Giving physical insight into the Butler–Volmer model of electrode kinetics: Part 2 – Nonlinear solvation effects on the voltammetry of heterogeneous electron transfer processes

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1. Introduction

Electron transfer (ET) reactions are key processes in chemistry and biology and a great effort has been made to understand the fundamental factors defining their characteristics. The interest and difficulty of this aim are evident given to the number of theoretical and experimental works devoted to it [1–3]. Among them, the model introduced by Marcus in the mid-1950s [4,5] is a landmark in the study of ET kinetics. Its application to electrode processes is known as the Marcus–Hush (or Marcus–Hush–Chidsey) model (MH) [6,7].

In the last few years the validity of the MH model has been questioned on the basis of experimental deviations documented for solution-phase and surface-bound electrode processes [8–23]. Spectroscopic measurements have also shown discrepancies with respect to the Marcus picture of electron transfer [24,25]. These indicate that the symmetric MH model does not reflect all the complexity of ET reactions and so there is a need to identify and consider the factors causing the experimental deviations.

As suggested by several authors [8,21,22,26–29], a reasonable explanation is related to asymmetric Gibbs energy curves for the initial and final species (oxidized and reduced forms) as a result of the change of charge in the ET process. Consequently, the vibrational modes and the interactions with the surroundings may differ significantly between the oxidized and reduced species. This affects the activation barrier and so the oxidation and reduction rate constants ($k_{\text{cat}}$ and $k_{\text{an}}$, respectively). Electrode processes are well placed to assess the incidence of these factors since compensating effects that can take place in homogeneous ET processes with several participating species are avoided.

Regarding the vibrational component of the reorganization energy (so-called inner-sphere reorganization energy), in recent papers we have made use of the asymmetric form of Marcus theory to derive relationships for the heterogeneous rate constants when the vibrational force constants of the electroactive species differ [21–23]. The resulting formalism for electrode reactions enabled a successful description of the deviations from the symmetric MH approach (including asymmetric Tafel plots) as well as very satisfactory fitting of the experimental voltammograms corresponding to the electroreduction of 2-methyl-2-nitropropane in acetonitrile [4,5], cyclooctatetraene in dimethylsulfoxide [3] and europium (III) in water solution [4,7] on mercury hemispherical microelectrodes, and the electrooxidation of tetraphenylethylene in dichloromethane on platinum microdisk electrodes [23]. In all the above cases the fitting obtained with the symmetric MH model was not acceptable.

Nevertheless, the asymmetric MH model does not cover the possible asymmetric effects arising from the charge/solvent fluctuations accompanying the electron transfer reaction (so-called outer-sphere reorganization energy) [2]. In the original Marcus theory [4,5], the linear response approximation is assumed with equal
force constants of the oxidized and reduced forms for the solute–solvent interactions. Accordingly, the solvent reorganization energies of the oxidation and reduction reactions are the same. Later works [24,25,29–38] have considered a nonlinear solvent response in order to give a better understanding of the effect of the nature of the solvent on the electron transfer. Unfortunately, most of them require complex numerical simulation which has limited their application. Matyushov contributed by filling this gap and deriving closed-form, analytical equations for the bilinear solute–solvent coupling that enables the simulation of the ET free energy surface and easy calculation of the activation barrier [38].

In the present paper, Matyushov’s results are applied to evaluating the effects of nonlinear solvation in the voltammetry of heterogeneous electron transfer reactions. The influence of solvent nonlinear response (solvation saturation) on the oxidation and heterogeneous electron transfer reactions. The theoretical results are compared with those predicted by the two main kinetic models employed currently: Butler–Volmer (BV) and MH models [39,40]. Despite the fact that microscopic models like MH provide more physical insight about the physical and chemical nature of the system, the empirical BV approach is still the most widely used in Electrochemistry given its simplicity and ability to parameterize many experimental systems over decades.

The connection between the transfer coefficient, $x$, and nonlinear effects is also studied. This enables the investigation of the incidence of nonlinear solvation on electron transfer processes by electrochemical experiments, as well as giving new possible physical interpretation to a large number of kinetic data available.

2. Theory

The theory developed by Matyushov [37,38] assumes bilinear solute–solvent coupling and so it accounts for the effects of nonlinear solvation on electrode reactions. Although the original model also considers the solution-electrode electronic coupling, for the sake of simplicity we will assume in this work that the electronic coupling is very weak (i.e., nonadiabatic processes).

According to Matyushov nonlinear model, for the general case of a one-electron transfer process (Eq. (1)) without formation or breaking of bonds, the Gibbs energy surface of the electron transfer ($G(X)$) for nonadiabatic processes can be calculated from Eq. (2) [24,38,41]:

$$ \text{Ox}^{2+} + e^- \rightarrow \text{Red}^{2+} \quad (1) $$

$$ \frac{\mu_{\text{cat}}}{k_B T} = \frac{\mu_{\text{act}}}{k_B T} + \left( \sqrt{\gamma \left| X + \gamma z_{\text{Ox}} \right| - \left| \gamma \right| \sqrt{\lambda^2(\gamma)} - \ln[1 + \exp(-\nu(X))] \right) \quad (2) $$

where $\mu_{\text{cat}}$ is the thermodynamic chemical potential of the oxidized species, $X$ is the reaction coordinate, and:

$$ \nu(X) = X_0 - X + \eta \quad (3) $$

with

$$ X_0 = -\gamma \left[ \frac{z_{\text{Ox}}}{\gamma - 1} \sqrt{\lambda^2(\gamma)} \right] \quad (4) $$

and $\lambda^2(\gamma)$ is the nonlinear solvent reorganization energy:

$$ \lambda^2(\gamma) = \frac{z_{\text{Ox}}^2}{\gamma} \quad (5) $$

with $z_{\text{Ox}} = \lambda/v_{\text{Ox}}/k_B T$ being the dimensionless solvent reorganization energy. $\eta = (E - E^0)F/RT$ the dimensionless applied potential, $E^0_i(V)$ the formal potential of the redox couple $\text{Ox}^{2+}/\text{Red}^{2+}$ and $z_{\text{Ox}}$ the charge of the oxidized species. The dimensionless parameter $\gamma = k_{\text{cat}} / (k_{\text{cat}} - k_{\text{act}})$ quantifies the difference between the solvent force constants ($k$) in the oxidized and reduced forms and so the deviation from the linear response regime (see Section 3). Note that $\gamma$-value is restricted to $\gamma > 1$ or $\gamma < 0$ [37,38].

As shown in Fig. 1, the ET free energy curves have two minima corresponding to the oxidized ($X_{\text{Ox}}$) and reduced ($X_{\text{Red}}$) species, and one maximum at the transition state ($X$). The activation barriers for the cathodic and anodic reactions can be easily calculated from Eq. (2):

$$ G_{\text{cat}}(\eta) = G(X') - G(X_{\text{Ox}}) $$

$$ G_{\text{an}}(\eta) = G(X') - G(X_{\text{Red}}) $$

(6)

For the case of electrode reactions, after considering the continuum of electronic levels at the electrode [6] the following general relationships are obtained for the heterogeneous rate constants of the cathodic (reduction) and anodic (oxidation) processes:

$$ k_{\text{cat}} = k^0 \frac{k_{\text{act}}(\eta, \gamma)}{k_{\text{act}}(0, \gamma)} $$

$$ k_{\text{an}} = k^0 \frac{k_{\text{act}}(\eta, \gamma)}{k_{\text{act}}(0, \gamma)} $$

(7)

where $k^0$ is the standard electrochemical rate constant and $l(\eta, \lambda, \gamma)$ is an integral of the form:

**Fig. 1.** Effect of the $\gamma$ value (indicated on the graphs) on the free energy surfaces (Eq. (2)) of the one-electron reduction of (A) a monopositive species: $\text{Ox}^+ + e^- \rightarrow \text{Red}^0$, and (B) a neutral species: $\text{Ox}^0 + e^- \rightarrow \text{Red}^-$. $\lambda = 1$ eV, $\eta = 0$. 
$$I_{cat/an}(\eta, \gamma) = \int_{-\infty}^{\infty} \frac{\exp[-C_{cat/an}^\alpha(\eta + x)/K_B]}{1 + \exp(\gamma x)} \, dx$$

with $x$ being an integration variable. Where two signs appear, the upper sign refers to the reductive process; the lower one to the oxidative reaction.

Cyclic voltammetry experiments were simulated with programs made in-house by finite difference numerical methods as described in previous publications [42,43]. Crank–Nicholson algorithm with four preceding extrapolation steps was employed for time integration and an exponentially expanding grid with high expansion factors and four-point formulae for the spatial discretization in the case of semi-infinite diffusion.

3. Discussion

For a given electrode process Ox$^{\infty}$/Red$^{\infty}$, the parameter $\gamma$ quantifies the extent of nonlinear solvation. Thus, the $\gamma$ value is inversely proportional to the difference between the solvent force constants in the oxidized and reduced species such that small absolute values of $\gamma$ correspond to more significant asymmetric effects. On the other extreme, the model reproduces the results corresponding to the linear solvation regime (Marcus model) for $\gamma \rightarrow \infty$ (i.e., equal force constants in Ox and Red).

The above behavior can be observed in Fig. 1, where the ET Gibbs energy surface is plotted for different $\gamma$ values. The Gibbs energy surface deviates from the symmetric and parabolic shape corresponding to the linear response (dotted line) as the absolute value of $\gamma$ diminishes. The sign of $\gamma$ indicates the relative magnitude of the solvent force constants in the oxidized and reduced species. Positive $\gamma$ values (Fig. 1A) correspond to a tighter free energy curve for the oxidized species, that is, greater force constant in the oxidized form. On the other hand, negative $\gamma$ values (Fig. 1B) relates to a greater force constant for the reduced species.

Obviously, the “asymmetries” of the Gibbs energy surface affects the values of the oxidation and reduction rate constants and, ultimately, the voltammetric response. The variation of the rate constants with the applied potential (Tafel plot) is studied in Fig. 2. For positive $\gamma$ values ($K_{Ox} > K_{Red}$) the reduction rate constant at a given applied potential is greater than that predicted by the linear model (Marcus model, grey line) whereas the oxidation rate constant is smaller. The opposite effect is seen for negative $\gamma$ values ($K_{Red} > K_{Ox}$). The divergences with respect to the linear model are more apparent as the applied potential increases and, logically, as the absolute value of the parameter $\gamma$ diminishes.

The symmetry of the slopes of the cathodic and anodic branches of Tafel plots is another important aspect. According to the symmetric MH model (Fig. 2, grey line), these branches are symmetrical with respect to the axis $\eta = 0$ such that:

Fig. 2. Variation of the heterogeneous rate constants (Eq. (7)) with the applied potential according to Matyushov nonlinear model (black lines) and the symmetric Marcus–Hush model (grey solid line) [21]. Different $\gamma$ values are considered (indicated on the graphs) for the one-electron reduction of (A) a monopositive species: Ox$^+$ + e$^- \rightleftharpoons$ Red$^0$, and (B) a neutral species: Ox$^0$ + e$^- \rightleftharpoons$ Red$^-$. $\Delta_0 = 2$ eV.

Fig. 3. Variation of the transfer coefficient at the formal potential, $\alpha(0) = -(\omega_0/2) \ln(\eta_{0/0})$ with the parameter $\gamma$ for the one-electron reduction of (A) a monopositive species: Ox$^+$ + e$^- \rightleftharpoons$ Red$^0$, and (B) a neutral species: Ox$^0$ + e$^- \rightleftharpoons$ Red$^-$. $\Delta_0 = 2$ eV.
This equality is also predicted by the Butler–Volmer model for \( \alpha = 0.5 \) [21].

Nevertheless, experimental deviations from Eq. (9) are well documented in the literature. Thus, asymmetric Tafel plots have been found experimentally for metal aquo complexes in solution [8] as well as for osmium [9,10] and ferrocene [11–13] complexes attached to the electrode surface. According to Fig. 2, nonlinear effects can account for these behaviors both when the slope of the cathodic branch is greater than the anodic one (\( c > 1 \), Fig. 2A) and when the slope of the anodic branch is greater (\( c < 0 \), Fig. 2B). Both situations have been observed experimentally in the electrochemical response of electroactive monolayers [44].

In Electrochemistry, the above effects are usually analyzed in terms of the value of the transfer coefficient: \( \alpha = -\frac{\partial \ln k_{\text{cat}}}{\partial \eta} \). From Fig. 2 it can be concluded that the nonlinear solvation model predicts a potential-dependent transfer coefficient giving rise to curved Tafel plots. Experimental confirmation of this behavior was first documented by Savéant et al. for the electroreduction of nitrocompounds [45], and later by Fletcher et al. for the electroreduction of hexamminecobalt(III) at carbon microdisc electrodes [46] and by several authors for different electroactive self-assembled monolayers [6,47–49].

In summary, the results obtained with the nonlinear model points out its flexibility to describe the curved and asymmetrical anodic/cathodic branches in Tafel plots found experimentally. Note that neither the symmetric MH model nor BV model account for this behavior of the electrochemical rate constants. Whereas the former predicts symmetrical Tafel plots, BV cannot reproduce the curvature of such plots. On the other hand, the asymmetric Marcus–Hush model does predict curved, asymmetrical plots as a result of different vibrational force constants between the oxidized and reduced species [21,22].

The relationship between the transfer coefficient at the formal potential \( \alpha(\eta = 0) \) and the extent of nonlinear effects (through the parameter \( \gamma \)) is analyzed in Fig. 3. Establishing the connection between \( \alpha \) and nonlinear solvation is of great interest since the parameterisation of the electrode kinetics has been carried out extensively with Butler–Volmer such that there exists a vast number of data for the transfer coefficient. So, this enables us to revise the experimental data with this new physical interpretation and to use the BV formalism for a simpler quantitative analysis of the experimental results complemented by physical insight not available from the original, phenomenological BV model [39,40,50,51].

Fig. 3 shows that the case \( \alpha(0) > 0.5 \) corresponds to positive \( \gamma \) values, that is, a greater solvent force constant in the oxidized form. The situation where the solvent frequency of the reduced species is greater than that of the oxidized species relates to \( \alpha(0) < 0.5 \). The greater the nonlinear effects (i.e., the smaller the absolute value of \( \gamma \)), the greater the deviation of the transfer coefficient from 0.5. It is also found that \( \alpha(0) \) is mainly defined by \( \gamma \).

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Fig. 4. Variation of the cyclic voltammograms with the parameter \( \gamma \) for solution phase (A and C) and surface attached (B and D) redox couples. (A and B) Ox\(^+\) + e\(^-\) \rightarrow \text{Red}^-. \lambda_s = 2.5 \text{ eV}. Solution-phase: \( k^0 \sqrt{F} = 0.01, \Psi = I/(\sqrt{F} A C \sqrt{D/RT}) \), planar electrode; Surface-attached: \( k^0 \sqrt{F} = 0.013, \Psi = I/(FAF^+ PV/RT) \).
whereas the influence of the solvent reorganization energy on the $\alpha(0)$-value is less significant for the typical range $\lambda_s = 1 - 4 \text{ eV}$. Though a detailed description of adiabatic processes is beyond the aim of this work, it is worth noting that nonlinear effects are predicted to be more noticeable in the electrochemical response as the ET process is more adiabatic [38], more extreme $\alpha$-value being expected.

The influence of nonlinear solvation on the cyclic voltammograms is shown in Fig. 4 for solution-phase (Fig. 4A and C) and surface-attached (Fig. 4B and D) electrode processes. In general, kinetic effects are more apparent for surface-attached systems since they are not masked by rate-limiting mass transport like when the electroactive species are dissolved in an electrolyte solution.

The effects of different solvent force constants for positive $\gamma$ values (i.e., $K_{\text{Ox}} > K_{\text{Red}}$) are analogous to those associated to $\alpha > 0.5$ in the BV model. Thus, the cathodic peak current increases with respect to that of the anodic peak, and the cathodic peak potential shifts towards lower overpotentials whereas the anodic peak potential moves to more positive values. The opposite effect is observed for negative $\gamma$ values (i.e., $K_{\text{Red}} > K_{\text{Ox}}$) where the magnitude of the oxidative signal increases relative to the reductive one as expected for $\alpha < 0.5$.

In light of the above results it is interesting to reconsider the results recently obtained in our group for the electroreduction of 2-methyl-2-nitropropane (MeNP), cyclooctatetraene (COT) and europium(III) (Eu$^{3+}$) on mercury microelectrodes [22] and the electrooxidation of tetraphenylethylene (TPE) on platinum microdisk electrodes [23]. In all cases, the reductive and oxidative experimental peaks could not be fitted adequately with the symmetric MH model. The magnitude of one of the peaks was overestimated whilst underestimating the other one. On the other hand, the electrode kinetics were parameterized satisfactorily for all the systems with the Butler–Volmer formalism, which shows greater flexibility to act on the relative magnitudes of the reductive and oxidative peaks. The values obtained for the standard heterogeneous rate constant and the transfer coefficient of each process are shown in Table 1.

For the electroreduction of neutral species (MeNP/MeNP$^+$ and COT/COT$^+$) a transfer coefficient less than 0.5 is obtained whereas $\alpha > 0.5$ for the redox couples Eu$^{3+}$/Eu$^{2+}$ and TPE'/TPE. Taking into account the physical insight given above to $\alpha$, these results indicate that the interaction with the solvent increases with the solute charge such that the solvent frequency is greater in the more charged form, that is, the reduced species for MeNP/MeNP$^+$ and COT/COT$^+$, and the oxidized species for Eu$^{3+}$/Eu$^{2+}$ and TPE'/TPE. This is the behavior expected when considering Coulombic interactions [34,30,52]. The quantitative application of the present results is not suitable for these systems since for all of them it is well documented that the inner-sphere component is not negligible [8,53,54], and it is a source of asymmetries in the free energy surface in the case Eu$^{3+}$/Eu$^{2+}$ [8]. Other redox systems (like those involving aromatic molecules) show very small contribution of the inner reorganization energy and so the nonlinear model can be applied to the quantitative parameterization of the results. However, in general the vibrational component has to be considered with the interplay between the possible asymmetric effects arising from the solvent and inner-sphere reorganization energy [55]. This will make the model more complex and may require the use of numerical simulation. In addition, the unambiguous determination of the kinetic parameters will likely require additional information about the redox system.

Finally, the variation of the peak current with the scan rate of the cyclic voltammograms of irreversible electrode processes is analyzed in Fig. 5. This analysis is of great interest in electrochemistry since it enables us to discriminate between diffusional and surface processes. According to the Butler–Volmer model, the peak current ($I_{\text{peak}}$) of an irreversible process at a planar electrode scales with the square root of voltage scan rate (Randles–Sevcik equation) whereas when the redox couple is adsorbed on the electrode surface $I_{\text{peak}}$ is proportional to the scan rate [39,40].

However, we have demonstrated that a system obeying Marcus–Hush kinetics does not follow the behaviors above described [18,44]. Thus, the peak current is smaller than expected, this deviation being more apparent for systems with small reorganization energies deviation and at greater overpotentials (that is, higher scan rates and/or slower electrode kinetics). Indeed,

![Table 1](image_url)

Table 1: Kinetic parameters obtained from the fitting of cyclic voltammograms with the Butler–Volmer (BV) model. Error bars calculated from the standard deviation of the best fittings at several scan rates [22,23]. TBAP: tetrabutylammonium perchlorate; MeCN: acetonitrile; TEABr: tetrabutylammonium bromide; DMSO: dimethylsulfoxide; TBAPF6: tetrabutylammonium hexafluorophosphate; DCM: dichloromethane.

![Fig. 5](image_url)

Fig. 5. Variation of the peak current of the forward scan with the scan rate for an irreversible electrode processes involving solution phase (A) and surface attached (B) redox couples. $\lambda_s = 2.5 \text{ eV}$. The results from Matyushov nonlinear model (black line), symmetric Marcus–Hush model (grey solid line) and Butler–Volmer model (grey dashed line) are shown. Solution-phase: $k_0 = 10^{-2} \text{ cm}^3 \text{s}^{-1}$; $T = 1/(F \Delta f/RT)$, planar electrode; surface-attached: $k_0 = 0.5 \text{ s}^{-1}$, $\Psi = [(F \Delta f/RT)$. 

there are several experimental evidences of these deviations for electroactive redox monolayers [9,10,56,57].

As can be seen in Fig. 5, the nonlinear model also predicts curved Randles–Sevcik plots for small absolute values of $\gamma$. For positive and negative $\gamma$ values the value of the peak current is smaller than that expected by the BV model and the divergence increases continuously as the scan rate is increased and the peak moves towards greater overpotentials.

4. Conclusions

The effect of nonlinear solvation on the electrochemical response of electrode reactions has been considered with the Matyushov model that includes bilinear solute–solvent coupling. In contrast with other nonlinear approaches, the Matyushov model offers an analytical equation for easier simulation of the case where the solvent frequencies in the oxidized and reduced species differ significantly due to the change of charge. The model introduces a new kinetic parameter, $\gamma$, which accounts for the deviations with respect to the linear response regime (Marcus model). This gives the model a greater flexibility to parameterize the kinetics of those systems where deviations with respect to the symmetric Marcus–Hush model have been recently reported. Nonlinear effects also give rise to asymmetric, curved Tafel plots and curved Randles–Sevcik plots. Both behaviors have been observed experimentally and they contrast with the results predicted by the widely-used Butler–Volmer model.

The application to electrode processes has been carried out and the effects on the rate constants and cyclic voltammograms of solution-phase and surface-attached redox systems have been analyzed. The results show that the electrochemical response is sensitive to the occurrence of nonlinear solvation such that the symmetry between the oxidation and reduction processes is affected. Thus, when the oxidized form interacts more strongly with the solvent, the magnitude of the cathodic signal increases relative to the anodic one. The opposite situation is found when the solvent force constant of the reduced species is greater.

Accordingly, the effects of nonlinear solvation can be analyzed from the value of the transfer coefficient, $\alpha$, considering it as an indicator of the differences between the solvent frequencies. The case $\alpha > 0.5$ relates to greater force constant for the oxidized species and $\alpha < 0.5$ for the reduced form. A qualitative analysis of the experimental results obtained for the electroreductions of 2-methyl-2-nitropropane, cyclooctatetraene and europium(III) on mercury microelectrodes and the electrooxidation of tetraphenylethylene on platinum microdisk electrodes are in agreement with the solvent force constant of the more charged species being greater. Thus, as a consequence of nonlinear solvation the fluctuation component of the reorganization energy depends on the charge of the species.

From the results presented here and in Refs. [21,22], the deviations from the symmetric Marcus model and the values of the transfer coefficient can be rationalized in terms of differences between the vibrational and solvent force constants in the oxidized and reduced species. The Matyushov nonlinear model and the asymmetric Marcus–Hush model enable separate evaluations of these effects from manageable, analytical equations. Unfortunately, both asymmetries may act simultaneously and the experimental discrimination between them is not straightforward. A careful analysis of each particular system attending to its microscopic properties and additional data available is required.

Acknowledgments

The authors thank Dr. D.V. Matyushov for his very helpful comments and ideas. E.L. thanks the Fundación SENECA for the grant received. MCH thanks EPSRC for funding (EP/H002413/1).

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