Redox systems obeying Marcus–Hush–Chidsey electrode kinetics do not obey the Randles–Ševčík equation for linear sweep voltammetry

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**Abstract**

The cyclic voltammetry of the reaction of a solution-phase species at a macroelectrode under semi-infinite diffusion is simulated assuming irreversible electrode kinetics within the Marcus–Hush–Chidsey model. The resulting peak currents are shown to deviate from the square root dependence on voltage scan rate predicted by the Randles–Ševčík equation. Simulated voltammetry of a surface-bound redox couple also shows deviations from the expected linear dependence of peak current on scan rate. These numerical findings are supported by analytical arguments and they provide simple method for a critical assessment of the Marcus–Hush–Chidsey model before it is suitable for the analysis of experimental voltammetry.

**1. Introduction**

The use of the Randles–Ševčík equation [1,2] is ubiquitous in experimental electrochemistry. Its prediction of peak current varying with the square root of voltage scan rate is an important analytical result, indicating that a redox couple is dissolved in solution rather than adsorbed on the electrode surface, the latter being identified by a linear relationship between peak current and scan rate [3].

While the behaviour of reversible redox systems is determined by thermodynamics, the analysis of irreversible systems as a function of scan rate can yield electrode kinetic data. The derivation of the Randles–Ševčík equation for irreversible couples assumes, however, that "the rate of electron transfer is an exponential function of the electrode potential" [4], i.e. it assumes Butler–Volmer kinetics. For an irreversible, one-electron, solution-phase oxidation the peak current, \( I_p \), assuming Butler–Volmer kinetics is given by:

\[
I_p = 0.4958 \left( \frac{1 - \alpha}{RT} \right) F A c' D^{1/2} \nu^{1/2}
\]

where \( A \) is the geometric area of the electrode, \( c' \) is the bulk reactant concentration, \( D \) is the reactant diffusion coefficient, \( \nu \) is the voltage scan rate and \( \alpha \) is the transfer coefficient. \( F, R \) and \( T \) have their usual meanings.

In this work we use both numerical and analytical methods to examine whether the equations governing the variation of peak current with scan rate hold when using a different kinetic model, namely the Marcus–Hush–Chidsey model [5,6], for both solution-phase and surface-bound redox systems. In the limit of irreversible kinetics the peak current for a one-electron surface-bound redox couple is given by [7]:

\[
I_p = \frac{F \alpha F A \Gamma^0}{RT 2.718 \nu}
\]

where \( \Gamma^0 \) is the initial coverage of reactant.

We examine the conditions under which significant differences may be expected, with deviations from classical Randles–Ševčík behaviour providing an experimental method for the critical assessment of the Marcus–Hush–Chidsey kinetic formalism.

**2. Theory**

2.1. Electrode kinetics

The variation of electron transfer rate constants with overpotential depends upon the kinetic model employed. Within the Butler–Volmer (BV) model these rate constants are given by [3]:

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

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

where \( k_0 \) is the standard electrochemical rate constant, \( \alpha \) is the transfer coefficient and \( \theta \) is a dimensionless overpotential, defined thus:
\[ \theta = \frac{F}{RT} (E - E^\circ) \]  
where \( E \) is potential, \( E^\circ \) is the formal potential.

Within the Marcus–Hush–Chidsey (MHC) formalism these rate constants are given by [5,6,8]:

\[ k_{\text{red}}^\text{MHC} = k_0 \exp \left[ \frac{\lambda}{2} \frac{S(A,0)}{S(A,0)} \right] \]  
\[ k_{\text{ox}}^\text{MHC} = k_0 \exp \left[ \frac{\lambda}{2} \frac{S(A,0)}{S(A,0)} \right] \]  

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

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

The function

\[ S(A,0) = \int_{-\infty}^{\infty} \exp \left[ -e \frac{-(c-x)^2}{4} \right] \, de \]  
in which \( e \) is an integration variable, is evaluated numerically using the trapezium rule. It should be noted that in the limit of very high reorganisation energy the Marcus–Hush–Chidsey rate constants tend to their Butler–Volmer equivalents for the case when \( \lambda = \frac{1}{2} \).

As can be seen in Fig. 1, there is a major difference in the potential dependence of rate constants between the two kinetic models. For Butler–Volmer kinetics the rate constant continues to increase exponentially with increasing overpotential, whereas for Marcus–Hush–Chidsey kinetics the rate constants reach a limiting value at high overpotentials. As will be seen later, this difference determines the fulfilment, or otherwise, of Randles–Ševčík behaviour.

3. Numerical simulation

3.1. Solution-phase reaction

We consider the reaction \( A = B + e^- \) taking place at a macroelectrode in a solution containing a large excess of supporting electrolyte such that mass transport is entirely diffusional [9]. For simplicity the diffusion coefficients of reactant and product are assumed equal (i.e. \( D_A = D_B = D \)). For such a system diffusion may be approximated as linear, hence

\[ \frac{\partial C}{\partial t} = D \frac{\partial^2 C}{\partial x^2} \]  

where \( C \) is concentration of species, \( t \) is time and \( x \) is the coordinate normal to the electrode surface. Additionally, at the electrode surface:

\[ \partial C_A \bigg|_{x=0} = k_{\text{ox}} c_{A,0} - k_{\text{red}} c_{B,0} \]  
\[ \partial C_A \bigg|_{x=0} = -\partial C_B \bigg|_{x=0} \]  

where \( c_{i,0} \) denotes concentration at the electrode surface.

Cyclic voltammetry at a macrodisc was considered for this system, where the applied potential varies as:

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

where \( E_1 \) and \( E_2 \) are the starting and vertex potentials respectively. This is simulated numerically by solving Fick’s second law (Eq. (10)) via the backwards implicit (BI) finite difference method [10]. The boundary condition at the electrode surface (Eq. (11)) was chosen to be either the Butler–Volmer equation or its equivalent from Marcus–Hush–Chidsey kinetics as appropriate.

3.2. Surface-bound reaction

We also consider the reaction \( A = B + e^- \) taking place on the surface of an electrode. For this system:

\[ \frac{d \Gamma_A}{dt} = -k_{\text{ox}} \Gamma_A + k_{\text{red}} \Gamma_B \]  

where \( \Gamma \) is surface coverage.

Cyclic voltammetry was simulated via numerical solution of this equation using the backwards implicit (BI) finite difference method [10].

4. Scan rate dependence of the peak current

4.1. Dimensionless units

We define the following dimensionless units in order to simplify the following analysis:

<table>
<thead>
<tr>
<th>Unit</th>
<th>Dimensionless Unit</th>
<th>Scale</th>
</tr>
</thead>
<tbody>
<tr>
<td>Concentration</td>
<td>( C = \frac{C_0}{C^\circ} )</td>
<td>( \text{c} )</td>
</tr>
<tr>
<td>Distance</td>
<td>( X = \frac{x}{L} )</td>
<td>( \text{L} )</td>
</tr>
<tr>
<td>Potential</td>
<td>( \theta = \frac{E}{E^\circ} )</td>
<td>( \text{V} )</td>
</tr>
<tr>
<td>Standard rate</td>
<td>( K_0 = \frac{L^2}{4D} )</td>
<td>( \text{S} )</td>
</tr>
<tr>
<td>Time</td>
<td>( \tau = \frac{L^2}{\nu D} )</td>
<td>( \text{t} )</td>
</tr>
<tr>
<td>Scan rate</td>
<td>( \sigma = \frac{\nu}{\sqrt{2D}} )</td>
<td>( \text{V} )</td>
</tr>
<tr>
<td>Current</td>
<td>( j = \frac{1}{\sqrt{2DD_Ac_0}} )</td>
<td>( \text{A} )</td>
</tr>
</tbody>
</table>

4.2. Development of a general integral equation

Diffusion-only mass transport is given by Fick’s 2nd law, which for a linear space is:

\[ \frac{\partial C}{\partial t} = D \frac{\partial^2 C}{\partial x^2} \]  

If the applied overpotential is perturbed as:

\[ \theta = \theta_0 + \sigma \tau \]  

then we can define a coordinate \( \theta \) which is scaled to scan rate:
\[ \vartheta = \theta - \theta_i = \sigma \tau \]  

Hence  

\[ \frac{\partial (C \vartheta)}{\partial \vartheta} = \frac{\partial^2 C}{\partial \vartheta^2} \]  

Now, if \( C = 1 \) initially, and the outer boundary condition is \( C \to 1 \) as \( X \to \infty \), the general solution for \( C \) in the Laplace space is:  

\[ \mathcal{L}_X^{-\vartheta}(C(X, \vartheta')) = \mathcal{L}(X, s') = \frac{1}{s'} + B(s') \exp(-X\sqrt{s'}) \]  

Hence  

\[ \frac{\partial C}{\partial X} = -\sqrt{s'}\sigma B(s') \exp(-X\sqrt{s'}) \]  

and  

\[ \mathcal{C} = \frac{1}{s'} - \frac{\sqrt{s'}}{s'\sigma} \]  

On inverse transformation, from application of the convolution theorem it follows that:  

\[ \mathcal{C}(X, \vartheta') = \mathcal{C}(0, 0') + \mathcal{J}(\vartheta') = (\partial C/\partial X)_{X=0} \]  

we derive the following general relationship:  

\[ C_0 = 1 - \int_0^\vartheta \frac{\partial C(X, u)}{\partial X} \sqrt{s'\sigma} \vartheta - u \]  

This general mass transport relation is of direct use to the solution for the current if the surface flux obeys a simple first-order relationship:  

\[ f(\vartheta) = K_0 f(0) C_0(\vartheta) \]  

Both the irreversible Butler–Volmer and irreversible Marcus–Hush–Chidsey boundary conditions obey this general form, hence, transforming into the coordinate \( \vartheta' \):  

\[ f(\vartheta') = K_0 f(\theta_i + \vartheta') C_0(\vartheta') \]  

On substitution into the integral expression, an integral equation for \( C_0 \) results, which is a Volterra equation of the second kind:  

\[ C_0(\vartheta') + \frac{K_0}{\sqrt{\pi \sigma}} \int_0^{\vartheta'} f(\theta_i + \vartheta') \frac{C_0(u)}{\sqrt{\vartheta' - u}} \frac{du}{\sqrt{\vartheta' - u}} = 1 \]  

or equivalently  

\[ C_0(\vartheta') + \frac{K_0}{\sqrt{\pi \sigma}} \int_0^{\vartheta'} f(\theta_i + \vartheta' - u) C_0(\vartheta' - u) \frac{du}{\sqrt{u}} = 1 \]  

4.3. Analysis of the integral equation for special cases of \( f \)

In general the solution to Eq. (27) depends on the coefficients \( K_0, \sigma \) and \( \theta_i \). However, let us suppose a special case in which multiplying the function \( f(x) \) by a constant shifts it on the abscissa, but does not otherwise affect it. This is true for the exponential function. This property may be expressed:  

\[ \Delta f(x) = f(x + g(\lambda)) \]  

Therefore the constants may be absorbed into the function \( f \):  

\[ C_0(\vartheta') + \int_0^{\vartheta'} f(\vartheta' + A\vartheta - u) C_0(\vartheta' - u) \frac{du}{\sqrt{u}} = 1 \]  

and so a general solution \( C_0(\vartheta', A\vartheta) \) can be defined. Defining the voltammetric waveform function \( \chi(x, A\vartheta) \) as:  

\[ \chi(x, A\vartheta) = f(x + A\vartheta) C_0(x) \]  

we ensure that the unknown \( \chi(x, A\vartheta) \) tends to zero when negligible current is drawn, i.e. where \( f(x + A\vartheta) \to 0 \). Then the integral equation can be written as:  

\[ \chi(\vartheta', A\vartheta) + \frac{f(0) + A\vartheta} \int_0^{\vartheta'} \left( \frac{\vartheta' - u, A\vartheta} \sqrt{u} \right) \right] \frac{du}{\sqrt{u}} = f(0 + A\vartheta) \]  

Is \( \chi \) a strong function of \( A\vartheta \)? This can be assessed by altering the coefficient by an addition by \( \lambda \), so considering \( \chi(\vartheta', A\vartheta + \lambda) \), which from definition (Eq. (31)) satisfies:  

\[ \chi(\vartheta' + \lambda, A\vartheta + \lambda) + \frac{f(0 + \lambda) + A\vartheta + \lambda} \int_0^{\vartheta'} \chi(\vartheta' - u, A\vartheta + \lambda) \frac{du}{\sqrt{u}} \right) \right] \frac{du}{\sqrt{u}} = f(0 + A\vartheta + \lambda) \]  

Now considering the original function with an offset of \( \lambda \) in the abscissa, i.e. \( \chi(\vartheta' + \lambda, A\vartheta) \), we can see that the offset in potential affects the function \( f \) identically to altering \( A\vartheta \):  

\[ \chi(\vartheta' + \lambda, A\vartheta + \lambda) + \frac{f(0 + \lambda) + A\vartheta + \lambda} \int_0^{\vartheta'} \chi(\vartheta' - u, A\vartheta + \lambda) \frac{du}{\sqrt{u}} \right) \right] \frac{du}{\sqrt{u}} = f(0 + A\vartheta + \lambda) \]  

If the rate of reaction \( f(\vartheta' + \theta_i) \) is negligible between \( \vartheta = 0 \) and \( \vartheta = \theta_i \), then the potential \( \vartheta \) tends to zero in this domain, then equally \( \chi \) is zero in range. This can be ensured by requiring that \( \theta_i \to 0 \). Hence  

\[ \int_0^{\vartheta'} \chi(\vartheta' - u, A\vartheta) \frac{du}{\sqrt{u}} \approx 0 \]  

Therefore  

\[ \chi(\vartheta' + \lambda, A\vartheta + \lambda) \approx f(0 + A\vartheta + \lambda) \]  

from which it follows that, subject to the above conditions:  

\[ \chi(\vartheta' + \lambda, A\vartheta + \lambda) \approx f(0 + A\vartheta + \lambda) \]  

because the defining equations for these two functions, given by Eqs. (32) and (35) respectively, are identical. We conclude that \( \chi(\vartheta') \) is only affected by the exact value of \( A\vartheta \) in terms of a horizontal shift of the waveform on the potential axis, so long as the condition of initially negligible rate of reaction remains satisfied. Hence, the maximal value of \( \chi(\vartheta') \) does not depend on \( K_0, \sigma \) or \( \theta_i \), although the absolute potential where this maximum occurs does depend on these parameters.

Therefore, if the maximum current is \( J_{\text{max}} \) and its associated potential is \( \theta_{\text{max}} \), and the maximum value of the general function \( \chi \) is \( \chi_{\text{max}} \),  

\[ J_{\text{max}} = K_0 f(\theta_{\text{max}}) C(\theta_{\text{max}}) = K_0 f(\theta_{\text{max}}) \frac{\chi_{\text{max}}}{\sqrt{\pi \sigma}} \]  

thus demonstrating that peak current is proportional to \( \sqrt{\sigma} \), irrespective of the actual value of \( \sigma \).

This above analysis is entirely dependent on the condition of Eq. (28), which is satisfied for the exponential Butler–Volmer boundary condition but not for the parabolic Marcus–Hush–Chidsey integral. Therefore, we can expect the peak current to be a more complex function of \( \sigma \) (as well as the other parameters) if Marcus–Hush–Chidsey boundary conditions are applied, and the simple relation \( J_{\text{max}} \propto \sqrt{\sigma} \) does not hold.
5. Solution-phase results

Cyclic voltammetry was simulated using Marcus–Hush–Chidsey kinetics for a range of scan rates and compared with the Randles–Ševčík equation. A macrodisc radius, \( r_e \), of 1 mm was assumed and the diffusion coefficient, \( D \), was set to be \( 10^{-5} \) cm s\(^{-1}\). Voltammetry was simulated over the range 100 mV s\(^{-1}\) up to 1000 V s\(^{-1}\).

From previous work [11] Randles–Ševčík behaviour is expected over this range of scan rates.

The Randles–Ševčík equation (Eq. (1)) predicts \( \frac{I_p}{f} \propto \sqrt{v} \). Consequently plotting peak current against square root of scan rate, as in Fig. 2, ought to yield a linear trend. Voltammetry simulated using MHC kinetics, however, shows deviation from the expected linearity which is particularly marked for reorganisation energies of 1 eV and smaller and for high scan rates. The extent of this non-linearity, which was predicted by the analytical treatment above, is highlighted in Fig. 3 which shows a plot of the variation of \( \frac{dI_p}{d\sqrt{v}} \) vs \( \sqrt{v} \). Note that a very significant variation in Randles–Ševčík slope occurs in the range \( 10 < \vartheta < 200 \), where

\[
\vartheta = \frac{1}{k_0} \sqrt{\frac{vFD}{RT}} \tag{38}
\]

For this range, which corresponds to 0.25 V s\(^{-1}\) to 100 V s\(^{-1}\) in Fig. 3, the change in slope is given in Table 1 for some typical values of reorganisation energy.

This deviation from Randles–Ševčík is also evident in the transition from reversible to irreversible voltammetry with increasing scan rate, as shown in Fig. 4. The Randles–Ševčík equations (for \( \varphi = 0.5 \)) predict at most a ca. 30% difference in peak current upon the transition from reversible to irreversible (Figurerev-irrev(a)). However, as shown in Figs. 4, for MHC kinetics the normalised peak current continues to decrease with scan rate and not reaching a limiting value as with BV. This observation has implications for electroanalysis in terms of the study of the analytical benefits expected from electrocatalytic effects, for example due to modification of the electrode surface. According to these results, under MHC kinetics the increase in analytical sensitivity can be significantly greater than the 30% predicted by the BV model.

6. Surface-bound results

Eq. (2) predicts a linear relationship between peak current and scan rate for voltammetry of a surface-bound species. Cyclic voltammetry simulated for a surface-bound couple over the scan rate...
range 1 mV s\(^{-1}\) to 1 kV s\(^{-1}\) yielded significant deviations from Eq. (2) in a similar fashion to that observed for solution-phase voltammetry. The extent of deviation is much greater for surface-bound species, however, because the electrode kinetics are not masked by rate-limiting mass transport.

Fig. 5. Plots of peak current against scan rate for a surface-bound redox couple: (a) \(k_0 = 1 \times 10^{-1} \text{ s}^{-1}\), (b) \(k_0 = 10^0 \text{ s}^{-1}\), and (c) \(k_0 = 10^1 \text{ s}^{-1}\). Dotted line shows Eq. (2) for \(\lambda = 0.5\), solid lines are simulated peak currents using MHC kinetics: \(\lambda \text{ (eV)} = 0.5, 0.6, 0.8, 1.0, 2.0, 5.0\). \(A = 0.1 \text{ cm}^2\), \(\Gamma^* = 10^{-9} \text{ mol cm}^{-2}\).

7. Discussion

Marcus-Hush-Chidsey kinetics have proven somewhat successful for the analysis of surface-bound redox systems\(^{[5]}\) through the ability to reproduce the curvature evident in experimental Tafel plots, consequently a curved Tafel plot is taken to be evidence of MHC kinetics over BV kinetics. Recent work has also studied
MHC kinetics applied to solution-phase voltammetry both under diffusion-only\[12\] and diffusion-convection mass transport\[13\]. These works have compared MHC and BV kinetics by fitting of diffusion-only\[12\] and diffusion-convection mass transport \[13\].

This work suggests that, according to the Marcus–Hush–Chidsey kinetic model, a curved Randles–Ševčík plot is predicted under certain experimental conditions. This observation should be most apparent for systems with small reorganisation energies in the range $10 < \nu < 200$. Our findings also suggest that such a deviation would be particularly evident for a surface-bound redox couple.

According to Marcus theory a small reorganisation energy leads to a fast rate constant, and vice versa, making the task of observing such a curved plot more difficult as the deviation is most apparent to a fast rate constant, and vice versa, making the task of observing such a curved plot more difficult as the deviation is most apparent for small values of both $\lambda$ and $k_0$. Nevertheless through the use of high scan rates one ought to be able to study systems with relatively high $k_0$ values (and therefore low $\lambda$ values) under the appropriate conditions to observe deviations from Randles–Ševčík.

The literature, however, is replete with linear plots in accordance with Eqs. (1) and (2) and, to the authors’ knowledge, there are no reports of significant deviations from linearity such as the ones reported in this work for MHC kinetics. This, however, could potentially be a result of examining only a narrow range of scan rates, as is commonplace experimentally. In this case the trends in Figs. 2 and 5 would appear almost linear, albeit with a non-zero intercept, and can be analysed using either Eq. (1) or Eq. (2). If all other variables are known ($r_e$, $c$, $D$, etc.) then analysing the slope will yield a value for $\alpha$. In this situation it is prudent to check the consistency of this $\alpha$. This could be done via comparison with the value extracted via Tafel analysis.

An illustrative example of this comparison is shown in Fig. 7 which shows voltammetry simulated for a dissolved redox couple using MHC kinetics with $\lambda = 1$ eV at a scan rate of $1$ V s$^{-1}$. Tafel analysis ($\ln$ vs $E$) of this voltammogram yields $\alpha \approx 0.5$. Fig. 7a shows a comparison with BV kinetics for this value and the discrepancy in peak current is plainly visible. While the value of diffusion coefficient affects peak current, this may be fixed using a method such as potential step chronoamperometry which is independent of electrode kinetics. As such there are no parameters whose values may be “tweaked” to improve the quality of fit.

Fig. 7b shows a comparison with BV for a larger value of $\alpha = 0.616$, which was extracted from Randles–Ševčík analysis of the slope in Fig. 2. While Fig. 7b shows close agreement between the two forward peaks after shifting the formal potential slightly, the back peaks differ markedly in both current and potential. The fitting of both oxidative and reductive peaks serves as another helpful check on the consistency of an $\alpha$ value extracted from Randles–Ševčík analysis.

8. Conclusion

Through numerical simulation of cyclic voltammetry we have demonstrated that a system obeying Marcus–Hush–Chidsey kinetics does not obey the Randles–Ševčík equation for an irreversible system. We have shown analytically that peak current scales with the square root of scan rate only when the rate of electron transfer depends exponentially on potential, as is the case for Butler–Volmer kinetics. We have also shown a similar deviation from Butler–Volmer theory for surface-bound redox systems.

The optimal experimental conditions for the verification of these results have been discussed, suggesting $10 < \nu < 200$. Where the deviation from linearity is not marked, assessment of the consistency of the $\alpha$ value extracted from Randles–Ševčík is recommended, e.g. via Tafel analysis.

Analogous deviations from classical Butler–Volmer theory are being investigated experimentally for pulse voltammetry and hydrodynamic voltammetry.

References