On the adiabaticity of electrode processes: Effect of the supporting electrolyte cation on the kinetics of electroreduction of 3-nitrophenolate

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The comparative analysis of voltammetric responses at different temperatures through the asymmetric Marcus–Hush theory provides physical insight into the changes upon the electron transfer mechanism and the electronic interaction between the electrode and the electroactive species. Herein this approach is applied to the assessment of the influence of the nature of the supporting electrolyte on the kinetics of electrode processes.

In particular, the electroreduction of the 3-nitrophenolate anion is studied in dimethylsulfoxide solutions via the use of a mercury hemispherical working microelectrode. Three different tetra-alkyl-ammonium perchlorates are employed as supporting electrolyte: tetraethylammonium, tetrabutylammonium and tetrarehexitlammonium. From these kinetic studies undertaken at different temperatures the reorganization energy, force constant symmetry and the strength of the electronic coupling are determined and analyzed for the different conditions. The results presented show a significant effect of the identity of the supporting electrolyte cation on the electrode kinetics that can be attributed to the change of the distance of closest approach between the electroactive species and the electrode as well as to ion-pairing effects. The experimental behavior observed suggests that the process has a non-adiabatic character.

1. Introduction

Much insight into electrode processes is available from kinetic studies at different temperatures. Microscopic kinetic models, and particularly the asymmetric Marcus–Hush (aMH) [1,2], enable one to rationalize the kinetics of heterogeneous electron transfers in terms of the difference between the configurations of the reactant and product species (reorganization energy), the difference between their vibrational force constants, and the strength of the electronic interaction between the electrode and the electroactive species (adiabaticity).

In the literature, varying theoretical approaches to the adiabatic character of outer-sphere electrode processes can be found [3–5]. Herein there is a need for new experimental investigations to assist the development of suitable holistic models. Usually [6–8] the sensitivity of the electrode kinetics to the electronic density of the electrode material and the solution viscosity has been criteria to examine the degree of adiabaticity of a given process. The first approach [6] is based on the simplifying idea that the rate constant of the processes increases with the density of states up to a limit value corresponding to the adiabatic regime. Therefore, the kinetics of non-adiabatic processes is expected to scale with the electrode density of states whereas adiabatic reactions should be independent of this parameter and therefore independent of the electrode material. Schmickler et al. found the latter behavior when studying the electroreduction of several ions in aqueous solutions under turbulent flow and, consequently, these reactions were classified as adiabatic [6,7]. This strategy requires a precise knowledge of the density and nature of electronic states of the electrode material [3].

With respect to the study of the electronic coupling through viscosity variable studies [8], the rate constant of a non-adiabatic process is expected to be independent of the solution viscosity, whereas for adiabatic processes the electron transfer rate should be enhanced as the solution viscosity decreases. This simplifying criterion does not reflect the complexity of the effect of viscosity on the electrode kinetics and can lead to misinterpretation [8].

The study of the variation of the standard heterogeneous rate constant (k0) with temperature is an interesting and valuable alternative that has been applied to the study of several electrode reactions [9–13]. Apart from enabling the evaluation of the degree of adiabaticity, the value of the reorganization energy can also be better estimated with superior accuracy compared to voltammetry at constant temperature.

In the present work, this methodology is applied to explore the effect of the size of the supporting electrolyte cation on the kinetics of...
of electroreduction of 3-nitrophenolate anion at the interface between a mercury microelectrode and a dimethylsulfoxide solution. As has been reported for other nitrocompounds [9,14], at the negative potentials where the electrode process takes place the size of the cation is expected to establish the distance of closest approach between the electroactive species and the electrode. The resulting effect on the rate constants is predicted to be significant for non-adiabatic processes and to decrease as the reaction is more adiabatic [15].

2. Experimental

2.1. Chemical reagents

3-Nitrophenol (Pb(OH)NO₂, Aldrich, 99%), tetra-n-ethylammonium perchlorate (TEAP, Fluka, Puriss grade), tetra-n-butylammonium perchlorate (TBAP, Fluka, Puriss grade), tetra-n-hexylammonium perchlorate (THAP, Alfa Aesar), tetra-n-butylammonium hydroxide (TBAOH, Alfa Aesar, >98%), mercury(I) nitrate dihydrate (Hg₂(NO₃)₂·2H₂O, Aldrich, >97%), nitric acid (HNO₃, Fisher scientific, 70%), ferrocene (Fe(C₅H₅)₂, Aldrich, 98%), cobalt(III) sepulchrate trichloride ([CoSep]Cl₃, Aldrich, 95%), potassium nitrate (KNO₃, Aldrich, >99%), dimethylsulfoxide (DMSO, Alfa Aesar, >98%), mercury(I) nitrate trihydrate (Hg₂(NO₃)₂·3H₂O, Aldrich, >97%), nitric acid (HNO₃ [17]).

2.2. Instrumentation

All the electrochemical experiments were carried out with a computer-controlled Autolab PGSTAT12 (Metrohm-AutoLab BV, Utrecht, Netherlands) and a three-electrode set-up where a platinum mesh acted as the counter electrode and a silver wire as the reference electrode.

A mercury hemisphere was employed as the working electrode. This was electrodeposited onto a microdisc electrode of 23 μm radius by applying a potential pulse at −0.25 V (vs Ag wire) in a 50 mM Hg₂(NO₃)₂ and 0.1 M KNO₃ solution acidified to 0.5% with HNO₃ [17].

The amount of charge passed enabled a first control of the size of the hemisphere. After deposition, the size and shape of the mercury deposit were confirmed by both electrochemical and optical methods as detailed in previous works [12,13]. The results confirmed the deposition of a 23 μm-radius mercury drop with hemispherical shape.

An air heater-controller system fabricated in-house was used for thermal control of the electrochemical experiments within a precision of ±0.1 °C.

2.3. Determination of the reactant concentration and diffusion coefficients

For the current study, DMSO solutions containing ca. 1 mM of 3-nitrophenolate monoanion and ca. 0.1 M of a different background electrolyte (TEAP, TBAP or THAP) were used for electrochemical measurements at different temperatures in the ranges: 24–49 °C for TEAP; 24–47.5 °C for TBAP; and 23–53 °C for THAP.

The diffusion coefficient of the electroactive species and the concentration of the 3-nitrophenolate anion were determined at each temperature through independent measurements prior to the kinetic study in order to reduce the number of unknown variables. Note that these magnitudes vary with temperature given the temperature-dependent nature of diffusion coefficients and solvent thermal expansion.

Double potential step chronoamperometry [18] was carried out at each temperature. The potential was initially set at −0.25 V (vs Ag wire) where no Faradaic process takes place. Then, the potential value was stepped to a potential corresponding to diffusion-limited conditions for the electroreduction of the 3-nitrophenolate monoanion for 0.5 s. In the second pulse the applied potential was stepped back to −0.25 V for 0.5 s such that the radical dianion electrogenerated during the first pulse is oxidized under limiting current conditions.

The analysis of the first step chronoamperogram yields the diffusion coefficient and bulk concentration of the 3-nitrophenolate monoanion and, once this is known, the diffusion coefficient of the radical dianion is obtained from the second step chronoamperogram. The reactant concentrations studied ranged between 0.84 and 1.13 mM, and the results for the diffusion coefficients (D) are shown in Fig. 1 in the form of Arrhenius plots of ln(D) vs 1/T and they will be discussed in Section 4.1.

2.4. Temperature variable cyclic voltammetry

Cyclic voltammograms within the scan rate range of 50 mV s⁻¹ to 2 V s⁻¹ were recorded between −0.2 and −0.92 V (vs Ag wire) on 23 μm radius mercury hemispherical electrode. Thus, the electrode kinetics was investigated in a very wide experimental time scale from a nearly purely linear diffusional regime at high scan rates to a nearly purely convergent diffusion at low scan rates. For each

Fig. 1. Arrhenius plots of lnD vs 1/T for 3-nitrophenolate⁻⁻ (A) and 3-nitrophenolate⁻ (B) in DMSO containing 0.1 M TXAP.
solution, four sets of voltammograms each recorded at a different temperature (24–49 °C for TEAP; 24–47.5 °C for TBAP; and 23–53 °C for THAP), were obtained.

3. Theory

3.1. Kinetic model

The electroreduction of the 3-nitrophenolate anion on mercury in DMSO solutions will be simulated as a simple, outer-sphere electron transfer according to the following scheme:

\[
\text{Ph(O}^\cdot\text{NO}_2^- + e^- \rightarrow \text{Ph(O}^-\text{NO}_2^-)
\]

where \(k_{\text{red}}\) and \(k_{\text{ox}}\) are the rate constants for reduction and oxidation, respectively. As will be discussed in Section 3.2, this reaction scheme leads to very satisfactory fittings of experimental voltammograms in all the systems for a wide range of scan rates (from 50 mVs\(^{-1}\) to 2 V s\(^{-1}\)). Nevertheless, the temperature dependence of the diffusion coefficients suggests the occurrence of ion-pairing when TEAP and TBAP (see Section 4.1), and its possible incidence in the kinetic parameters is discussed below.

The rate constants in scheme (1) can be written as:

\[
k_{\text{red}/\text{ox}} = \nu_n k_{\text{red}} k_n
\]

with \(\nu_n\) being the nuclear vibration frequency factor, \(k_{\text{el}}\) the electronic transmission coefficient and \(k_n\) the nuclear reorganization factor. The standard heterogeneous rate constant, \(k^0\), is defined as the value of the reduction and oxidation rate constants at the formal potential: \(k^0 = k_{\text{red}}(E = E^0_{\text{red}}) = k_{\text{ox}}(E = E^0_{\text{ox}})\).

The electronic transmission coefficient contains the information about the electronic coupling of the redox couple with the metal electrode. An approximate and simple expression was given by Feldberg and Sutin [15] for electron transfer reactions between a metal electrode and a free-moving species in solution:

\[
k_{\text{el}} \approx \frac{1}{\beta} \ln \left(1 + \frac{4\pi^2 \rho_{M} H_{AB}^0}{\nu_{M} h \sqrt{4\pi \rho_{M} H_{AB}^0}}\right)
\]

where \(F\), \(R\) and \(T\) have the usual meanings, \(\beta\) is the reorganization energy, \(\rho_{M}\) is the tunneling factor, \(\rho_{M}\) the density of electronic levels in the electrode, \(h\) the Planck's constant and \(H_{AB}^0\) the electronic coupling element at the plane of closest approach.

At the potentials corresponding to the electroreduction of 3-nitrophenolate, the surface of the mercury microelectrode is negatively charged such that the concentration of supporting electrolyte cations around the electrode surface will be large. Consequently, the size of the cations will define the plane of closest approach and then the \(H_{AB}^0\) value: the larger the cation, the smaller the \(H_{AB}^0\) value. Indeed, the decrease of the standard heterogeneous rate constant with increasing size of the SE cation has been previously reported for the electroreduction of nitrocompounds [9,14].

Considering the continuum of electronic levels of the metallic electrode, the nuclear factor can be written as:
\[ \kappa_n = \int_{-\infty}^{\infty} \exp\left[ -\Delta G_{\text{red/ox}}^\omega(x) \right] \frac{1}{1 + \exp(x)} \, dx \]

where the upper sign refers to the reductive process whereas the lower one to the oxidative reaction, and \( x = \frac{F(e - E)}{RT} \) is an integral variable. Within the asymmetric Marcus–Hush formalism (aMH), the activation energies of the reduction and oxidation processes given by:

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

with \( \lambda = \frac{F}{RT} \) being the dimensionless reorganization energy, \( \eta = \frac{F(E - E^\text{eq})}{RT} \) the dimensionless overpotential and \( \gamma \) the dimensionless parameter that informs about the differences between the inner-shell force constants of oxidized and reduced species:

\[ \gamma = \frac{\lambda i}{\lambda} \sum_k k_i (\Delta q_i^0)^2 I_i \]

where \( \lambda_i \) is the inner-sphere reorganization energy, \( \Delta q_i^0 \) the difference of the equilibrium values for the sth normal mode coordinate of reactants and products, and \( k_i \) and \( I_i \) symmetric and antisymmetric combinations of the force constants of the sth mode of reactants and products, \( f_i^\text{ox} \) and \( f_i^\text{red} \) respectively.

\[ k_i = \frac{2f_i^\text{red} f_i^\text{ox}}{I_i} \]

\[ I_i = \frac{f_i^\text{ox} - f_i^\text{red}}{f_i^\text{ox} + f_i^\text{red}} \]

Note that the lowering of the energy barrier due to the electronic coupling is not considered given that this is small according to the results below.

### 3.2. Fitting methodology

The quality of the fitting of the experimental cyclic voltammograms was evaluated through the value of the mean scaled absolute deviation (MSAD); the smaller the MSAD value, the better the quality of the fitting:

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

where \( i_{\text{exp}} \) and \( i_{\text{sim}} \) are experimental and simulated current, respectively, and \( N \) is the number of data points. In order to avoid large contributions to the MSAD of very small signal values only the points where \( i_{\text{exp}} \) is at least 10% of the peak current has been considered.

Given that the concentration and diffusion coefficients of the electroactive species are known, the fitting parameters are reduced to four: \( \{ E^\text{eq}_i, k_i^0, \lambda, \gamma \} \). For the sake of consistency, the activation
parameters $\lambda$ and $\gamma$ were kept constant for a given solution (i.e., a given supporting electrolyte) across all the temperature range.

For a given temperature, the voltammograms are relatively insensitive to the $k$-value and so the effective fitting parameters are $(E^0_0, k^0, \gamma)$, the optimum values of which were determined from minimization of the MSAD value for each experimental set. The limits of the integral in Eq. (4) were restricted to the range of $x$-values $\pm 50$ where the value of the integrand is significant.

However, as shown in Section 4 the $k$-value can be accurately obtained from the variation of $k^0$ with temperature. The $E^0_0$ value is considered as a floating variable due to the actual shift that accompanies the use of the Ag wire pseudo-reference electrode. The results are shown in Figs. 2–4 and Tables 2–4, and in all cases the agreement between theory and experiments is very satisfactory (average MSAD <4%).

4. Results and discussion

4.1. Activation energy for diffusion

The activation energy for diffusion, $E_{a,d}$, of the electroactive species was calculated from the Arrhenius-like variation of the $D$-value with temperature:

$$D = D_{\infty} \exp \left(-\frac{E_{a,d}}{RT}\right)$$  \hspace{1cm} (10)

where $D_{\infty}$ is the hypothetical diffusion coefficient at infinite temperature. The $E_{a,d}$ values obtained are given in Table 1, showing significantly larger activation energy for both electroactive species in presence of TEA$^+$ and TBA$^+$ compared to those obtained when using THAP as supporting electrolyte. Given that the smaller cations (TEA$^+$ and TBA$^+$) are expected to have stronger Coulombic interactions with the negatively charged electroactive species, these results can be assigned to larger effective molecular volume [19] due to ion-pairing in the case of TEA$^+$ and TBA$^+$ but not in the case of THA$^+$. Indeed, as a result of these interactions the $E_{a,d}$ value in presence of TEA$^+$ and TBA$^+$ is larger than the activation energy of viscosity for DMSO, $E_{a,g} = 14.1$ kJ mol$^{-1}$ [20]. Given that the $E_{a,d}$ and $D_{\infty}$ values (dependent on the molecule size [19]) for the oxidized and reduced species are very similar, we can conclude that there is no change of the ion-pair stoichiometry after the electron transfer and so the process can be modeled as shown in Eq. (1) (i.e., E mechanism).

The activation energy for diffusion of the electroactive species in THAP solutions is approximately half of the $E_{a,g}$-value, which indicates that the electroactive molecules deviate significantly from macroscopic hydrodynamic theory in this medium. Assuming that there is no ion-pairing between the electroactive species and

### Table 1
<table>
<thead>
<tr>
<th>Supporting electrolyte</th>
<th>$E_{a,d}$ (kJ mol$^{-1}$)</th>
<th>$\ln[D_{\infty}$(m$^2$s$^{-1}$)]</th>
</tr>
</thead>
<tbody>
<tr>
<td>3-NP</td>
<td>7.9 ± 0.7</td>
<td>$-18.1 ± 0.3$</td>
</tr>
<tr>
<td>3-NP$^\text{2-}$</td>
<td>7 ± 1</td>
<td>$-18.7 ± 0.5$</td>
</tr>
</tbody>
</table>
THA\(^{+}\), this behavior can be ascribed to the more planar shape and smaller size of 3-nitrophenolate with respect to the ion pairs with TEA\(^{+}\) and TBA\(^{+}\), such that its diffusion is less affected by the solvent viscosity [21].

The above possibility was investigated by UV–vis spectroscopy of 3-nitrophenolate solutions in presence and absence of supporting electrolyte with a U-2001 spectrophotometer (HITACHI, UK). The spectra obtained (not shown) show two peaks at 291 nm (with an extinction coefficient, \(\varepsilon = 4380 \text{M}^{-1}\text{cm}^{-1}\)) and 496 nm (\(\varepsilon = 1380 \text{M}^{-1}\text{cm}^{-1}\)), the heights of which do not change significantly when varying the concentration of TXAP between 0 and 100 mM. However, the study of ion-pairing through UV–vis spectroscopy has been reported to be inconclusive, especially for non-contact ion pairs [22]. Therefore, in spite of the UV–vis results and on the basis of the values obtained for the activation energy for diffusion, the possible incidence of ion-pairing on the kinetics will be present in the following discussions.

### 4.2. Reorganization energy and symmetry parameter

The fitting of the cyclic voltammograms at different scan rates (50–2000 mV s\(^{-1}\)) yielded the best-fit set of parameters \(\{E_p, k_1, k_2, \lambda, \gamma\}\) reported in Tables 2–4. As discussed in Section 3.2, the \(k_1, k_2\) and \(\gamma\) values were determined from the fitting of the voltammogram position, peak-to-peak separation and peak heights at each scan rate and temperature.

A negative \(\gamma\) value is obtained in all cases which indicates greater vibrational force constants of the reduced form (i.e., radical dianion) than for the oxidized form (i.e., monoanion), which follows the behavior reported for the electroreduction of other nitrocompounds [22,23]. The correlation between the size of the supporting electrolyte cation and the value of the symmetry parameter \(\gamma\) is not clear, \(\gamma\) being effectively in TEA\(^{+}\) and THA\(^{+}\) solution, and greater (in absolute value) for TBA\(^{+}\).

Once \(k_0\) is known, the value of the reorganization energy was determined from the slope of the variation of \(\ln(k_0)\) value with \(T^{-1}\) (Fig. 5):

\[
\ln(k_0) = \ln(Z) - \frac{\lambda F}{4k} \left(1 + \frac{\lambda}{4}\right) \frac{1}{T}
\]

where \(Z\) is a pre-exponential factor that, according to Eqs. (2)–(5), is given by:

\[
Z = \frac{C_V n}{\beta} \ln \left(1 + \frac{4\pi^2 \rho M_p^2}{v_e \hbar \sqrt{4\pi \lambda^2}}\right)
\]

![Arrehnius plot of ln(k_0) vs 1/T for 3-nitrophenolate electroreduction on mercury in DMSO containing 0.1 M TXAP. k_0 values obtained through the fitting of experimental cyclic voltammograms.](image)

### Table 2

<table>
<thead>
<tr>
<th>Experiment</th>
<th>24.0 °C</th>
<th>31.0 °C</th>
<th>40.5 °C</th>
<th>49.0 °C</th>
</tr>
</thead>
<tbody>
<tr>
<td>(k_0) (cm s(^{-1}))</td>
<td>0.025</td>
<td>0.031</td>
<td>0.039</td>
<td>0.049</td>
</tr>
<tr>
<td>(\lambda) (eV)</td>
<td>0.88 ± 0.02</td>
<td>0.88 ± 0.02</td>
<td>0.88 ± 0.02</td>
<td>0.88 ± 0.02</td>
</tr>
<tr>
<td>(\gamma)</td>
<td>-0.26</td>
<td>-0.26</td>
<td>-0.26</td>
<td>-0.26</td>
</tr>
<tr>
<td>MSAD (%)</td>
<td>4.3 ± 0.5</td>
<td>4 ± 1</td>
<td>4 ± 1</td>
<td>4 ± 1</td>
</tr>
</tbody>
</table>

### Table 3

<table>
<thead>
<tr>
<th>Experiment</th>
<th>24.0 °C</th>
<th>30.8 °C</th>
<th>39.0 °C</th>
<th>47.5 °C</th>
</tr>
</thead>
<tbody>
<tr>
<td>(k_0) (cm s(^{-1}))</td>
<td>0.020</td>
<td>0.021</td>
<td>0.025</td>
<td>0.028</td>
</tr>
<tr>
<td>(\lambda) (eV)</td>
<td>0.52 ± 0.03</td>
<td>0.52 ± 0.03</td>
<td>0.52 ± 0.03</td>
<td>0.52 ± 0.03</td>
</tr>
<tr>
<td>(\gamma)</td>
<td>-0.42</td>
<td>-0.42</td>
<td>-0.42</td>
<td>-0.42</td>
</tr>
<tr>
<td>MSAD (%)</td>
<td>1.9 ± 0.3</td>
<td>8 ± 1</td>
<td>6.1 ± 0.3</td>
<td>7 ± 1</td>
</tr>
</tbody>
</table>

### Table 4

<table>
<thead>
<tr>
<th>Experiment</th>
<th>23.0 °C</th>
<th>32.0 °C</th>
<th>43.0 °C</th>
<th>53.0 °C</th>
</tr>
</thead>
<tbody>
<tr>
<td>(k_0) (cm s(^{-1}))</td>
<td>0.0040</td>
<td>0.0048</td>
<td>0.0058</td>
<td>0.0064</td>
</tr>
<tr>
<td>(\lambda) (eV)</td>
<td>0.53 ± 0.04</td>
<td>0.53 ± 0.04</td>
<td>0.53 ± 0.04</td>
<td>0.53 ± 0.04</td>
</tr>
<tr>
<td>(\gamma)</td>
<td>-0.25</td>
<td>-0.25</td>
<td>-0.25</td>
<td>-0.25</td>
</tr>
<tr>
<td>MSAD (%)</td>
<td>2.9 ± 0.9</td>
<td>3 ± 1</td>
<td>2 ± 1</td>
<td>3 ± 1</td>
</tr>
</tbody>
</table>

where \(C\) is approximately constant for the temperature range here considered, and it is calculated from Eq. (4) and the \(\lambda\) and \(\gamma\) values of each redox couple. As can be seen in Fig. 5, the experimental results follow the linear behavior indicated by Eq. (11) and the value of the reorganization energy is calculated from the slope.

The \(\lambda\) values obtained are shown in Tables 2–4. In all cases the reorganization energy is significantly smaller than that determined for the electroreduction of nitroaliphatics such as 2-methyl-2-nitropropane (\(\lambda = 1.74\text{eV}\) [10]) and 1-nitropentane (\(\lambda = 1.74\text{eV}\) [12]). According to the conclusions reached by Kraiya et al. [24], this difference is due to the different origin of the inner-sphere changes upon the electron transfer process, which is the nitrogen pyramidalization for nitroaliphatics and the turning of the nitro group out of the aromatic ring plane for nitroaromatics.

The influence of the size of the supporting electrolyte cation on the \(\lambda\) value is quite significant, the reorganization energy of the smaller cation, TEA\(^{+}\), being larger than that for TBA\(^{+}\) and THA\(^{+}\). Given that no change of ion-pair stoichiometry is expected either for TEA\(^{+}\) or TBA\(^{+}\), the difference between the corresponding \(\lambda\) values may be ascribed to the stronger coulombic interactions of TEA\(^{+}\), resulting in the reorganization of the ion-pair being energetically more expensive.

### 4.3. Degree of adiabaticity

The intercept of the linear regressions (\(Z\)) in Fig. 5 is closely related to the magnitude of the electronic coupling between the electrode and the electroactive molecules. According to Feldberg and Sutin’s approximate treatment [15], the \(Z\) value increases as the
electronic interaction is stronger until reaching a limit value corresponding to the adiabatic regime (see solid line in Fig. 6).

Making use of Eq. (12), and considering adequate values for the different variables (\( \beta = 10^4 \text{ cm}^{-1} \) [15], \( \rho_{\text{el}} \approx 0.3 \text{ eV}^{-1} \) [25], \( v_{\text{n}} = 10^{12} \text{ s}^{-1} \) [26]), the theoretical and experimental values for the pre-exponential factor are compared in Fig. 6, in the three cases the electrode reaction lying in the non-adiabatic regime. Accordingly, the effect of the size of the supporting electrolyte cation on the Z value is remarkable such that Z increases as the cation is smaller and then the distance of closest approach to the electrode surface diminishes and \( H_{\text{AB}} \) increases. This experimental behavior reinforces the idea of adiabaticity as a variable property of an electrode reaction that can be “modulated” through, for example, the electron-tunneling distance [27]. Therefore, the degree of adiabaticity must not be ascribed only to the processes itself but also to the medium (including the supporting electrolyte) and electrode material.

As shown in this study, this can be carried out easily by varying the nature of the supporting electrolyte such that the subsequent variation of the kinetic parameters informs about the degree of adiabaticity of the process. In the future it is of interest to extend this methodology to the study of nitroaliphatics (such as 1-nitropropane) for which a more adiabatic character has been reported [13].

5. Conclusions

Kinetic study of electrode processes through temperature-variable cyclic voltammetry is a valuable alternative for the estimation of the reorganization energy and degree of adiabaticity of the process. In this paper, this approach has been applied to study the effect of the size of the supporting electrolyte cation on the kinetics of electroreduction of 3-nitrophenolate on a mercury hemispherical microelectrode in DMSO. Thus, the kinetics of this reaction has been investigated with the asymmetric Marcus–Hush model and three different supporting electrolytes: tetra-n-ethylammonium perchlorate, tetra-n-butylammonium perchlorate and tetra-n-hexylammonium perchlorate.

The results obtained show a significant effect on the electrode kinetics: the smaller the cation, the faster the process. Considering that the size of the cation establishes the minimum distance for electronic interaction between the molecules and the electrode, this behavior confirms that the reaction has a non-adiabatic character given that the influence is predicted to be very small for adiabatic processes.

The experimental behavior is also consistent with the idea stated by Batchelor-McAuley et al. [5] according to which electrode processes are reported to be more adiabatic in aqueous solutions due to the smaller size of the supporting electrolyte ions employed in this medium. On the other hand, larger ions are usually employed in organic solvents (such as those considered in the present study) in such a way that the minimum electron-tunneling distance is longer and the electronic coupling weaker.

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References


Fig. 6. Variation of the intercept (Z) of the plot \( \ln(k^0) \) vs \( 1/T \) with the coupling constant (\( H_{\text{AB}} \)).