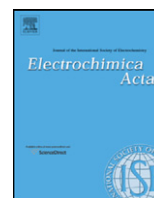




Contents lists available at SciVerse ScienceDirect

Electrochimica Acta

journal homepage: www.elsevier.com/locate/electacta



Variable temperature study of electro-reduction of 3-nitrophenolate via cyclic and square wave voltammetry: Molecular insights into electron transfer processes based on the asymmetric Marcus–Hush model

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ARTICLE INFO

Article history:

Received 5 November 2012

Received in revised form

27 December 2012

Accepted 30 December 2012

Available online xxx

Keywords:

Asymmetric Marcus–Hush model

Variable temperature experiments

Reorganization energy

Adiabaticity

ABSTRACT

In this study, variable temperature experiments have been used in conjunction with numerical fitting of cyclic and square wave voltammogram responses via the asymmetric version of Marcus theory to provide molecular insight into the electroreduction of the 3-nitrophenolate anion in DMSO on mercury hemispherical microelectrodes of 23 μm radius. As a result, the reorganization energy, differences between the inner-sphere force constants of the electroactive species, and the degree of adiabaticity have been evaluated.

Furthermore, a comparison between the quality of fitting obtained through the Butler–Volmer and asymmetric Marcus–Hush models is also presented to examine the relative ability of the kinetic models in predicting voltammetric responses in a range of temperatures and scan rates.

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1. Introduction

The study of molecular characteristics of electrochemical reactions through electrochemical measurements can be carried out using microscopic models of electron transfer processes [1–5]. The most widely used is the Marcus theory [6,7] that relates the rate of electron transfer to the reorganization energy, λ , which parameterizes the energy required to modify the reagent's inner (bond lengths and angles) and outer (orientation of solvent molecules surrounding the reactive species) configurations. However, weaknesses of the *symmetric* version of the Marcus theory (referred here as the Marcus–Hush model for electrode processes, MH) [6–9] have been reported in the literature for the quantitative description of the voltammetry of both diffusional and surface-bound electrode processes [10–26]. A possible explanation for this lies in the validity of the assumption of the inner-sphere and outer-sphere “force constants” of the reduced and oxidized species being equal, which does not necessarily hold true given the structural and charge changes that can take place upon the electron transfer.

In response to this, the *asymmetric* form of the Marcus theory (referred as asymmetric Marcus–Hush model) has been applied recently to the study of electrode reactions [23–26]. This version of the MH model introduces the symmetry parameter, γ , which is associated with the differences between the vibrational modes of the electroactive species.

In this paper the asymmetric MH model is used in variable temperature kinetic studies via cyclic and square wave voltammetry to determine the λ value as well as the degree of adiabaticity of the electroreduction of the 3-nitrophenolate anion in DMSO on a hemispherical mercury microelectrode (radius = 23 μm). Cyclic voltammetry was carried out with scan rates between 0.05 and 2 Vs^{-1} and square wave voltammetry with frequencies ranging between 25 and 200 Hz. Voltammetric measurements were taken within the temperature range of 24–47.5 °C and fitted with Butler–Volmer (BV) and asymmetric MH kinetic models. The kinetic parameters and the quality of the fittings obtained from the different models are quantified and compared at different temperatures. The results obtained offer an extension to the insight of how the reorganization energy and the standard rate constant are affected as the reagent transits from nitro-aliphatic compounds (explored in previous studies [16,24,26]) to nitro-aromatics.

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2. Experimental

2.1. Chemical reagents

3-Nitrophenol (Ph(OH)NO₂, Aldrich, 99%), tetra-n-butylammonium perchlorate (TBAP, Fluka, Puriss grade), tetra-n-butylammonium hydroxide (TBAOH·30H₂O, Aldrich, >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, >99%), acetonitrile (MeCN, Fisher Scientific, HPLC grade), were all used as received without further purification.

The 3-nitrophenolate anion solutions were prepared by adding an excess of base (TBAOH·30H₂O) to the corresponding 3-nitrophenol solutions in the molar ratio of 1.2:1 [27].

2.2. Instrumentation

Cyclic voltammetry with a scan rate range between 50 mV s⁻¹ and 2 V s⁻¹ and potential step chronoamperometry were performed with a computer-controlled Autolab PGSTAT12 (Metrohm-Autolab BV, Utrecht, Netherlands). Microdisc working electrodes of 23 μm radius was fabricated in-house by sealing Pt wire (Goodfellow Cambridge Ltd., UK) into soda glass capillary according to the published method [28]. The platinum disc 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 disc 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 [1,2,29]:

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

where $\tau = 4Dt/r_0^2$, A is the area of the disc (cm²), D the diffusion coefficient of the electroactive species (cm² s⁻¹), c_{bulk} its bulk concentration (mol cm⁻³) and r_0 the disc radius (cm). A widely adopted literature diffusion coefficient for ferrocene of $D = 2.3 \times 10^{-9}$ m² s⁻¹ [30] was employed for the calculations.

A mercury hemisphere was then electrochemically deposited onto the microdisc from a 50 mM Hg₂(NO₃)₂ solution containing 0.1 M KNO₃ and acidified to 0.5% with HNO₃ following the method laid out by Mauzeroll et al. [31]. 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.

A platinum mesh 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 electrode was characterized by optical and electrochemical methods.

Visual measurement of the hemisphere was obtained through the use of 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



Fig. 1. Image of the 23 μm radius electrodeposited hemisphere immersed in DMSO.

adopted the radius of the microdisc. An image of the 23 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]Cl₃ and 0.1 M KNO₃, which is given by the following expression in the case of electrodes with spherical geometry [1,2]:

$$I = FADc_{\text{bulk}} \left(\frac{1}{\sqrt{\pi Dt}} + \frac{1}{r_0} \right) \quad (2)$$

where the symbols have their usual meaning.

The value of the diffusion coefficient of [CoSep]Cl₃ employed for the calculations was $D = 6.3 \times 10^{-10}$ m² s⁻¹. This was determined from chronoamperograms recorded at microdisc electrode of known dimensions from Eq. (2) and it is in close agreement with literature [32,33].

The radius obtained through the analysis of the chronoamperogram coincides with that determined with the optical measurements outlined previously.

2.4. Cyclic voltammetry, square wave voltammetry and potential step chronoamperometry measurements

Cyclic voltammograms within the scan rate range of 50 mV s⁻¹ to 2 V s⁻¹ were recorded between -0.35 and -0.90 V (vs Ag wire) on 23 μm radius mercury hemispherical electrode. Four sets of voltammograms, each recorded at a different temperature (24.0, 30.8, 39.0 and 47.5 °C), were obtained. All the solutions contained 0.1 M TBAP background electrolyte in DMSO solvent.

Square wave voltammograms were recorded between -0.48 and -0.95 V (vs Ag wire) with a potential step and amplitude of 15 mV. Frequencies used cover the range between 25 and 200 Hz.

Double potential step chronoamperometry was recorded for each experimental set conducted in the current study. The potential was stepped from -0.45 V where there is no faradaic current to -0.85 V (vs Ag wire) where the reduction current is fully controlled by diffusion and was held for 0.5 s and then abruptly stepped back to -0.45 V for further 0.5 s. The resulting chronoamperometric response was simultaneously fitted for both the diffusion coefficients and concentration of the electroactive species using the previously reported method [34–36].

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