is
even if not possible to simultaneously fit both forward and back peaks, Simulated square wave voltammetry for a surface-bound redox couple, Fig. 11. Simulated square wave voltammetry for a surface-bound redox couple obeying asymmetric MH kinetics. \( k_{f}/f = 0.01, \) pulse amplitude = 25 mV, step potential = 10 mV, \( \psi = 0.001 \), \( \lambda = 1 \text{ eV} \) and \( \beta/\lambda = -0.45 \) (black), \(-0.45\) (white) and 0 (grey).

not possible to simultaneously fit both forward and back peaks, even if \( E^a \) and \( k_0 \) are treated as variable. While the two models proved almost indistinguishable for typical solution-phase systems [22], this is evidently not the case for surface-bound systems.

4. Discussion

In recent work [22] we concluded that for diffusional voltammetry both the BV and asymmetric MH models can satisfactorily parameterise experimental data. Indeed, an approximate equivalence relationship between the electron transfer coefficient (\( \alpha \)) and the asymmetry parameter (\( \beta/\lambda \)) was established. This enables the use of the simpler BV model while maintaining the ability to gain physical insights about the system through the relationship with the asymmetric MH model.

However for the case of electroactive monolayers the two models are no longer indistinguishable (as shown in Figs. 9 and 11) due to the smaller values of reorganisation energy which are typical for surface-bound systems. Additionally experimental evidence has demonstrated numerous features which the Butler–Volmer is unable to account for and as such the use of this model should be restricted to systems with highly reversible electrode kinetics.

The symmetric MH model correctly predicts curved Tafel plots and deviations from the Butler–Volmer trends in peak current and potential, however it is unable to model the asymmetry evident in many experimental Tafel plots and cannot account for unequal cathodic and anodic peak currents or peak overpotentials. This model has been successfully employed for some systems, notably the ferrocene system studied by Chidsey [10], however the use of this model in the analysis of all experimental systems may not be appropriate. In particular the practice of independently fitting the cathodic and anodic branches of a Tafel plot to gain two values for the reorganisation energy is to be discouraged due to its thermodynamic inconsistency.

The asymmetric MH model has been compared to several features of experimental cyclic and square wave voltammetry and has been able to reproduce them all. Further, the use of this model enables the extraction of physically insightful kinetic data and conversely allows for predictions based upon previously known data. Given that this model encompasses the symmetric version, but with greater flexibility, we recommend that the analysis of surface-bound redox couples should be performed using the asymmetric Marcus–Hush model.

5. Conclusions

The asymmetric Marcus–Hush (MH) model has been applied to the simulation of surface-bound redox systems by cyclic voltammetry (CV) and square wave voltammetry (SWV). This microscopic kinetic model allows physical insights to be gained from the values of the kinetic parameters, conversely it permits predictions on the basis of properties of the system under study.

Comparison has been made with both the empirical BV model and the symmetric MH model. The asymmetric MH model has been shown to most accurately reproduce the experimentally observed features of surface-bounds redox systems: it yields asymmetric curved Tafel plots and predicts the correct non-linear trends in both peak current and peak potential for both cyclic and square wave voltammetry.

While the voltammetry of reversible and quasireversible systems may be parameterised satisfactorily using the Butler–Volmer model, for systems with irreversible electrode kinetics (or for high scan rate/frequency) the use of the asymmetric Marcus–Hush model is strongly recommended.

Acknowledgments

M.C.H. thanks EPSRC for funding (EP/H002413/1). E.L. thanks the Fundacion SENECA for support.

Appendix A. Supplementary material

Supplementary data associated with this article can be found, in the online version, at http://dx.doi.org/10.1016/j.jelechem.2012.04.006.

References