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Electrochemical investigations of dissolved and surface immobilised 2-amino-1,4-naphthoquinones in aqueous solutions

L. Bouffier [a,b], K.E. Lister [a], S.J. Higgins [a], R.J. Nichols [a], Th. Doneux [a,c,*]

[a] Department of Chemistry, University of Liverpool, Crown Street, Liverpool L69 7ZD, United Kingdom
[b] Université de Bordeaux, ISM, CNRS UMR 5255, F-33400 Talence, France
[c] Chimie Analytique et Chimie des Interfaces, Faculté des Sciences, Université Libre de Bruxelles, Boulevard du Triomphe, 2, CP 255, B-1050 Bruxelles, Belgium

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ABSTRACT

The electrochemistry of proton coupled electron transfer phenomena is an important contemporary topic in molecular and interfacial electrochemistry, due to its significance in important organic and bioelectrochemical processes. We report here on the synthesis, self-assembly and electrochemical characterisation of amino-naphthoquinones derivatives on gold electrodes, which provide strong test-beds for such electrochemical processes. Voltammetric analysis of these systems and comparisons between buffered and unbuffered solutions give insights in the electrochemistry of the proton coupled electron transfer phenomenon. The solution electrochemistry of three of these derivatives is analysed with respect to the different side groups on the amino moiety, while the fourth derivative can be self-assembled on the gold electrode through a thiol attachment. The latter enables a Laviron analysis and quantification of the apparent electron transfer rate constant $k_s \approx 2 \times 10^2\ s^{-1}$, this value being barely affected by the buffering conditions. However, switching from buffered to non-buffered solution markedly changed the voltammetric features of the redox active monolayer. While only one cathodic peak and one anodic peak were recorded in phosphate buffer solutions, one or two anodic peaks were observed in $KClO_4$ depending on the scan rate, in very good agreement with recent theoretical works.

1. Introduction

The electrochemistry of quinones has enjoyed a long standing interest from the scientific community dating back to the early days of polarography to the present days [1,2]. Such sustained interest has been maintained through the many applications of quinones, ranging from their biochemical role in photosynthesis and biological activity to their use in industrial processes or the development of nanoscience-based devices. This latter aspect is mainly concerned with the fabrication of self-assembled monolayers (SAMs) containing quinone moieties. Like other redox-active SAMs, these monolayers take advantage of the redox properties of quinones to confer some particular functionalities to the modified surface. For example, quinones have been used as building blocks for electrochemically controlled post-assembly strategies [3–9] or, conversely, for the electrochemically triggered release of biochemical ligands [10,11].

At a more fundamental level, quinones are currently used, both in solution and immobilised on surfaces, as model systems to understand the electrochemistry of proton coupled electron transfer phenomena [12–19]. Our work takes place in this context, presenting the electrochemical behaviour in buffered and non-buffered conditions of a novel quinone compound, 2,2′-dithiobis[ethyl-amino(naphthalene-1,4-dione)], self assembled on gold electrodes. Other 2-amino-1,4-naphthoquinones, dissolved in solution, are used as reference systems to help interpret the voltammetric response of the immobilised naphthoquinone (NQ). A few reports have already been devoted to the synthesis, self-assembly and electrochemical characterisation of NQ derivatives immobilised on gold electrodes [18,20–27]. Naphthoquinone occurs naturally as the core structure of the vitamin K family, involved in various biological processes. The biological activity of NQ derivatives, including 2-amino-naphthoquinones, is related to their electrochemical properties and has thus been investigated for years [28,29], most recently as photosystem I electron acceptors [30] and as potential anti-tumor agents [31–33].

2. Experimental

2.1. Reagents and chemicals

Cystamine dihydrochloride (Aldrich, purum, ⩾99.0%), 4-aminobenzoic acid (Aldrich, 99.0%); glycine, ethanolamine, KH_2PO_4,

* Corresponding author at: Chimie Analytique et Chimie des Interfaces, Faculté des Sciences, Université Libre de Bruxelles, Boulevard du Triomphe, 2, CP 255, B-1050 Bruxelles, Belgium. Tel.: +32 2 650 57 18; fax: +32 2 650 29 34.
E-mail address: tdoneux@ulb.ac.be (Th. Doneux).

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$K_2HPO_4.3H_2O$, KOH, $HClO_4$ 70% (all from Fluka, puriss., p.a.) and 1,4-naphthoquinone (Alfa Aesar, 97 + %) were used without further purification. Potassium perchlorate (Fluka, puriss. ⩾99.0%) was recrystallized in ultrapure water. Aqueous solutions were prepared with ultrapure water from a Milli-Q® system (Millipore), and the other solvents were of analytical grade. The phosphate buffer solution was 0.025 M KH_2PO_4 + 0.025 M K_2HPO_4, with a resulting pH of 6.9. For the unbuffered solution, the pH was adjusted to 6.9 ± 0.2 by addition of KOH in the 0.1 M $KClO_4$ solution containing the dissolved naphthoquinone.

2.2. Apparatus and methods

2.2.1. NMR spectroscopy

NMR spectroscopy was recorded on a Bruker (400 MHz) machine equipped with a 5 mm QNP $^1H/^{13}C$ probe. The chemical shift (δ) was referred either to the signal of TMS (δ_H = 0.00 ppm) or to the residual signal of the DMSO (δ_H = 2.50 ppm and δ_C = 39.52 ppm).

2.3. Mass spectrometry

Mass spectrometry was recorded onto an electrospray instrument (Micromass Liquid Chromatography Time-of-flight) in positive ionisation mode (ES+) from solutions in methanol +0.1–0.2% formic acid.

2.3.1. Fourier transform infrared spectrometry

Fourier transform infrared (FTIR) spectra were obtained from powder samples on a JASCO FT/IR-4200 type A spectrometer equipped with a standard source and a TGS detector. In each case, 100 spectra in the region from 600 to 4000 cm^{-1} were accumulated at a resolution of 4 cm^{-1}. Automatic baseline correction was applied using the JASCO spectra manager version 2 software.

2.3.2. Electronic absorption spectroscopy

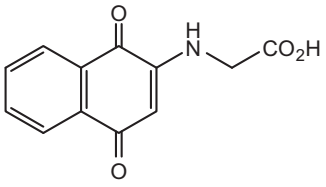
Electronic absorption spectra were obtained from powder samples on a Perkin-Elmer Lambda 650S UV/VIS spectrometer equipped with deuterium and tungsten halogen light sources, high-sensitivity photomultiplier and Peltier-controlled PbS detectors. Spectra were recorded in the region from 190 to 900 nm with a resolution of one point per nm. The naphthoquinone sample was ground with potassium bromide at a concentration of about 1–2 weight percent. The electronic spectrum is plotted taking the maxima of the lowest-energy absorption arbitrarily as 1.00.

2.3.3. Electrochemical measurements

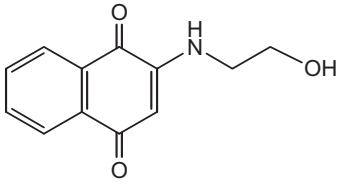
The electrochemical experiments were conducted in a three-electrode cell, comprised of a gold wire as the working electrode, a saturated calomel electrode (SCE) as the reference electrode and a platinum grid as the counter electrode, connected to an Autolab PGSTAT 20 (EcoChemie, Metrohm) potentiostat. Prior to each experiment, the working and counter electrode were cleaned in a Bunsen flame, and nitrogen was bubbled for 20 min through the solution to remove dissolved oxygen. A nitrogen atmosphere was kept above the solution throughout the measurements.

2.4. Synthesis

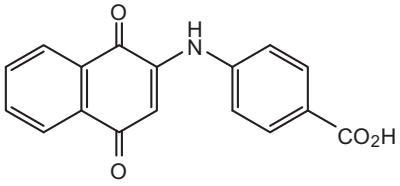
Regioselective mono-functionalisation of 1,4-naphthoquinone was achieved by a nucleophilic addition reaction (i.e. Michael addition) using primary amines as nucleophiles. The structures of the synthesized compounds are depicted in Scheme 1.



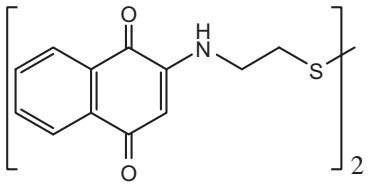
NQ1 = 2-([1-Carboxymethylamino])naphthalene-1,4-dione



NQ2 = 2-([2-Hydroxyethyl]amino)naphthalene-1,4-dione



NQ3 = 2-[4-Carboxyanilino]naphthalene-1,4-dione



NQ4 = 2,2'-Dithiobis[ethyl-amino(naphthalene-1,4-dione)]

Scheme 1. Structure of the investigated 2-amino-1,4-naphthoquinones (NQ1–4).

2.4.1. 2-([1-Carboxymethylamino])naphthalene-1,4-dione (NQ1)

A solution of glycine (0.3832 g, 5.10 mmol) in water (5 mL) was added to a solution of 1,4-naphthoquinone (0.7988 g, 5.05 mmol) in ethanol (95 mL). Then DIPEA (1 mL, 5.74 mmol) was added to the mixture which was stirred for 4 days at room temperature. After evaporation to dryness, the crude mixture was extracted with H_2O/HCl (150 mL, pH ≈ 2–3) and CH_2Cl_2 (3 × 100 mL). The organic layers were collected, dried over sodium sulphate and concentrated under vacuum. The product NQ1 (0.3859 g, 1.67 mmol) was thus isolated in 33% yield.

The NMR spectra were consistent with previously reported data [34].

^1H NMR (400 MHz, DMSO-d6 + TMS) δppm = 8.01 (1H, dd, J = 7.6 and 1.3 Hz), 7.94 (1H, dd, J = 7.6 and 1.3 Hz), 7.84 (1H, td, J = 7.5 and 1.3 Hz), 7.75 (1H, td, J = 7.5 and 1.3 Hz), 7.43 (1H, t broad, $J \approx 6.2$ Hz, NH), 5.63 (1H, s), 3.99 (2H, d, J = 6.2 Hz, CH_2). ^{13}C NMR (100 MHz, DMSO-d6) δppm = 181.6 C═O), 181.3 (C═O), 170.0 (CO_2H), 148.2, 134.9, 132.8, 132.3, 130.1, 125.9 (CH), 125.3 (CH), 100.7 (CH), 43.4 (CH_2). HRMS (TOF ES+) m/z $[M + H]^+$ calculated for $C_{12}H_{10}NO_4$ 232.0610, found 232.0617.