Molecular insights into electron transfer processes via variable temperature cyclic voltammetry. Application of the asymmetric Marcus–Hush model

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The study of the variation of the kinetics of electrode processes with temperature is performed considering the asymmetric version of the Marcus theory for the first time. This kinetic model introduces a new symmetry parameter that takes into account possible differences between the inner-sphere force constants of the oxidized and reduced electroactive species. Variable temperature measurements in fast-scan cyclic voltammetry are employed to gain further insights into the molecular properties of the electroreduction of 1-nitropentane in acetonitrile on mercury hemispherical microelectrodes of 28.5 μm radius. Thus, the values of the reorganization energy of the electron transfer process and the symmetry parameter as well as the degree of adiabaticity of the electron transfer reaction are evaluated. The results are also analyzed in terms of the ability of the different kinetic models employed in Electrochemistry (Butler–Volmer, symmetric Marcus–Hush and asymmetric Marcus–Hush) to fit the experimental voltammograms with consistent values for the kinetic parameters in a range of temperatures and scan rates.

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1. Introduction

The application of microscopic models of electron transfer processes to electrode reactions potentially enables the use of electrochemical measurements to gain information about the molecular characteristics of the electron transfer reaction [1–5]. Through these models the electrode kinetics can be related to the molecular properties of the electroactive species in a particular medium as well as to the electronic characteristics of the electrode material. Among them, the Marcus theory is the most widely used [6,7]. In this model, the reorganization energy, λ, is related to the energy required to modify the inner (angles and bonds) and outer (solvent) configurations of the reagent species into those of the product. However, several experimental discrepancies from the symmetric version of the Marcus theory (known as the Marcus–Hush model, MH) [6–9] has been reported in the literature for both diffusional and surface-bound electrode processes [10–25].

Differences between the inner-sphere and outer-sphere “force constants” of the reduced and oxidized species can be responsible for the deviations mentioned above. Thus, the asymmetric form of the Marcus theory (referred as asymmetric Marcus–Hush model) has been applied recently to the study of electrode reactions [23–25]. This version of the MH model introduces the symmetry parameter γ which is associated with the difference between the vibrational modes of the electroactive species:

\[ \gamma = \frac{\lambda_i}{\lambda} \frac{\sum_{n=1}^{N} k_n (\Delta q_n^o)^2}{\sum_{n=1}^{N} k_n (\Delta q_n^o)^2} \]

with \( \lambda_i \) being the inner-sphere reorganization energy, \( \Delta q_n^o \) the difference of the equilibrium values for the s-th normal mode coordinate of reactants and products, and \( k_i \) and \( l_i \) symmetric and antisymmetric combinations of the force constants of the s-th mode of reactants and products, \( f_{\text{ox}}^\text{Red} \) and \( f_{\text{ox}}^\text{Red} \), respectively:

\[ k_i = \frac{2f_{\text{ox}}^\text{Red}f_{\text{ox}}^\text{Red}}{f_{\text{ox}}^\text{Red} + f_{\text{ox}}^\text{Red}} \]

\[ l_i = \frac{f_{\text{ox}}^\text{Red} - f_{\text{ox}}^\text{Red}}{f_{\text{ox}}^\text{Red} + f_{\text{ox}}^\text{Red}} \]

In this paper the asymmetric MH model is used in variable temperature kinetic studies for the first time. Electrochemical measurements at different temperatures are very valuable in order to obtain microscopic information about a given electrode reaction. Whereas the symmetry parameter can be determined with satisfactory accuracy from voltammetric measurements at constant temperature, this may not be the case of the value of the reorganization energy [24]. Voltammetric experiments at different temperatures enable more accurate determination of the \( \lambda \) value as well as the estimation of the degree of adiabaticity of the electrode
reaction [26,27]. This information is of fundamental interest in the understanding of the factors determining electron transfers which are key processes in chemistry and biology. Moreover, it offers a more thorough evaluation of the soundness of the different kinetic models employed in Electrochemistry.

The electroreduction of 1-nitropentane in acetonitrile is studied experimentally in this work by using hemispherical mercury microelectrodes and fast scan rate cyclic voltammetry. Cyclic voltammograms have been recorded at several temperatures in the range of 26–37 °C and fitted considering different kinetic approaches: Butler–Volmer (BV), symmetric MH and asymmetric MH models. The kinetic parameters and the quality of the fittings obtained from each model are quantified and compared. Finally, the value of the reorganization energy and the degree of adiabaticity are determined from the variation of the standard electrochemical rate constant with temperature.

2. Experimental

2.1. Chemical reagents

1-Nitropentane (CH$_3$(CH$_2$)$_3$CH$_2$NO$_2$, Aldrich, 97%), tetra-n-butylammonium perchlorate (TBAP, Fluka, Puriss grade), mercury(I) nitrate dihydrate (Hg$_2$(NO$_3$)$_2$·2H$_2$O, Aldrich, >97%), nitric acid (HNO$_3$, Fisher scientific, 70%), ferrocene (Fe(C$_5$H$_5$)$_2$, Aldrich, 98%), cobalt(III) sepulchrate trichloride ([CoSep]Cl$_3$, Aldrich, 95%), potassium nitrate (KNO$_3$, Aldrich, >99%), acetonitrile (MeCN, Fisher Scientific, HPLC grade), were all used as received without further purification.

2.2. Instrumentation

Cyclic voltammetry with a scan rate range between 30 mV s$^{-1}$ and 5 V s$^{-1}$ and potential step chronoamperometry were performed with a computer-controlled Autolab PGSTAT12 (Metrohm-Autolab BV, Utrecht, Netherlands). Fast-scan cyclic voltammograms encompassing scan rates between 180 and 1844 V s$^{-1}$ were recorded with a fast-scan potentiostat constructed in-house conforming to the design developed by Amatore et al. [28]. This potentiostat is capable of ohmic drop compensation by means of an internal positive feedback circuit. Microdisk working electrodes of 28.5 μm radius was fabricated in-house by sealing Pt wire (Goodfellow Cambridge Ltd., UK) into soda glass capillary according to the published method [29]. The platinum disk was polished prior to hemisphere deposition using 1.0, 0.3 and 0.05 μm alumina-water slurry on soft lapping pads (Buehler, Illinois). The disk size was calibrated by numerical fitting of the chronoamperometric response of the 1.0 mM ferrocene solution in acetonitrile supported by 0.1 M TBAP using the Shoup and Szabo expression [1,2,30]:

$$I = 4FAD_{\text{bulk}} \left( \frac{1}{\sqrt{\pi Dt}} + \frac{1}{r_0} \right)$$

(5)

where the symbols have their usual meaning.

The value of the diffusion coefficient of [CoSep]Cl$_3$ employed for the calculations was $D = 6.3 \times 10^{-10}$ m$^2$ s$^{-1}$. This was determined from chronoamperograms recorded at microdisk electrode of known dimensions from Eq. (5) and it is in close agreement with literature [33,34].

The radius obtained through the analysis of the chronoamperogram was found to be 28.5 μm. This coincides with that determined with the optical measurements outlined previously.

A platinum foil counter electrode was employed for all electrochemical measurements while a silver wire was used as the reference electrode. Stringent thermal control of the electrochemical cell was achieved through the use of an air heater-controller system fabricated in-house. With this system, temperature control was achieved within the precision of ±0.1 °C.

2.3. Characterization of the hemispherical mercury electrode

The size and shape of the mercury deposit was characterized by optical and electrochemical methods.

Visual measurement of the hemisphere was obtained through the use of a JVC digital video camera TK-C921EG. To allow the appraisal of size and shape of the hemisphere in the environment of the reagent solution, the working electrode was submerged in the solution sealed within a UV/vis cuvette, and visual image taken. It was found that the mercury droplet formed a hemisphere which adopted the radius of the microdisk. An image of the 28.5 μm hemisphere is shown in Fig. 1.

The electrochemical characterization of the mercury hemispheres was carried out through analysis of the limiting current chronoamperogram of an aqueous solution containing 2 mM [CoSep]Cl$_3$ and 0.1 M KNO$_3$, which is given by the following expression in the case of electrodes with spherical geometry [1,2]:

$$I = \frac{FAD_{\text{bulk}}}{\pi r_0} \left( 0.7854 + 0.8862 \tau^{-1/2} + 0.2146 \exp(-0.7823 \tau^{-1/2}) \right)$$

(4)

where $\tau = 4Dt/r_0^2$, $A$ is the area of the disk (cm$^2$), $D$ the diffusion coefficient of the electroactive species (cm$^2$ s$^{-1}$), $C_{\text{bulk}}$ its bulk concentration (mol cm$^{-3}$) and $r_0$ the disk radius (cm). A widely adopted literature diffusion coefficient for ferrocene of $D = 2.3 \times 10^{-7}$ m$^2$ s$^{-1}$ at 25 °C [31] was employed for the calculations.

A mercury hemisphere was then electrochemically deposited onto the microdisk from a 50 mM Hg$_2$(NO$_3$)$_2$ solution containing 0.1 M KNO$_3$ and acidified to 0.5% with HNO$_3$ following the method laid out by Bard et al. [32]. For deposition, the potential was stepped to −0.25 V vs. Ag wire. The size of the hemispherical drop was controlled by the amount of charge passed.

Fig. 1. Image of the 28.5 μm radius electrodeposited hemisphere immersed in acetonitrile.
2.4. Cyclic voltammetry and potential step chronoamperometry measurements

Cyclic voltammograms at typical scan rates (within the range of 30 mV s\(^{-1}\) to 5 V s\(^{-1}\)) were recorded between –1.00 and –1.90 V (vs. Ag wire) on 28.5 μm radius mercury hemispherical electrode in 1.5, 0.5 and 0.073 mM 1-nitropentane solution containing 0.1 M TBAP supporting electrolyte in MeCN solvent.

Fast-scan cyclic voltammograms encompassing the scan rates of 180–1844 V s\(^{-1}\) were recorded between –1.00 and –2.10 V (vs. Ag wire) on 28.5 μm radius mercury hemispherical electrode. Ohmic drop compensation was set by the on-screen adjustment relative to the onset of observed oscillations as described in [35]. Care was taken to ensure that the circuit was not over-compensated to avoid large amplitude oscillations which often have deleterious effects on the electrode surface.

Six sets of voltammograms, each recorded at a different temperature, were obtained with fast-scan cyclic voltammetry: (1) \(T = 26 \degree C\), scan rates: 187–1844 V s\(^{-1}\); (2) \(T = 27.5 \degree C\), scan rates: 142–1300 V s\(^{-1}\); (3) \(T = 30 \degree C\), scan rates: 180–1495 V s\(^{-1}\); (4) \(T = 32 \degree C\), scan rates: 180–1494 V s\(^{-1}\); (5) \(T = 35 \degree C\), scan rates: 145–1337 V s\(^{-1}\); and (6) \(T = 37 \degree C\), scan rates: 182–1491 V s\(^{-1}\). All the solutions contained 0.1 M TBAP background electrolyte in MeCN solvent.

Potential step chronoamperometry was recorded for each experimental set conducted in the current study. The potential was stepped from –1.30 V where there is no faradaic current to –1.80 V (vs. Ag wire) where the reduction current is fully controlled by diffusion and was held for 0.5 s. The resulting chronoamperometric response was simultaneously fitted for both the diffusion coefficient and concentration of the electroactive species using the previously reported method [36–38].

2.5. Fitting methodology

Simulation programs written in-house were used to simulate cyclic voltammograms on a hemispherical electrode based on the BV, symmetric MH and asymmetric MH formalisms. These were used, in conjunction with the value of diffusion coefficients determined through numerical fitting of chronoamperometric responses, to model cyclic voltammograms over the full range of experimental conditions. Fitting of the electrochemical reduction processes was carried out by matching the peak potentials, thereby fixing the formal potential (\(E^0\), which over the course of our experiment is found to shift within ±30 mV range due to the use of Ag wire pseudo reference electrode), the standard electrochemical rate constants of thermally activated electron transfers can be expressed as [27,39,40]:

\[
\kappa_{\text{red}} = v_n\kappa_{\text{el}}\kappa_n
\]

where \(v_n\) is the nuclear vibration frequency factor, \(\kappa_{\text{el}}\) is the electronic transmission coefficient and \(\kappa_n\) is the nuclear reorganization factor. The \(\kappa_n\) value is related to the electronic coupling between the electroactive species and the energy levels of the electrode, thus defining the adiabaticity character of the electron transfer process. Thus, \(\kappa_n = 1\) for adiabatic processes and \(\kappa_n < 1\) in the non-adiabatic limit.

The nuclear reorganization factor, \(\kappa_n\), considering the continuum of electronic levels of the metallic electrode is given by:

\[
\kappa_n = \int_{-\infty}^{\infty} \frac{\exp(-\Delta G_{\text{red}}(\alpha, x))}{1 + \exp([\gamma]x)} \, dx
\]

with \(x = \frac{F(e - E)}{RT}\) being an integral variable. Where two signs appear, the upper sign refers to the reductive process; the lower one to the oxidative reaction. The nuclear factor introduces the dependence of the rate constants with the applied potential, \(E\), such that the standard rate constant, \(k^0\), corresponds to the value of the reduction and oxidation rate constants at the formal potential:

\[
\kappa_{\text{el}}(E = E^0) = \kappa_{\text{ox}}(E = E^0) = k^0.
\]

To evaluate the activation energy of the electroreduction and electrooxidation processes we will make use of the asymmetric Marcus–Hush model [7,23,24]. Accordingly, \(\Delta G_{\text{red}}(\alpha, x)\) is given by:

\[
\Delta G_{\text{red}}(\alpha, x) = \frac{\lambda^2}{4} \left(1 \pm \frac{\eta + x}{\lambda} \right)^2 + \frac{\gamma(\eta + x)}{4} \left(1 - \left(\frac{\eta + x}{\lambda} \right)^2 \right) + \frac{\gamma^2 \lambda}{16}
\]

where \(\lambda = F\bar{z}/RT\) is the dimensionless reorganization energy, \(\eta = (E - E^0)/RT\) the dimensionless overpotential and \(\gamma\) the symmetry parameter (see Eq. (1)). The latter accounts for the differences between the inner-shell force constants of oxidized and reduced species such that the \(\gamma\) absolute value increases with the disparity between the force constants. Note that when \(\gamma = 0\) the above equation reproduces the activation energy predicted by the symmetric version of Marcus theory, the most widely used so far.

Assuming that only the value of the nuclear factor \(\kappa_n\) varies significantly with temperature under the experimental conditions, one can infer that the natural logarithm of the standard rate constant \(\ln(k^0)\) has a linear dependence with the inverse of temperature \((1/T)\). The slope of which is mainly defined by the reorganization energy, whereas the intercept relates to the degree of adiabaticity of the process (see Section 4). On the other hand, the numerical evaluation of the temperature behaviour of \(k^0\) shows that the symmetry parameter does not have a significant effect
on the values of the slope and intercept for not very extreme $\gamma$ values ($|\gamma| \leq 1/3$).

4. Results and discussion

First, cyclic voltammetry was carried out at typical scan rates (0.03, 0.1, 0.3 and 5 V s$^{-1}$) with a mercury hemispherical electrode as working electrode immersed in a solution containing 1.5 mM 1-nitropentane and 0.1 M TBAP in MeCN from -1.0 to -1.9 V (vs. Ag wire reference electrode) at 26°C. Voltammograms obtained are displayed in Fig. 2.

The voltammograms obtained reveal a single reduction wave with the reversibility of the process in the reverse scan being dependent on the value of the scan rate applied. In particular, the reverse scan does not show any oxidative peak at 0.1 V s$^{-1}$, it displays a modest peak at 0.3 V s$^{-1}$, and finally the oxidation counterpart is clearly observed at 5 V s$^{-1}$. This indicates the presence of a follow-up chemistry of the radical anion whose contribution becomes negligible when a scan rate beyond 5 V s$^{-1}$ is applied.

The fitting of chronoamperometric response of the system simultaneously for the number of electrons transferred, $n$, and the diffusion coefficient of 1-nitropentane, $D_{\text{nitropentane}}$, yields the values: $n = 1.00 \pm 0.06$ and $D_{\text{nitropentane}} = (2.5 \pm 0.1) \times 10^{-3}$. In order to eliminate the contribution of the follow-up chemistry of the radical anion, fast-scan cyclic voltammetry was used to collect 6 sets of voltammograms, each taken at a different temperature. The specific experimental conditions are described in Section 2. All the voltammograms are recorded on a 28.5 $\mu$m radius Hg hemispherical electrode from -1.00 to -2.10 V (vs. Ag wire) (representative fast-scan voltammograms are shown in Fig. 3). All solutions contain 0.1 M TBAP background electrolyte in MeCN solvent.

4.1. Determination of the concentration and diffusion coefficient

Under the experimental conditions of each of the 6 fast-scan experiments described in the previous section, potential step chronoamperometry was employed to determine both the concentration and diffusion coefficient of 1-nitropentane simultaneously using a previously reported method [36–38]. This is necessary as heating of the original solution prepared at room temperature up to the desired experimental temperature results in the decrease of concentration due to solvent expansion, and the increase of diffusion rates. The results from the fitting of chronoamperometric responses are presented in Table 1.

From the values of the diffusion coefficient obtained at different temperatures diffusional activation energy, $E_{\text{a,d}}$, can be calculated according to the following Arrhenius-like equation:

$$D = D_{\infty} \exp \left(\frac{-E_{\text{a,d}}}{RT}\right)$$

where $D_{\infty}$ is the hypothetical diffusion coefficient at infinite temperature. Note that the obtaining of the $E_{\text{a,d}}$ value is very helpful since it enables the determination of the diffusion coefficient of a species for a given temperature. Fig. 4 shows that the experimental points are consistent with Eq. (11) such that the $D$ value decreases linearly with temperature in the range under study. From the best-fit linear regression a value for $E_{\text{a,d}}$ of 14 ± 1 kJ mol$^{-1}$ was obtained.

Fig. 2. Experimental cyclic voltammograms for the reduction of 1.5 mM 1-nitropentane in acetonitrile at mercury hemisphere electrode. The solution is thermostated at 26 °C and supported by 0.1 M TBAP. Scan rate (V s$^{-1}$): (A) 0.03, (B) 0.1, (C) 0.3, and (D) 5.
4.2. Determination of kinetic parameters

The study of the kinetics of the electroreduction of 1-nitropentane in acetonitrile on a mercury microelectrode was first carried out employing the asymmetric MH model. The determination of the kinetic parameters \( E_0, k^0, \lambda, \gamma \) was performed following an iterative procedure. Thus, given that the voltammograms were remarkably insensitive to changes in \( \lambda \) above 1 eV, a hypothetical value of \( \lambda = 1 \) eV was initially assumed and the results from fast-scan experiments 1–6 were fitted by minimization of the MSAD value (see Eq. (6)) with \( \gamma \) and \( k^0 \) as fitting parameters. The symmetry of the oxidative and reductive peak is mainly dependent on the \( \gamma \) value whereas the peak-to-peak separation of the voltammograms is established almost exclusively by the rate constant. Once the \( k^0 \) value for each temperature was known, a value of the reorganization energy of \( 1.7 \pm 0.1 \) eV was extracted from the slope of the best-fit linear regression of \( \ln(k^0) \) vs. \( 1/T \) (see Fig. 5). Accordingly, the fitting procedure was repeated with \( \lambda = 1.7 \) eV confirming that it is consistent with the experimental results and can be accepted as

Table 1

Diffusion coefficients of 1-nitropentane at different temperatures.

<table>
<thead>
<tr>
<th>Temperature (°C)</th>
<th>Concentration (mM)</th>
<th>( D_{\text{nitropentane}} ) (m²/s)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Fast-scan experiment 1</td>
<td>26.0</td>
<td>3.13</td>
</tr>
<tr>
<td>Fast-scan experiment 2</td>
<td>27.5</td>
<td>1.89</td>
</tr>
<tr>
<td>Fast-scan experiment 3</td>
<td>30.0</td>
<td>3.25</td>
</tr>
<tr>
<td>Fast-scan experiment 4</td>
<td>32.0</td>
<td>2.97</td>
</tr>
<tr>
<td>Fast-scan experiment 5</td>
<td>35.0</td>
<td>1.89</td>
</tr>
<tr>
<td>Fast-scan experiment 6</td>
<td>37.0</td>
<td>3.00</td>
</tr>
</tbody>
</table>

Fig. 3. Experimental fast-scan cyclic voltammograms for the electroreduction of 2.97 mM 1-nitropentane in acetonitrile at 28.5 μm radius mercury hemisphere electrode. The solution is thermostated at 32 °C and is supported by 0.1 M TBAP. Scan rate (V s⁻¹): (A) 180, (B) 380 (C) 762, and (D) 1494.

Fig. 4. Arrhenius plots of ln \( D \) vs. \( 1000 \times T^{-1} \) for 1-nitropentane in acetonitrile containing 0.1 M TBAP.
the “true” value of the reorganization energy. The “best-fit” kinetic parameters are shown in Table 2 and some of the fittings are displayed in Fig. 6. As can be observed in Fig. 6 the values of the kinetic parameters obtained give rise to a very satisfactory agreement of the theoretical and experimental results (MSAD < 5%) in a wide range of scan rates (between 180 and 1844 V s\(^{-1}\)) and at the different temperatures considered. Whereas the value of the standard rate constant increases with temperature, the temperature-independent values for the reorganization energy (1.7 eV) and the symmetry parameter (–0.14) are physically consistent.

According to the physical meaning of the parameter \(\gamma\), the negative value –0.14 obtained indicates that the force constants of the reduced species are (in average) greater than those of the oxidized species. We have also reported this behaviour for the electoreductions of 2-methyl-2-nitropropane and cyclooctatetraene\(^{[24]}\) where neutral species are reduced into radical anions. The likely stronger interactions of the anion with the solvent as compared with the neutral parent molecule can justify the negative \(\gamma\) values obtained for all these redox systems.

4.3. Degree of adiabaticity

Variable temperature experiments also enable us to estimate the degree of adiabaticity of the electron transfer process. This is of fundamental interest since it informs about the magnitude of the electronic interaction between the reactant species and the electrode, which is a major question for the understanding of electrode reactions\(^{[41–44]}\).

As can be deduced from Eq. (8), the degree of adiabaticity of the process is accessible from the value of the pre-exponential constant that increases with the electronic coupling between the electroactive species and the electrode. In order to gain information about the magnitude of this coupling we will make use of the approximate expression for the electronic transmission coefficient reported by Feldberg and Sutin for heterogeneous electron transfers\(^{[39]}\):

\[
\kappa_{el} = \frac{1}{\beta} \ln \left(1 + \frac{4\pi^2 \rho_M H_{0,AB}^2}{\gamma_e h^2/4\pi^2}\right)
\]

where \(\beta\) is the tunnelling factor, \(\rho_M\) the density of electronic levels in the electrode, \(H_{0,AB}\) electronic coupling element at the plane of closest approach and \(h\) the Planck’s constant. From Eqs. (9) and (10) we obtain that for our system (\(\lambda\) and \(\gamma\) values given in Table 2) the nuclear reorganization factor at the formal potential can be approximated as:

\[
\kappa_{el}(E = E^\circ) \approx 2.9 \times \exp\left(-\frac{1}{4RT}\left(1 + \frac{\gamma^2}{4}\right)^{13}\right)
\]

Note that the lowering of the energy barrier as a consequence of the electronic coupling is not considered in the present study.

Considering reasonable values for the tunnelling factor \(\beta = 10^8\) cm\(^{-1}\)\(^{[39]}\), the density of states of s-band metals \(\rho_M\) \(\approx 0.3\) eV\(^{-1}\)\(^{[45]}\) and the nuclear vibration frequency factor of the system \(\nu_n = 10^{13}\) s\(^{-1}\)\(^{[46,47]}\), we have calculated the variation of the intercept (\(Z\)) of the plot \(\ln(k^0)\) vs. \(1/T\) with the coupling constant \((H_{0,AB})\) from Eqs. (8), (12), and (13) (see Fig. 7). The linear domain at small \(H_{0,AB}\) values corresponds to a non-adiabatic behaviour (weak electronic coupling) whereas the adiabatic region (strong electronic coupling) corresponds to the plateau observed at large \(H_{0,AB}\) values.

From the best-fit linear regression shown in Fig. 5, a value for the intercept of \(\ln[Z(\text{cm s}^{-1})] = 13\pm1\) is obtained. As can be seen in Fig. 7, this value lies in the transition region between the non-adiabatic and the adiabatic domains. This suggests a moderate adiabatic character for the electron transfer process considered in this work and it can ask for the use of quantum–mechanical models\(^{[48–50]}\) that take into account the effect of the resonance energy on the activation energy.

4.4. Comparison between BV, symmetric MH and asymmetric MH models

In previous papers\(^{[16–25]}\), the weaknesses of the symmetric MH model in the description of several electrode processes have been pointed out via cyclic and square wave voltammetry at constant temperature. Here, the consistency of the different kinetic models will be further examined from the experimental results obtained in fast-scan cyclic voltammetry at different temperatures.

The BV, symmetric MH and asymmetric MH kinetic approaches were used to systematically simulate cyclic voltammograms of the experimental set obtained through fast-scan experiments 1–6. The “true” value of \(\lambda\) determined in the previous section was used in conjunction with the symmetric and asymmetric MH models. A common set of parameters that provided the “best fit” between the simulated and experimental voltammograms is then determined for each model. These “best fit” parameters are presented in Tables 2–4. A comparison between the BV and symmetric MH

*Fig. 5. Arrhenius plots of \(\ln(k^0)\) vs. 1000 \(\times\) \(T\)\(^{-1}\) for 1-nitropentane in acetonitrile containing 0.1 M TBAP.*

### Table 2

<table>
<thead>
<tr>
<th>Kinetic parameters obtained with the asymmetric Marcus–Hush model.</th>
<th>Fast-scan experiment 1 (26°C)</th>
<th>Fast-scan experiment 2 (27.5°C)</th>
<th>Fast-scan experiment 3 (30°C)</th>
<th>Fast-scan experiment 4 (32°C)</th>
<th>Fast-scan experiment 5 (35°C)</th>
<th>Fast-scan experiment 6 (37°C)</th>
</tr>
</thead>
<tbody>
<tr>
<td>(k^0) (cm s(^{-1}))</td>
<td>0.013</td>
<td>0.0115</td>
<td>0.017</td>
<td>0.019</td>
<td>0.021</td>
<td>0.025</td>
</tr>
<tr>
<td>(\lambda) (eV)</td>
<td>1.7</td>
<td>1.7</td>
<td>1.7</td>
<td>1.7</td>
<td>1.7</td>
<td>1.7</td>
</tr>
<tr>
<td>(\gamma)</td>
<td>–0.14</td>
<td>–0.14</td>
<td>–0.14</td>
<td>–0.14</td>
<td>–0.14</td>
<td>–0.14</td>
</tr>
<tr>
<td>(E^0) (V)</td>
<td>–1.61 ± 0.03</td>
<td>–1.41 ± 0.02</td>
<td>–1.57 ± 0.01</td>
<td>–1.380 ± 0.002</td>
<td>–1.475 ± 0.007</td>
<td>–1.58 ± 0.01</td>
</tr>
<tr>
<td>MSAD (%)</td>
<td>5 ± 1</td>
<td>4 ± 1</td>
<td>4 ± 1</td>
<td>2.9 ± 0.8</td>
<td>5 ± 1</td>
<td>3 ± 1</td>
</tr>
</tbody>
</table>
The optimized simulated voltammograms obtained with the BV model give excellent quality of fit across all experimental sets. At 26°C, the value of $k_0 = 0.011 \text{ cm s}^{-1}$ is extracted for the current compound. In comparison with an electrochemical system whose heterogeneous reaction is predominantly limited by the change in geometry required in the formation of the product species (e.g. $k_0 = 0.014 \text{ cm s}^{-1}$ for cyclooctatetraene in DMSO at 25°C [19]), the value of $k_0$ extracted for the current compound is within a similar order. This relatively slow standard heterogeneous reaction rate is consistent with the findings of Peover and Powell [51] which states that the concentration of negative charge on the nitro group of aliphatic nitro compounds is responsible for a high value of outer-sphere reorganization energy.

With the value of $\dot{i}$ obtained in the previous section ($\dot{i} = 1.7$ eV), the optimum $k_0$ extracted from the fitting with the symmetric MH model (see Table 4) gives rise to an average MSAD value of 6% which is poorer than with the BV model. The asymmetric MH simulations were carried out with fixed values of $\dot{i} = 1.7$ eV and $\gamma = -0.14$ with excellent quality of fit (average MSAD = 4%) comparable to that obtained with the BV formalism. The optimum $k_0$ value is identical to that of the symmetric MH fitting as the peak-to-peak separation between the forward and reverse scan is almost exclusively fixed by $k_0$ whereas the effect exerted by the parameter $\gamma$ is negligible under these conditions.

According to the above results, the quality of the fittings with the BV and asymmetric MH models are comparable but superior to that obtained with the symmetric version of the MH model. This agrees with previous results [24] where we showed the inability of the symmetric MH approach to describe properly the voltammetry of different solution-phase redox couples, including the electroreduction of 2-methyl-2-nitropropane in acetonitrile, cyclooctatetraene in dimethylsulfoxide and europium (III) in water solution on mercury hemispherical microelectrodes, and the electrooxidation fits is given in Fig. 8, and between that of the symmetric and asymmetric MH in Fig. 9.
of tetraphenylethylene in dichloromethane on platinum microdisk electrodes.

As a result of these works the relationship between the BV transfer coefficient ($\alpha$) and the symmetry parameter ($\gamma$) was revealed. Thus, $\alpha$ values smaller than 0.5 are related to force constants of the reduced species greater than those of the oxidized one whereas the opposite situation applies for $\alpha > 0.5$. This enables the use of the simpler BV approach for the parameterization of the electrochemical response of solution-phase systems in terms of $\{E_0^f, k_0, \alpha\}$ complemented by the physical interpretation of these kinetic parameters given by the asymmetric MH model.

### Table 3

<table>
<thead>
<tr>
<th>Kinetic parameters obtained with the Butler–Volmer model.</th>
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<tr>
<td>1 (26 °C)</td>
</tr>
<tr>
<td>$k_0$ (cm s$^{-1}$)</td>
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<tr>
<td>$\gamma$</td>
</tr>
<tr>
<td>$E_0^f$ (V)</td>
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<tr>
<td>MSAD (%)</td>
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### Table 4

<table>
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<th>Kinetic parameters obtained with the symmetric Marcus–Hush model.</th>
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<tr>
<td>1 (26 °C)</td>
</tr>
<tr>
<td>$k_0$ (cm s$^{-1}$)</td>
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<tr>
<td>$\gamma$ (eV)</td>
</tr>
<tr>
<td>$E_0^f$ (V)</td>
</tr>
<tr>
<td>MSAD (%)</td>
</tr>
</tbody>
</table>

**Fig. 8.** Experimental (solid line) and simulated cyclic voltammograms with Butler–Volmer (open circles) and symmetric Marcus–Hush (dashed line) models for the reduction of 1-nitropentane in acetonitrile at 28.5 µm radius mercury hemisphere electrode: (A) 3.13 mM 1-nitropentane at 26 °C (scan rate = 187 V s$^{-1}$); (B) 3.25 mM 1-nitropentane at 30 °C (scan rate = 377 V s$^{-1}$); (C) 2.97 mM 1-nitropentane at 32 °C (scan rate = 762 V s$^{-1}$); and (D) 3.00 mM 1-nitropentane at 37 °C (scan rate = 1491 V s$^{-1}$). All solutions are supported with 0.1 M TBAP.
5. Conclusions

The asymmetric Marcus–Hush (MH) model has been employed in variable temperature voltammetry in order to extend the physical insights into electron transfer processes available via electrochemical measurements. With this aim, the electroreduction of 1-nitropentane in acetonitrile has been investigated through fast-scan cyclic voltammetry and using mercury microhemispheres as working electrodes.

From the fitting of the voltammograms at different temperatures with the asymmetric MH model, the values of the reorganization energy ($\lambda = 1.7$ eV) and the symmetry parameter ($\gamma = 0.14$) have been extracted. The negative $\gamma$ value indicates greater force constants for the radical anion electrogenerated than for the initial neutral species. The above $\lambda$ and $\gamma$ values lead to very satisfactory agreement of simulated and experimental results in all the range of temperatures and scan rates considered. The variation of the standard rate constant with the temperature also informs that the system has an intermediate behaviour between the adiabatic and non-adiabatic limits.

The comparison of the different kinetic models has been carried out obtaining comparable fit qualities for the Butler–Volmer (with $\alpha = 0.42$) and asymmetric MH models, whereas the symmetric MH approach gives rise to worse description of the voltammograms.

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Fig. 9. Experimental (solid line) and simulated cyclic voltammograms with asymmetric Marcus–Hush (open squares) and symmetric Marcus–Hush (dashed line) models for the reduction of 1-nitropentane in acetonitrile at 28.5 µm radius mercury hemisphere electrode: (A) 3.13 mM 1-nitropentane at 26 °C (scan rate = 187 V s$^{-1}$); (B) 3.25 mM 1-nitropentane at 30 °C (scan rate = 377 V s$^{-1}$); (C) 2.97 mM 1-nitropentane at 32 °C (scan rate = 762 V s$^{-1}$); and (D) 3.00 mM 1-nitropentane at 37 °C (scan rate = 1491 V s$^{-1}$). All solutions are supported with 0.1 M TBAP.

References
