Discussion


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This response article aims to provide an overview of the literature highlighting experimental work that, in contrast to the account by Luque and Schmickler, evidences the non-adiabatic nature of the electron transfer process.

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1. Introduction

Experimental evidence as to the magnitude of a molecule’s electronic coupling to a bare electrode surface – and hence the ‘adiabaticity’ of the electron transfer – is both limited and conflicting. It is this question of adiabaticity which forms the basis of Luque and Schmickler’s comments [1] upon the previous work published by the authors in Chemical Communications [2]. As correctly highlighted by Luque and Schmickler, the main argument for outer-sphere electron transfers operating via an adiabatic pathway is predominantly predicated upon two papers published by Schmickler et al. during the mid-1980s [3,4]. Here for a series of aqueous redox ions, the ‘insensitivity’ of the rate of electron transfer to the electrode material was demonstrated. Hence, prima facie, the electron transfer was taken to be adiabatic in nature [6].

These conclusions pertaining to the adiabatic nature of the electron transfer have been questioned by, amongst others, Marcus [7]. Marcus demonstrated that even with a surface tethered ruthenium complex, where the electron transfer is almost certainly non-adiabatic in nature (due to the redox centre being situated at a relatively large distance from the electrode surface), there is still no major difference in the electron transfer rate between a gold and platinum electrode (a ratio of 1.8 was reported). Of importance is the fact that the density-of-states (DOS) for these two materials differs by a factor of 7.5, this is primarily due to the d-orbital contribution for platinum. Consequently, Marcus proposed that the underlying assumption that the electronic coupling strength to all of the electronic bands is equal, may not be valid.

Beyond the comparison of the relative rates of electron transfers on different substrates an alternative, independent approach presented within the literature is to assess the rate of electron transfer for a given system as a function of temperature. Assuming Arrhenius type behaviour, the pre-exponential factor is then used to give a measurement of the ‘adiabaticity’ of the electron transfer. On this basis Savéant et al. have confirmed the likely non-adiabatic nature of a number of systems including the reduction of tert-nitrobutane, C10H17NO and a phenol derivative in non-aqueous media on a mercury electrode [8,9].

As shall be discussed later in this response article a number of other groups – beyond those mentioned above – including those of Lewis [10] and McCreery [11] take a different view upon the magnitude of the electronic coupling matrix to that presented by Luque and Schmickler. The conclusion that the electron transfer for quinones at both gold and carbon electrodes in aprotic media is non-adiabatic is consistent with most of the literature. The following

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1 Note that more recent experimental work has reinvestigated the ruthenium hexamine system as reported by Schmickler et al. [3,4]. This more accurate data shows there to be a statistically significant difference between the electron transfer rate at a gold and platinum surface, with a measured ratio of 1.27 [5].
sections act, in part, as a rebuttal to Luque and Schmickler’s points but also serve to highlight associated reported areas impacting the issue.

2. Discussion

2.1. The transition from adiabatic to non-adiabatic regime

It is helpful to start by making a comment on electron transfer, specifically regarding the adiabatic/non-adiabatic transition. A key issue is the differing opinion on how to treat the influence of the electronic coupling upon the expression for the electron transfer rate constant. Importantly, the two main literature models are not equivalent [12]. The Anderson–Newns approach as taken by Schmickler [6] directly considers the reduction in the activation energy as a function of the coupling strength. Alternatively, in the Gerischer type model as presented by Feldberg [13], an explicit term for the activation energy is not formulated, here the rate of electron transfer is related to the overlap integral between the oxidised and reduced species. Coupling to the electrode surface acts to broaden the distribution of energy levels for the two species, hence in doing so increasing the overlap integral. The formalism for the later model as discussed by Feldberg and Sutin [14] is – although a simplification – in good agreement with the more holistic (non-DOS) approach taken by Medvedev et al. [15].

In accordance with the work of both Feldberg and Sutin [14], and Savéant et al. [8], the variation of the pre-exponential factor ($z_{het}$) with coupling strength may be approximated by the following equation,

$$z_{het} = \frac{\nu_{n}}{\beta} \frac{\pi}{\sqrt{1 + (\pi k_{B} T / \lambda)}} \ln \left( 1 + \frac{4\pi^{2} \rho H_{DA}^{2}}{\hbar \nu_{n}^{4} \sqrt{4\pi (\lambda / k_{B} T)}} \right)$$

(1)

where $\nu_{n}$ is the nuclear vibrational frequency, $\beta$ is the coupling attenuation coefficient, $\lambda$ is the heterogeneous reorganisation energy, $\rho$ is the metallic density of states and $H_{DA}^{2}$ is the coupling strength. Fig. 1 depicts the variation of this pre-exponential rate constant as a function of coupling strength, where the value of $\nu_{n}$ has been given a lower bound value of $10^{12}$ s$^{-1}$ [16]. Two distinct regions are observed, one at small values of $H_{DA}^{2}$ where the value of $z_{het}$ is strongly dependent upon the coupling strength, this is the non-adiabatic limit. The other is at ‘high’ coupling strengths where the pre-exponential value is effectively invariant with the coupling strength, this represents the adiabatic limit. Note that the transition between the two regimes occurs gradually over roughly an order of magnitude of the coupling strength.

From Eq. (1) we recognise two important features. First, for a given reorganisation energy the adiabatic regime may be viewed as representing the ‘upper’ limiting rate for an electron transfer. Consequently, this implies that in this limit the rate of electron transfer is both virtually independent of the coupling strength and is also independent of the electron transfer distance [14]. To this end the electron transfer inhibiting effects of tert-alkyl-ammonium cations in polar aprotic media have been interpreted in terms of increasing the electron transfer distance due to the increased double layer thickness; implying a non-adiabatic process is operative [17,8]. If these conclusions are both valid and extended further, then due to the smaller size of the supporting electrolyte ions in aqueous media, this may give insight into why the redox chemistry of aqueous ions appears to be adiabatic – as inferred in the earlier Schmickler papers [3,4]. Second, the non-adiabatic limit may be viewed as being the situation under which the electron hopping frequency ($\nu_{et}$) is significantly less than the effective nuclear vibration frequency ($\nu_{n}$). Due to the band structure of the electrode material, electron transfer may occur to and from a multitude of energy levels. Consequently the magnitude of $\nu_{et}$ is proportional to both the magnitude of the electronic coupling element ($H_{DA}^{2}$) and also the density of electronic states ($\rho$) [14]. This proportionality to the density of states is of paramount importance and is reflected in the variation of the pre-exponential factor ($z_{het}$) as given by Eq. (1). It can be seen that as the density of states decreases the ‘adiabaticity’ of the electron transfer will also decrease for a given set of parameters, this provides insight as to why electron transfers at semiconducting electrodes are treated as non-adiabatic [18].

2.2. The electrochemistry of quinones on gold

The first question that arises in respect to Luque and Schmickler’s comment is the issue of the non-adiabaticity of the quinone electron transfer on a gold substrate. The rate of electron transfer for benzoquinone on a gold electrode has been previously measured by Jaenicke et al. as a function of temperature in both DMF and acetonitrile [19]. From this data it can be seen that the rate of electron transfer in DMF exhibits a strong supporting electrolyte dependence (note the acetonitrile data is only measured using tetraethyl ammonium perchlorate [TEAP]). As discussed in the above section such a result is consistent with the electron transfer being non-adiabatic.

Fig. 2 plots the experimentally measured rate of electron transfer versus the inverse of temperature for benzoquinone in acetonitrile (0.1 M TEAP) [19], also shown is the datum point provided by Nissim et al. [2] relating to the use of 0.1 M tetrabutyl ammonium perchlorate (TBAP) both are studied using a bare gold electrode. From the data provided by Jaenicke et al. the reorganisation energy ($\lambda$) for the electron transfer in acetonitrile can be estimated as being equal to $1.24 \pm 0.11$ eV. Given that within the Marcusian treatment the gradient of the plot should be independent of the identity of the supporting electrolyte [17], then we are able to estimate a value for the pre-exponential factor for benzoquinone in acetonitrile with 0.1 M TBAP as being $8 \pm 4 \times 10^{4}$ cm$^{-1}$ s$^{-1}$.

It should be commented here that the ionic strength is known to influence the electron transfer rate, however in the present case the concentration of supporting electrolyte is constant [20]. This value of $8 \pm 4 \times 10^{4}$ cm$^{-1}$ s$^{-1}$ for the pre-exponential factor is very comparable to that found by Savéant et al. for other electroactive species exhibiting non-adiabatic electron transfer in polar aprotic

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\[2\] The current treatment neglects the effect of the lower activation energy with strong electronic coupling strength.
solvents [8,9]. Moreover, from comparison with Fig. 1 it can be seen that the pre-exponential factor is, significantly, below the value for the adiabatic limiting case (~10^5 cm s⁻¹). Hence, given the above justification one may conclude that the electron transfer for benzoquinone on gold in acetonitrile (0.1 M TBAP) is non-adiabatic.

Given the apparent non-adiabatic nature of the electron transfer for benzoquinone on gold, it is not unreasonable that the electron transfers for the other quinones are also non-adiabatic on this substrate. Moreover, recognising the lower DOS associated with carbon it is justifiable to predict that the quinone electron transfer on this material will also likely be non-adiabatic. We return to this question of the adiabaticity of the electron transfer on carbon in Section 2.4.

2.3. The density of electronic states of graphite

In their response to our work Luque and Schmickler [1] provide a DFT based calculation for the carbon electronic density of states. This ‘improved’ DOS exhibits significantly more structure than the originally presented data [21], or for that matter, data found within the literature from both theoretical [22,23] and especially experimental [24,25] sources. Fig. 3 depicts a scanning tunnelling spectroscopic measurement for HOPG, as adapted from Červenka et al. [24], where the plot of dI/dV reflects the experimental DOS. Also depicted in Fig. 3 is the ratio of the carbon DOS to that of gold as presented by both the original paper and by Luque and Schmickler. It is of note that Luque and Schmickler’s DOS deviates significantly at both negative and positive potentials. Given that DFT results are only as good as their approximations [26] and noting that the DOS as presented by Luque and Schmickler is calculated using merely four carbon layers [27], one might question its accuracy.

Nuances aside, a more important consideration is the relative change in the DOS from −0.35 V (versus PZC) to −1.68 V (versus PZC) i.e. over the range of the quinone study. As outlined in our original article this change should be reflected in the ratio of the measured rate constants. From the originally presented DOS a change of a factor of 4.7 is found, from Schmickler’s DOS a value of 7.9 is obtained, however interestingly from extrapolation of the experimental data presented by Čajkova et al. the ratio is found to be as low as 3.9 [25]. Clearly even in the non-adiabatic limit one is not expecting to observe a large change in the relative rate constants for the quinone electron transfer (gold versus carbon) as a function of potential. Experimentally from the original paper the relative rate constants on the two materials are found to change by a factor of

3.1. This value is below that predicted theoretically, however, even using Luque and Schmickler’s DFT DOS the experimental data can be shown to be in reasonable agreement (Fig. 4).

2.4. Electron transfer at graphitic electrodes: adiabaticity

Work by Royea et al. [10], has previously led to the conclusion that electron transfers from a series of aqueous redox ions at graphitic electrodes are non-adiabatic. This result firmly contradicts Schmickler’s conclusions [1]. However, within the comments of Luque and Schmickler these discrepancies are ascribed as being due to differing electron transfer distances [1]. It is argued by Luque and Schmickler that for the more highly charged species – as used by Royea et al. – the plane of electron transfer occurs further from the electrode surface as compared to the quinone case. Hence, this increased distance reduces the electronic coupling to the electrode surface resulting in a more non-adiabatic electron transfer. This argument ignores the fact that for our experimental quinone work undertaken in acetonitrile, the supporting electrolyte cations are significantly larger than those used in aqueous media. In accordance with the literature it would be reasonable to conclude that

![Graph showing the variation of the standard rate constant with temperature](image1)

**Fig. 2.** Variation of the standard rate constant (cm s⁻¹) with temperature (K) for the one-electron reduction of benzoquinone in acetonitrile (0.1 M TBAP) (black squares) on a gold electrode. The red line represents the line of best fit giving an intercept of 11 ± 1. Data taken from Table 3 of Rüssel and Jaenicke [19]. The star represents the rate of electron transfer for benzoquinone in acetonitrile (0.1 M TBAP) as reported by Nissim et al. on a gold microelectrode [2]. (For interpretation of the references to colour in this figure legend, the reader is referred to the web version of the article.)

![Graph showing the differential conductance spectra of graphite](image2)

**Fig. 3.** Left hand axis: the differential conductance (dI/dV) spectra of graphite as adapted from Červenka et al. (the black line) [24]. Right hand axis: the ratio of the carbon and gold density of states, the green line – the DOS as presented within the original Chemical Communications paper [2], the red line – the DOS as presented by Luque and Schmickler from DFT calculations. (For interpretation of the references to colour in this figure legend, the reader is referred to the web version of the article.)

![Graph showing the comparison between the ratio of the standard electron transfer rate constants](image3)

**Fig. 4.** The comparison between the ratio of the standard electron transfer rate constants for a series of quinones (acetonitrile, 0.1 M TBAP) and the ratio of the carbon and gold densities of states as presented by Schmickler (the axes have been rescaled from the original text, noting that the ratio of the coupling strengths has been treated as a variable).
the electron transfer distance is approximately 8 Å due to the structure of the double layer [8]. This point significantly undermines the arguments of Luque and Schmickler. In light of the above discussion it seems reasonable to conclude that for quinones in a non-aqueous environment, the electron transfer on carbon is a non-adiabatic process. Moreover, the variation in the ratio of the electron transfer rates on carbon and gold as a function of potential would seem to be best explained, within the frames of our current model, as being due to the non-constant electronic structure of carbon near its Fermi level.

2.5. Electron transfer at graphitic electrodes: heterogeneity

Within the electrochemical field there is continuing discussion and active research into the varying rates of electron transfer at the ‘basal’ and ‘edge’ plane sites present upon the graphitic electrode surface [11]. It should be commented that the carbon microelectrode, as used in the Chemical Communications article [2], will exhibit a large number of edge plane sites upon its surface. In general the consensus is that the rate of electron transfer is greatest at the edge sites as compared to the basal [28]. However, as highlighted by Schmickler, one recent paper by Unwin et al. seems to buck this trend, where the electron transfer of ruthenium hexaamine is found – through the use of a so-called theta electrode – to be reversible on the basal plane sites [29]. This paper is certainly of interest, however, an important challenge that has not been realised in [29] is the correlation of this local microscopic result to that of the well documented macroscopic response of a HOPG electrode; i.e. if such ‘pristine’ HOPG surfaces, as used within [29], are used in a conventional cyclic voltammetric experiment do the voltammograms appear fully reversible or not? If so what sites are reproduced by other groups? If not, then why not?

Finally, we note that understanding the magnitude of the electronic coupling to these heterogeneous electrode surface sites and their differing electronic structure may yet yield significant understanding into both the regularly observed varying rates of electron transfer and the apparent contradictions present within the literature.

3. Conclusions

This article made in response to the comments of Luque and Schmickler, highlights why for both the gold and carbon electrodes it is reasonable to conclude that the electron transfer for the given quinone system is non-adiabatic. These conclusions are in agreement with a significant amount of literature from various independent groups [7,8,10,11].

References