An experimental comparison of the Marcus–Hush and Butler–Volmer descriptions of electrode kinetics applied to cyclic voltammetry. The one electron reductions of europium (III) and 2-methyl-2-nitropropane studied at a mercury microhemisphere electrode

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ABSTRACT

We present a comparative experimental evaluation of the Butler–Volmer and Marcus–Hush models using cyclic voltammetry at a microelectrode. Numerical simulations are used to fit experimental voltammetry of the one electron reductions of europium (III) and 2-methyl-2-nitropropane, in water and acetonitrile, respectively, at a mercury microhemisphere electrode. For Eu (III) very accurate fits to experiment were obtained over a wide range of scan rates using Butler–Volmer kinetics, whereas the Marcus–Hush model was less accurate. The reduction of 2-methyl-2-nitropropane was well simulated by both models, however Marcus–Hush required a reorganisation energy lower than expected.

1. Introduction

The Butler–Volmer theory [1,2] of electron transfer kinetics has proved very successful in the analysis of electron transfer for a wealth of systems and has become the standard kinetic model for electrochemical simulation. The model relates the rate of electron transfer to a standard heterogeneous rate constant, $k_0$, and two transfer coefficients $\alpha$ (for reduction) and $\beta$ (for oxidation), which obey $\alpha + \beta = 1$ for a one-electron process. This leads to the familiar classical interpretation of the transfer coefficients as indicating the ‘position’ of the transition state on the reaction coordinate between reactants and products [3].

Despite its widespread usage and numerous successes, Butler–Volmer theory does have its defects. Notably it predicts that the rate of electron transfer should continue following an exponential dependence on overpotential ad infinitum. A further drawback of the Butler–Volmer approach is that, due to its phenomenological nature, it offers limited physical insight into the process it describes.

By way of contrast, Marcus theory [4–9] has developed to cover a huge variety of electron transfer reactions, many aspects of which have been verified experimentally, not least the prediction of the existence of the so-called ‘inverted region’ and the theoretical basis of curved Tafel plots [10,11]. By relating the standard heterogeneous rate constant to a reorganisation energy, it has provided a more insightful physical model for understanding the rate of electron transfer as well as a means of its calculation. The total reorganisation energy may be divided into inner sphere and outer sphere contributions, the inner sphere reorganisation energy may then be calculated by consideration of changes in molecular geometry (e.g., using density functional theory) and the outer-sphere (solvent) reorganisation energy from the Born–Marcus solvation equation.

Following Chidsey’s work [11], which built upon earlier theoretical works [12] and is widely regarded as seminal, the Marcus–Hush approach has become increasingly widespread. This treatment considers Marcusian electron transfer between the redox species and the continuum of energy levels in the electrode. Its prediction of a finite limiting rate constant at high overpotential, which is in contrast to both the Butler–Volmer model and conventional Marcus theory, has been observed experimentally for many systems within the context of potential step chronoamperometry for surface bound species [11,13–16]. Feldberg has recently published theoretical work concerning the limits in which Butler–Volmer and Marcus–Hush formalisms are indistinguishable for steady state voltammetry in solution [17] and Oldham has published work concerning an approximation to the Marcus–Hush integral [18], but comparative experimental studies have been limited for redox systems in the solution phase [19].

The authors have previously compared the Marcus–Hush (MH) and Butler–Volmer (BV) formalisms using pulse voltammetry [20]. The one electron reduction of 2-methyl-2-nitropropane (MeNP) was studied using reverse scan square wave voltammetry. Using BV kinetics it was possible to fit the experimental data satisfactorily, however MH kinetics could not fit both peaks simultaneously for any value of reorganisation energy.
Given the clear distinction made between BV and MH kinetics under pulse voltammetry the question arises as to the extent to which similar contrasts might be revealed by using cyclic voltammetry. In this Letter we undertake a similar comparison of the two kinetic formalisms using cyclic voltammetry. We again study the one electron reduction of MeNP in acetonitrile, as well as the one electron reduction of europium (III) chloride in aqueous solution, both at a mercury microhemisphere electrode. These systems were chosen due to their irreversible kinetics and the literature values which deviate from those [21,22], such systems are predicted to produce the most marked differences in the two kinetic models [17]. Experimental voltammetry was fitted using numerical simulations for both the BV and MH models. In particular we focus on fitting the entire cyclic voltammetric waveshape to identify significant differences between the two kinetic models. We do not seek curved Tafel plots [23] and no a priori assumptions are made, in contrast with earlier work [24] which extracts effective rate constants as a function of potential which are not inconsistent with Marcus theory.

The enhanced mass transport properties of microelectrodes (as opposed to macroelectrodes) make them ideal for use in kinetic investigations such as this [3]. The use of a mercury microhemisphere electrode made it possible to verify, via simulation using programs developed previously [25], that all experimental solutions contained sufficient supporting electrolyte to be considered diffusion-only systems. Owing to its one-dimensional symmetry, diffusion-only systems are transfer coefficients and \( \theta \) is a dimensionless potential, defined thus:

\[
\theta = \frac{F}{RT} (E - E^{\prime\prime})
\]

where \( E \) (V) is potential, \( E^{\prime\prime} \) (V) is the formal potential and \( F, R \) and \( T \) have their usual meanings. Within the Marcus–Hush formalism for electron transfer at a metallic electrode [11,17,18] these rate constants are given by:

\[
\kappa^{\text{MH}}_{\text{red}} = k_0 \exp \left( -\frac{\theta}{2} \frac{I(A,0)}{I(A,0)} \right)
\]

\[
\kappa^{\text{MH}}_{\text{ox}} = k_0 \exp \left( +\frac{\theta}{2} \frac{I(A,0)}{I(A,0)} \right)
\]

where \( A \) is a dimensionless reorganisation energy, defined thus:

\[
A = \frac{F}{RT} \lambda
\]

in which \( \lambda \) (eV) is the reorganisation energy and the integral

\[
I(A,0) = \int_{-\infty}^{\infty} \exp \left( -\frac{\epsilon^2}{4\lambda^2} \right) d\epsilon
\]

in which \( \epsilon \) is an integration variable, is evaluated numerically using the trapezium rule. It should be noted that in the limit of very high reorganisation energy (i.e., \( A \to \infty \)) the ratio of integrals in Eqs. 9 and 10 tends to unity. Thus in this limit the Marcus–Hush rate constants are reduced to their Butler–Volmer equivalents for the case when \( \lambda = \frac{1}{2} \).

In this Letter we consider cyclic voltammetry, thus the potential applied at the electrode varies as a function of time according to:

\[
E(t) = |E_1 - \sigma t - E_2| + E_2
\]

where \( E_1 \) and \( E_2 \) (V) are the starting and vertex potentials, respectively, and \( \sigma \) (V s\(^{-1}\)) is the scan rate.

Rate constants are calculated at each timestep and the resulting set of simultaneous equations, which can be formulated as a diagonal matrix, is then solved using the Thomas algorithm [26].

Both the Butler–Volmer and Marcus–Hush program variants were written in C++ and run on a desktop PC. Due to the inherent extra calculation required in numerically evaluating the integral in Eq. 12 when calculating the rate constants for the Marcus–Hush model, these simulations were slower than those for the Butler–Volmer model, taking approximately twice the time to run. However for both programs typical simulation times were below five seconds.

2. Theory

We consider the redox reaction \( A + e = B \) taking place in solution at a hemispherical electrode. For this system the appropriate mass transport equation, neglecting migration [25], is therefore:

\[
\frac{\partial C_i}{\partial t} = D_i \left[ \frac{\partial^2 C_i}{\partial r^2} + \frac{2}{r} \frac{\partial C_i}{\partial r} \right]
\]

where \( C_i \) (mol cm\(^{-3}\)) and \( D_i \) (cm\(^2\) s\(^{-1}\)) are, respectively, the concentration and diffusion coefficient, \( r \) (s) is time and \( r \) (cm) is radial distance from the centre of the hemisphere of radius \( r_e \). This equation is solved numerically using the backwards implicit finite difference method [26] over an expanding grid of points subject to the following:

\[
t = 0 \quad r \geq r_e \quad C_A = C_A^0, C_B = 0
\]

\[
t > 0 \quad r \to \infty \quad C_A = C_A^0, C_B = 0
\]

\[
t > 0 \quad r = r_e \quad D_A \frac{\partial C_A}{\partial r} = k_{\text{red}} C_A - k_{\text{ox}} C_B
\]

\[
t > 0 \quad r = r_e \quad D_A \frac{\partial C_A}{\partial r} = -D_A \frac{\partial C_B}{\partial r}
\]

where \( C_A^0 \) (mol cm\(^{-3}\)) is the bulk concentration of \( A \) and \( k_{\text{red}} \) and \( k_{\text{ox}} \) (cm s\(^{-1}\)) are the rate constants for reduction and oxidation, respectively, which are defined differently within the Butler–Volmer and Marcus–Hush formalisms.

Within the Butler–Volmer model these rate constants are given by:

\[
k_{\text{red}}^{\text{BV}} = k_0 \exp \left( -\alpha \theta \right)
\]

\[
k_{\text{ox}}^{\text{BV}} = k_0 \exp \left( +\beta \theta \right)
\]

where \( k_0 \) (cm s\(^{-1}\)) is the standard electrochemical rate constant, \( \alpha \) and \( \beta \) are transfer coefficients and \( \theta \) is a dimensionless potential, defined thus:

\[
\theta = \frac{F}{RT} (E - E^{\prime\prime})
\]

where \( E \) (V) is potential, \( E^{\prime\prime} \) (V) is the formal potential and \( F, R \) and \( T \) have their usual meanings. Within the Marcus–Hush formalism for electron transfer at a metallic electrode [11,17,18] these rate constants are given by:

\[
\kappa^{\text{MH}}_{\text{red}} = k_0 \exp \left( -\frac{\theta}{2} \frac{I(A,0)}{I(A,0)} \right)
\]

\[
\kappa^{\text{MH}}_{\text{ox}} = k_0 \exp \left( +\frac{\theta}{2} \frac{I(A,0)}{I(A,0)} \right)
\]

3. Experimental methods

A three electrode cell was used. Hemispherical mercury ultramicroelectrodes were used (radius 50 \( \mu \)m for Eu (III) and radius 25 \( \mu \)m for MeNP) as the working electrode and was prepared according the procedure of Bard et al. [27,28]. A platinum wire was used as a counter electrode and a silver wire was used as the pseudo-reference electrode in non-aqueous solutions, a saturated calomel electrode (SCE, Radiometer, Copenhagen) was used instead in aqueous solutions. All electrochemical experiments were carried out using a PGSTAT 12 potentiostat (Autolab, the Netherlands) and thermostatted via immersion in a water bath at 298 K.

Europium (III) chloride (Aldrich, 99.99%), 2-methyl-2-nitropropane (Aldrich, 99%), potassium chloride (Aldrich, >99%), tetra-n-butylammonium perchlorate (TBAP, Aldrich, >99%) and acetonitrile (Fischer Scientific, HPLC grade) were all used as received with no
further purification. Aqueous solutions were made up using water of resistivity not less than 18.2 MΩ cm⁻¹ at 298 K (Millipore, UK). All solutions were thoroughly deoxygenated, for at least 30 min, with nitrogen pre-saturated with the corresponding solvent.

4. Theoretical results

Values of the Marcus–Hush oxidative rate constant calculated from Eq. 10 are shown in Figure 1 for a range of \( \lambda \) values, the Butler–Volmer rate constants for \( \lambda = \frac{1}{2} \) is also shown for comparison. The limiting value of rate constant predicted by the Marcus–Hush model can clearly be seen. For very small values of \( \lambda \), this plateau is reached at fairly low overpotentials, but with increasing \( \lambda \) the limiting rate constant increases, as does the overpotential required to reach it. Figure 1 also demonstrates graphically that in the limit of \( \lambda \to \infty \), Marcus–Hush kinetics yields rate constants equal to those of Butler–Volmer kinetics for \( \lambda = \frac{1}{2} \) for the same overpotential, assuming equal \( k_0 \) values.

In order to differentiate between the two kinetic formalisms voltammetrically there must be an appreciable difference in rate constants while the current is still under kinetic control. This is because the diffusion-limited current is inherently independent of the rate constant. As can be seen in Figure 1 the two models yield almost indistinguishable rate constants for potentials in the vicinity of \( E^* \), indeed at \( E = E^* \) the rate constants are exactly equal. For small reorganisation energies up to around 1 eV the two models begin to significantly diverge at overpotentials of the order of 50–100 mV, although as reorganisation energy increases so does the overpotential required for an observable difference in rate constants. Thus an experimental system must give a kinetically controlled current at an appreciable overpotential. For a totally reversible system the peak potential is approximately 29 mV [3], beyond which the current is under diffusional control. Therefore for a diffusion-only system, without employing extremely high scan rates, it is only redox systems with significantly irreversible electrode kinetics that will enable differentiation between the Butler–Volmer and Marcus–Hush kinetic models.

The effect \( \alpha \) and \( \lambda \) have on typical cyclic voltammetry when deviating from the \( \alpha = \frac{1}{2} \) (or \( \lambda \to \infty \)) limit is shown in Figure 2. Decreasing \( \lambda \) is seen to broaden and shorten both forward and back peaks. Within the BV formalism, however, when \( \alpha \) deviates from \( \frac{1}{2} \) one peak is seen to become broadened relative to the \( \alpha = \frac{1}{2} \) case, while the other peak becomes ‘sharper’ since \( \alpha + \beta = 1 \).

Excepting the case of steady-state voltammetry, where the current is always limited by the rate of mass transport, it is therefore not possible to exactly reproduce voltammetry simulated using BV kinetics with \( \alpha \neq \frac{1}{2} \) by using MH kinetics, regardless of the value of \( \lambda \) used. Equally, BV kinetics cannot precisely replicate voltammetry which is simulated using MH kinetics with a small reorganisation energy, no matter the value of \( \alpha \). Thus if a set of experimental data is fitted very accurately using one of either BV or MH kinetics (excepting the limiting cases discussed previously), the other model will likely yield a poor fit.

5. Experimental results

5.1. Quantifying quality of fit

In order to quantify agreement between simulation and experiment, a mean scaled absolute deviation (MSAD) was calculated for each voltammogram [29], which is defined by:

\[
\% \text{ MSAD} = \frac{1}{n} \sum_{i} \left| \frac{i_{\text{exp}} - i_{\text{sim}}}{i_{\text{exp}}} \right| \times 100
\]

where \( i_{\text{exp}} \) and \( i_{\text{sim}} \) are experimental and simulated current, respectively, and \( n \) is the number of data points. Since the points of the simulated voltammetry are not necessarily aligned at the same potential values as those of the experimental voltammetry, spline
interpolation was used to calculate $i_{\text{lim}}$ at the potentials of the experimental points. Additionally a narrow strip of the experimental voltammetry near $i = 0$ was omitted from the MSAD calculations because dividing by a very small value of $i_{\text{exp}}$ yields a very large value of MSAD even if $i_{\text{exp}} - i_{\text{lim}}$ is small.

5.2. The one electron reduction of Eu (III)

In order to study the system $\text{Eu}^{3+} + e^{-} \rightleftharpoons \text{Eu}^{2+}$, cyclic voltammetry (CV) was carried out over a wide range of voltage scan rates (10 mV s$^{-1}$ to 1 V s$^{-1}$) on a 1 mM aqueous solution of europium (III) chloride containing 0.4 M potassium chloride as supporting electrolyte. Prior to attempting theoretical fitting of the experimental data the diffusion coefficients of Eu$^{3+}$ and Eu$^{2+}$ were determined via double potential step chronoamperometry at the Hg microhemisphere. The resulting transient was fitted for both diffusion coefficients and the concentration using a previously reported program [30] based on the Shoup & Szabo expression [3]. The diffusion coefficients for Eu$^{3+}$ and Eu$^{2+}$ were found to be $6.4 \times 10^{-6}$ cm$^2$s$^{-1}$ and $9.0 \times 10^{-6}$ cm$^2$s$^{-1}$, respectively, at 298 K, in excellent agreement with the literature values [31–33].

Although the Shoup & Szabo expression assumes infinite electrode kinetics at high overpotentials, its use was justified as follows: the Shoup & Szabo value for the diffusion coefficient was used in fitting the experimental CV data. Once fitting was completed the best fit values for $k_0$ were substituted into a second potential step program, based upon finite electrode kinetics [34], to fit the same chronoamperometric transient fitted previously. For both BV and MH cases the diffusion coefficient was found to be effectively equal to that originally obtained from Shoup & Szabo.

Supplementary CV simulations were carried out to check the validity of simulating the system as ‘diffusion-only’. These simulations used a previously reported program which solves the Nernst–Planck–Poisson system of equations and thus does not neglect migration. There was no observable difference between the diffusion-only simulations and the diffusion-migration simulations for the support ratios used in the present experiments, thus we consider the system fully supported and the diffusion-only approximation assumed valid [35].

Additional experiments were also carried out to discount possible double layer effects, so-called ‘Frumkin effects’ [36], which could potentially have minor distorting effects on the voltammetry. Cyclic voltammetry was carried out for both 1 mM and 2 mM analyte in a range of supporting electrolyte concentrations (0.1–1.0 M). When this voltammetry was fitted (using Butler–Volmer kinetics) negligible and non-systematic variation was seen for both $k_0$ and $\alpha$. We therefore exclude possible Frumkin effects. This experimental justification is also supported by recent theoretical work [37] which considers electron transfer occurring at a range of distances from the electrode (rather than at a single distance as in Frumkin’s original work [36]). This work indicates that the inclusion of this range of tunneling distances acts so as to substantially mitigate the predicted effects. Thus the experimental voltammetry was further analysed without consideration of Frumkin effects.

Experimental Eu (III) voltammetry is shown for two different scan rates in Figure 3, along with best fit simulations using both Butler–Volmer and Marcus–Hush kinetics.

For the BV model, the best fit kinetic parameters were $k_0 = 3.5 \times 10^{-4}$ cm$^{-1}$s$^{-1}$ and $\alpha = 0.65$, which are in good agreement with values found in the literature [32]. Figure 3 clearly shows good agreement between simulation and experiment across a wide range of scan rates. At high scan rates a very close fit is achieved throughout the entirety of the voltammetric transient, with both the peak potential and peak current being accurately reproduced by simulations on the forward sweep, although at low scan rates the reverse peak current is overestimated by the simulations. Quantitative analysis of the fits yielded a small MSAD value of 9.4%.

The best fit achieved using MH kinetics used $k_0 = 2.0 \times 10^{-4}$ cm$^{-1}$s$^{-1}$ and $\lambda = 2.0$ eV. This value of $\lambda$ is equal to a value calculated using the Arrhenius and Marcus relations from $k_0$ by Elzanowska et al. [21]. Similar values for reorganisation energy, between 1.0 and 3.0 eV, have also been reported for numerous other metals [38].

Figure 3 shows that both high and low scan rates fits the experimental data is not fitted as accurately as was the case for BV kinetics. The forward peak current is too low and the peak too broad across the whole scan rate range. The simulated voltammetry fits the back peaks more closely than the forward, but the oxidative peak current is overestimated at all scan rates. Despite the large discrepancy between simulation and experiment, it was not possible to obtain a better fit. With both reactant and product diffusion coefficients fixed via double potential step experiments and $k_0$ fixed to a large degree by the peak separation, $\lambda$ is the only remaining parameter able to effect a change in the voltammetric waveshape. The MSAD value calculated for the MH model was 20.3%, more than double the value obtained for the BV simulations.

This relative inability of MH kinetics to accurately fit the experimental voltammetry is, perhaps, not surprising. As discussed in the Theoretical Results section, there is no equivalence between MH kinetics (for any $\lambda$) and BV kinetics using a value of $\alpha$ which
significantly deviates from $\frac{1}{6}$. Given that the experimental voltammetry was fitted well when using BV kinetics with $\alpha = 0.65$, it was unlikely that it would be possible to accurately fit the experimental data using MH kinetics (Table 1).

5.3. The one electron reduction of 2-methyl-2-nitropropane (MeNP)

Next, we consider the system MeNP + e$^-$ = MeNP$^-$. Cyclic voltammetry was next carried out on a 2 mM solution of 2-methyl-2-nitropropane in acetonitrile containing 0.1 M TBAP as supporting electrolyte. Again a wide range of scan rates was studied, from 10 mV s$^{-1}$ to 10 V s$^{-1}$, which encompassed steady-state to fully transient voltammetric responses. The diffusion coefficients of MeNP and MeNP$^-$ were determined via fitting of double potential step chronoamperometric transients using the same procedure described above for Eu (III). The values for MeNP and MeNP$^-$ were both found to be $2.7 \times 10^{-3}$ cm$^2$ s$^{-1}$, in excellent agreement with the literature values [39]. There was no observed systematic shift in either $E_0$ or $k_0$ with scan rate; thus ohmic drop was assumed to be negligible. Again, diffusion-migration simulations proved indistinguishable from diffusion-only simulations for the support ratio used in these experiments, as expected given that MeNP is uncharged.

The experimental voltammetry is shown for two different scan rates in Figure 4, along with best fit simulations for both Butler–Volmer and Marcus–Hush kinetics.

Figure 4 shows that, as was the case for Eu (III), the voltammetry of MeNP was fitted very well using BV kinetics. The best fit values of $k_0$ and $x$ were $3.2 \times 10^{-3}$ cm$^2$ s$^{-1}$ and 0.38, respectively, both in close agreement with the literature values [20,22,40,41]. It can be seen that these simulations fit the experimental peak potentials and peak currents at high scan rates very closely and accurate reproduction of the steady-state current is also observed at low scan rate. This impressive agreement between simulation and experiment is reflected by the small MSAD value of 4.3%.

The best fit achieved using the MH model used $x = 0.5$ eV and $k_0 = 3.2 \times 10^{-3}$ cm$^2$ s$^{-1}$ (Figure 4). These simulations yielded an MSAD value of 6.7% which is larger than was achieved by the BV fit. Almost perfect agreement is observed between simulation and experiment at high scan rate for the forward scan, but the simulated back peak is much smaller than experiment. At lower scan rates the MH fits are comparable to those produced by the BV model, but with a steady state current which is slightly larger than is observed experimentally.

This value of $x$, however, is smaller than the theoretical outer sphere reorganisation energy alone, calculated to be 1.6 eV using:

$$\lambda_{os} = \frac{N_A e^2}{8 \pi \varepsilon_0} \left( \frac{1}{\varepsilon_{op}} - \frac{1}{\varepsilon_s} \right)$$

(15)

using the spherical approximation of the Stokes–Einstein equation [42–45].

$$r = \frac{k_B T}{6 \pi \eta D}$$

(16)

where $r$ is the molecular radius here treated as the solvodynamic radius according to Clegg et al. [43], $\varepsilon_0$ is the permittivity of free space, $\varepsilon_{op}$ and $\varepsilon_s$ are the optical and static frequency components of the dielectric permittivity of the solvent, $\eta$ is the solvent viscosity and $D$ the diffusion coefficient. $N_A e^2 k_B$ and $T$ have their usual meanings.

From these equations $\lambda_{os}$ for this system was found to be much larger than the value used to obtain the best fit. Voltammetry simulated using this larger value of 1.6 eV, which still assumes a negligible inner sphere contribution to $\lambda$, is shown in Figure 5. It can be seen that while the agreement between simulation and experiment for the back peak at high scan rates is improved by a larger peak current, the forward peak is now too large and fits less well than for the lower $\lambda$ value. At lower scan rates the steady state current is also noticeably larger than the experimental value. The overall result is an increased MSAD value of 7.1%.

Furthermore, DFT calculations [41] have shown that the inner sphere reorganisation for the reduction of MeNP has a value of approximately 0.9 eV, far from negligible. Further increasing $\lambda$ to 2.5 eV, considering both inner and outer sphere reorganisation, results in an even higher overall MSAD value of 7.2% (Figure 5), demonstrating that simulations using MH kinetics with physically meaningful values of reorganisation energy may, in some cases, less accurately model the real physical process! (Table 2).

The inability of the MH formalism to fit both experimental peaks simultaneously for any value of $\lambda$, which has been reported previously for this system [20], is again not unexpected considering the

### Table 1

Simulation parameters for the reduction of Eu (III).

<table>
<thead>
<tr>
<th></th>
<th>Butler–Volmer</th>
<th>Marcus–Hush</th>
</tr>
</thead>
<tbody>
<tr>
<td>$k_0$/cm s$^{-1}$</td>
<td>$3.5 \times 10^{-4}$</td>
<td>$2.0 \times 10^{-4}$</td>
</tr>
<tr>
<td>$\alpha$</td>
<td>0.65</td>
<td>–</td>
</tr>
<tr>
<td>$\lambda$/eV</td>
<td>–</td>
<td>2.0</td>
</tr>
<tr>
<td>$E_0$/V</td>
<td>–0.59</td>
<td>–0.52</td>
</tr>
<tr>
<td>% MSAD</td>
<td>9.4 ± 2.3</td>
<td>20.3 ± 2.8</td>
</tr>
</tbody>
</table>

Figure 4. Comparison of experimental MeNP voltammetry (line) with best fit simulations using Butler–Volmer (blacksquare) and Marcus–Hush (circles) kinetics. Parameters are given in Table 2. (a) 50 mV s$^{-1}$ (b) 5000 mV s$^{-1}$.
fits for BV kinetics use a value of $x$ which significantly deviates from $\frac{1}{2}$. This is a key indication that when using simple three parameter models ($E^0_f$, $k_0$, $x$) in the case of BV kinetics or ($E^0_g$, $k_0$, $\gamma$) in the case of MH kinetics, while the Marcus–Hush model likely gives better physical insight, its application may not best parameterise voltammetric data in all cases.

A possible route to improving the ability of the MH model to parameterise experimental voltammetry would be to remove Chidsey’s assumption [11] that the forward and back reactions have the same reorganisation energy. Through the use of non-symmetrised Marcus theory [9], and the introduction of a second reorganisation energy (one for the forward reaction and another for the back reaction), it may be possible for the MHC model to better parameterise electrochemical reactions while still giving physical insight into the underlying processes. It is also possible, however, that an additional parameter would only make fitting more difficult and raise possible questions of the uniqueness of sets of parameters which fit experimental data.

6. Conclusions

We have undertaken a comparison of the Butler–Volmer and Marcus–Hush kinetic formalisms using cyclic voltammetry at a microelectrode. We have shown that for both experimental systems studied, despite its limitations, the use of Butler–Volmer kinetics using the literature values of $k_0$ and $x$ afforded accurate fitting of the experimental data. Comparable fitting was also possible for some systems using Marcus–Hush kinetics, however in order to achieve this it was necessary to discard both the literature and calculated values of reorganisation energy in favour of using $\gamma$ purely as a further fitting parameter, yielding physically unrealistic values. Thus, as was found to be the case using pulse voltammetry, the Marcus–Hush formalism, in its current form, has proven less well suited for the parameterisation of solution-phase voltammetry than the Butler–Volmer model. That said, the Marcusian approach arguably remains more physically insightful.

As discussed by Marcus in his 1965 Letter [9], the effect of the forward and back reactions having different reorganisation energies will be for $x$ to deviate from $\frac{1}{2}$ at zero overpotential. This could indicate that using this non-symmetrised formulation of Marcus theory, when applied to heterogeneous electron transfer, could lead to a kinetic model which retains its physical insight whilst also accurately parameterising electrochemical data [46]. Some work has been done in this area [47–51], but as yet there is no formulation which is as easily applied as the Marcus–Hush model considered in this work.

Acknowledgements

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