A theoretical and experimental approach to the adiabaticity of diffusional electron transfer processes. Electroreduction of 2-nitropropane on mercury microelectroelectrodes

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A B S T R A C T

A theoretical and experimental approach to the degree of adiabaticity of electrode processes is considered for the case where the electroactive species of the redox couple move freely in solution. Within a transition state-like framework, the adiabatic effect on the activation energy of electron transfer is included through the theory developed by Schmickler (W. Schmickler, J. Electroanal. Chem. 204 (1986) 31). The effect on the probability of electron tunnelling is also incorporated according to the Landau–Zener formalism (L. Landau, Phys. Z. Sowjetunion, 1932 [29]; C. Zener, Proc. R. Soc. London A 140 (1933) 660). In applying both aspects, it is recognised that the electron transfer takes place over a range of distances from the electrode surface.

The theory is applied to the study of the electroreduction kinetics of 2-nitropropane in fully-supported DMSO solutions on mercury hemispherical microelectrodes of 23 μm radius. By fitting of experimental cyclic voltammetry, the standard rate constant (k_0) is determined at different temperatures and for different supporting electrolytes. The reorganization energy and degree of adiabaticity from the variation of k_0 with temperature are evaluated.

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1. Introduction

In previous works electrochemical measurements have been employed to gain microscopic information about the electron exchange event between a species in solution and a metal electrode. In particular, the variation of the standard heterogeneous rate constant (k_0) with temperature provides molecular insight into the electroreduction of aliphatic and aromatic nitrocompounds [1–3]. The results obtained pointed out the need for evaluation of both the reorganization energy (λ) and the electronic interaction between the electroactive species and the electrode (i.e., the degree of adiabaticity) in order to fully understand the kinetics of a given electron transfer process. Thus, the variation of the experimental k_0 values with temperature indicated a higher adiabaticity and greater reorganization energy for 1-nitropentane than for 3-nitrophenolate, the difference in λ being associated with the different structural changes taking place upon the electron transfer [4].

Within a transition state-like framework, a higher degree of adiabaticity of the electroreduction of nitroaliphatics can lead to the lowering of the energy barrier in the model. In order to examine this question as well as the suitability of the model, herein we con-

sider the effect of the electronic interaction not only on the probability of electron tunnelling, but also on the energy barrier. Consequently, and given that the electron transfer involving a species in solution occurs over a solution region next to the electrode surface [5], the activation energy depends on the distance of electron transfer as will be shown in the formulation of the kinetics.

For the modelling of the potential energy curve of the system, the generalization of the Anderson–Newns model developed by Schmickler [6–8] will be used. Next, this theory will be assessed by investigating the kinetics of electroreduction of 2-nitropropane on mercury microelectrodes in fully-supported dimethylsulfoxide solutions. The value of the standard electrochemical rate constant is determined at different temperatures (between 22.0 °C and 44.5 °C) from the fitting of cyclic voltammetry. The values and temperature dependence of k_0 are fitted with the theoretical results and the degree of adiabaticity of the process is estimated. The procedure is applied in different media, with different supporting electrolyte cations, with the aim of analyzing the effect of the electron transfer distance on the kinetics of the process. This methodology can shed some light on the understanding of the adiabatic character of diffusional heterogeneous electron transfer processes and it can assist the development of models and experimental strategies for more realistic description of electron transfer.

2. Experimental

2.1. Chemical reagents

2-Nitropropane ($CH_3CH(NO_2)CH_3$, Aldrich, >96%), tetramethyl-ammonium perchlorate (TMAP, Fluka, Puriss grade), tetraethylammonium perchlorate (TEAP, Fluka, Puriss grade), tetra-n-butylammonium perchlorate (TBAP, Fluka, Puriss grade), mercury(I) nitrate dihydrate ($Hg_2(NO_3)_2\cdot 2H_2O$, Aldrich, >97%), nitric acid (HNO_3, Fisher scientific, 70%), ferrocene ($Fe(C_5H_5)_2$, Aldrich, 98%), cobalt(III) sepulchrate trichloride ([CoSep]Cl_3, Aldrich, 95%), potassium nitrate (KNO_3, Aldrich, >99%), dimethylsulfoxide (DMSO, Alfa Aesar, >99%), acetonitrile (MeCN, Fisher Scientific, HPLC grade), were all used as received without further purification.

2.2. Instrumentation

Cyclic voltammetry and potential step chronoamperometry were performed with a computer-controlled Autolab PGSTAT12

Table 1
Concentration and diffusion coefficients of the electroactive species in 0.1 M TMAP DMSO solution at the different temperatures examined determined by double potential step chronoamperometry.

T (°C)	Reagent concentration (mM)	$D_{\text{2-nitropropane}}$ ($m^2\,s^{-1}$)	$D_{\text{2-nitropropane}}^{\cdot-}$ ($m^2\,s^{-1}$)
22.0	1.9	5.4×10^{-10}	6.0×10^{-10}
29.5	1.9	6.3×10^{-10}	7.0×10^{-10}
34.8	1.9	6.7×10^{-10}	7.5×10^{-10}
41.0	1.8	7.6×10^{-10}	8.5×10^{-10}

Table 2
Concentration and diffusion coefficients of the electroactive species in 0.1 M TEAP DMSO solution at the different temperatures examined determined by double potential step chronoamperometry.

T (°C)	Reagent concentration (mM)	$D_{\text{2-nitropropane}}$ ($m^2\,s^{-1}$)	$D_{\text{2-nitropropane}}^{\cdot-}$ ($m^2\,s^{-1}$)
23.0	1.6	5.5×10^{-10}	6.2×10^{-10}
29.0	1.5	6.3×10^{-10}	7.0×10^{-10}
35.0	1.4	6.8×10^{-10}	7.7×10^{-10}
42.0	1.5	7.7×10^{-10}	8.6×10^{-10}

Table 3
Concentration and diffusion coefficients of the electroactive species in 0.1 M TBAP DMSO solution at the different temperatures examined determined by double potential step chronoamperometry.

T (°C)	Reagent concentration (mM)	$D_{\text{2-nitropropane}}$ ($m^2\,s^{-1}$)	$D_{\text{2-nitropropane}}^{\cdot-}$ ($m^2\,s^{-1}$)
23.0	1.5	5.6×10^{-10}	6.2×10^{-10}
28.5	1.4	6.4×10^{-10}	7.1×10^{-10}
34.0	1.5	6.9×10^{-10}	7.8×10^{-10}
44.5	0.8	8.0×10^{-10}	8.9×10^{-10}

Table 4
Diffusion activation energy ($E_{a,d}$) and diffusion coefficients at infinite temperature (D_∞) of the electroactive species in 0.1 M TXAP, DMSO solution obtained from the variation of the D-value with temperature.

Supporting electrolyte	$E_{a,d}$ (kJ mol^{-1})		$\ln[D_\infty(\text{cm}^2\,\text{s}^{-1})]$	
	2NPr	2NPr$^{-\cdot}$	2NPr	2NPr$^{-\cdot}$
TMAP	13.3 ± 0.8	13.8 ± 0.7	-6.7 ± 0.3	-6.4 ± 0.3
TEAP	13.2 ± 0.6	13.2 ± 0.6	-6.7 ± 0.2	-6.6 ± 0.3
TBAP	12.6 ± 0.9	13 ± 1	-6.9 ± 0.4	-6.8 ± 0.5

(Metrohm-Autolab BV, Utrecht, Netherlands). Microdisk working electrode of 23 µm radius was fabricated in-house by sealing Pt wire (Goodfellow Cambridge Ltd., UK) into soda glass capillary according to the method laid out by Amatore et al. [9]. The microdisk 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 [10–12]:

$$I = \frac{4FADc_{\text{bulk}}}{\pi r_0}(0.7854 + 0.8862\tau^{-1/2} + 0.2146 \\ \times \exp(-0.7823\tau^{-1/2})) \tag{1}$$

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_{bulk} its bulk concentration (mol cm^{-3}) and r_0 the disk radius (cm). A widely adopted literature diffusion coefficient for ferrocene of $D = 2.3 \times 10^{-9}$ m^2 s^{-1} at 25 °C [13] was used for the calculations.

A mercury hemisphere was then electrochemically deposited onto the microdisk from an aqueous solution of 50 mM $Hg_2(NO_3)_2$ containing 0.1 M KNO_3 acidified to 0.5% with HNO_3 following the
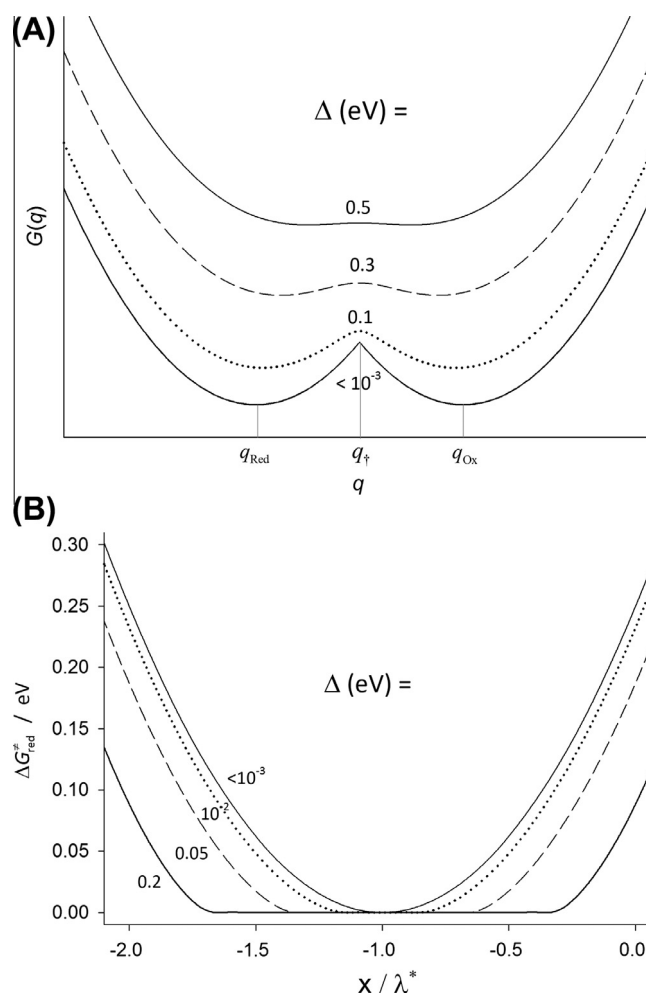

Fig. 1. (A) Potential energy curves corresponding to the redox couple Ox^0/Red^{-1} for different degrees of adiabaticity (Δ values indicated on the graph) calculated from Eq. (7). $\lambda = 1$ eV, $\eta + x = 0$, $T = 298$ K and (B) activation energy for the energy levels at the electrode, x, corresponding to the one-electron reduction of species Ox^0 for different degrees of adiabaticity (Δ values indicated on the graph) calculated from Eq. (10). $\lambda = 1$ eV, $\eta = 0$, $T = 298$ K.