



Nitroxyl radical self-assembled monolayers on gold: Experimental data vs. Laviron's interaction model

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ABSTRACT

Mixed SAMs of nitroxyl radical derivative and alkanethiol have been studied by cyclic voltammetry in both aqueous and non-aqueous solvents. Cyclic voltammograms exhibit shapes as a function of surface coverage deviating from an “ideal system”. Confronted to Laviron's interaction model, the agreement observed between theory and experiments provides evidence of a random distribution of electroactive centers on surface and indicates that the local ionic environment of charged redox centers plays a major role in the electrochemical behaviour of SAMs.

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1. Introduction

TEMPO (2,2,6,6-tetramethylpiperidine-1-oxyl) and its derivatives have been extensively studied in the search for organic synthesis as a redox mediator, mostly for the oxidation of primary alcohols [1–4]. The electrochemical oxidation of TEMPO is known to be a stable and reversible one-electron process in both aqueous [5–7] and non-aqueous electrolytes [8,9]. Despite the wide electrochemical applications of nitroxyl radical, rare works have been devoted to design and elaborate redox-responsive TEMPO self-assembled monolayers (SAMs) [10–12]. In 1997, Fuchigami et al. [10], then Kashiwagi et al. [11] in 1999, have reported the first electrocatalysis attempts of alcohols and amines in acetonitrile. In 2008, Finklea et al. [12] have worked on Au–S(CH₂)₁₀C(O)N(H)–TEMPO SAM to the first estimation of the standard rate constant and the reorganization energies of TEMPO/TEMPO⁺ in 1 M H₂SO₄. Recently, we have shown that nitroxyl radical SAMs afford a noteworthy electrocatalytic activity in both aqueous and organic media [13].

Here, we focused our attention on the shape of cyclic voltammograms (CVs) of mixed SAMs of nitroxyl radical derivative and alkanethiol in order to confront the experimental data with the Laviron's interaction model.

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2. Experimental

The synthesis and characterisations of nitroxyl radical derivatives **1a**, **1b** and **1c** (Scheme 1) were described in Ref. [13].

Electrochemical experiments were carried out with a Biologic SP-150 potentiostat at 293 K. Cyclic voltammetry was performed in a three-electrode cell equipped with a platinum-plate counter electrode. Reference electrodes were Ag/AgNO₃ (0.01 M CH₃CN) or Ag/AgCl/KCl_{sat}. CVs were recorded in dry HPLC-grade methylene chloride (CH₂Cl₂), HPLC-grade acetonitrile (CH₃CN) or H₂O (18 MΩ). Supporting electrolytes were tetrabutylammonium hexafluorophosphate (nBu₄NPF₆), sodium hexafluorophosphate (NaPF₆), tetrabutylammonium perchlorate (nBu₄NClO₄) or sodium perchlorate (NaClO₄).

The Au substrates were described in Ref. [14].

3. Results and discussion

3.1. Experimental data

In solution, cyclic voltammograms of **1a**, **1b** or **1c** exhibit a reversible one-electron process close to 0.56 V in CH₂Cl₂ and 0.41 V in CH₃CN (vs. Ag/AgNO₃ in 0.1 M Bu₄NPF₆), respectively [13].

Electrochemical behaviour of mixed SAMs was studied in CH₂Cl₂, in CH₃CN and H₂O. In aqueous and non-aqueous media, the shape of voltammetric waves and the linear dependency between peak intensities and scan rates were characteristic of surface-confined redox species [13]. CVs parameters are quasi

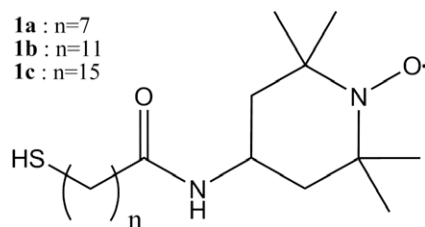
Scheme 1. Nitroxyl radical derivatives **1a**, **1b** and **1c**.

Table 1
CV parameters and interaction parameters of SAMs prepared from **1c**.

Media	At 0.1 V s ⁻¹	CH ₂ Cl ₂ ^a	MeCN ^a	H ₂ O ^b
0.1 M nBu ₄ NPF ₆	Γ (mol cm ⁻²)	4.7×10^{-10}	5.3×10^{-10}	–
	FWHM (mV)	36	113	–
	E_p (V)	0.48 ^a	0.51 ^a	–
	$r_{O_c}^c$	+1.14	–0.64	–
	$r_{R_c}^c$	0	0	–
0.1 M nBu ₄ NClO ₄	Γ (mol cm ⁻²)	4.7×10^{-10}	5.0×10^{-10}	–
	FWHM (mV)	32	71	–
	E_p (V)	0.48	0.45	–
	$r_{O_c}^c$	+1.25	+0.30	–
	$r_{R_c}^c$	0	0	–
0.1 M NaPF ₆	Γ (mol cm ⁻²)	–	4.8×10^{-10}	5.6×10^{-10}
	FWHM (mV)	–	104	84
	E_p (V)	–	0.45	0.69
	$r_{O_c}^c$	–	–0.27	+0.12
	$r_{R_c}^c$	–	0	0
0.1 M NaClO ₄	Γ (mol cm ⁻²)	–	5.7×10^{-10}	5.0×10^{-10}
	FWHM (mV)	–	71	94
	E_p (V)	–	0.44 ^a	0.71 ^b
	$r_{O_c}^c$	–	+0.34	~0
	$r_{R_c}^c$	–	0	0

^a vs. Ag/AgNO₃ (0.01 M).

^b vs. Ag/AgCl/KCl_{sat}.

^c vs. Standard deviation ~0.08.

chain-length (n) independent. Interestingly, shapes of voltammetric waves are solvent and supporting electrolyte dependent (Table 1). In CH₂Cl₂ and CH₃CN, the full width at half maximum (FWHM) deviate from the expected value (i.e. ~89 mV at 293 K) of an “ideal system”, corresponding e.g. to a Langmuir model.

The interfacial electron transfer process and the interactions between the immobilized functional moieties have been studied

widely to clarify the “non-ideality” of experimental data [15–24] but it still remains an open-ended question.

An approach to understand this striking behaviour is to dilute the electroactive species in the monolayer by mixing alkanethiols [25]. Indeed, CVs of mixed SAMs, prepared from **1a**, **1b** or **1c**:alkanethiol mixtures, exhibit a noteworthy surface coverage dependence (Fig. 1).

3.2. Laviron's interaction model

In experiments, the criteria for ideality are rarely met and interaction models have to be developed in order to extract information about the adsorbed redox system of interest. In the last 30–35 years, several models were developed [26–30]. Among these models, only two satisfy the diagnostic criteria [30] to predict current–voltage (i – E) wave shape in CV experiments on electroactive SAM: Laviron's model and Smith and White's approaches. In the Seventies, Laviron developed an interaction model, focused exclusively on non-idealities caused by lateral interactions [26]. This approach, refined by Anson [27], relied on finding values of interaction coefficients which produced good fits with experimental data. In 1992, the elegant electrostatic model of Smith and White [28], then refined by Yoneyama et al. [29], provided an analytical expression for the interfacial potential distribution. However, because electrostatic approaches require intricate mathematical treatments, we are focused on Laviron's model.

According to the specific hypothesis developed by Laviron (Frumkin model),

- The electroactive centers are random distributed on substrate, despite interactions,
- a_{OO} , a_{RR} and a_{OR} are the interaction constants between molecules of O, molecules of R and molecules of O and R, respectively (a_i is positive for an attraction and negative for a repulsion; the a values are assumed to be independent of the potential),

the i – E characteristic (IUPAC convention) can then be written [26a]:

$$\begin{cases} i(t) = nFAk_s \Gamma_{\max} [\theta_O(t) \eta^{-\alpha} \exp(-2a_{OO}\theta_O(t) - 2a_{OR}\theta_R(t)) \\ - \theta_R(t) \eta^{1-\alpha} \exp(-2a_{RR}\theta_R(t) - 2a_{OR}\theta_O(t))] \\ i(t) = -nFA \Gamma_{\max} \left[\frac{d\theta_O(t)}{dt} \right] = nFA \Gamma_{\max} \left[\frac{d\theta_R(t)}{dt} \right] \end{cases}$$

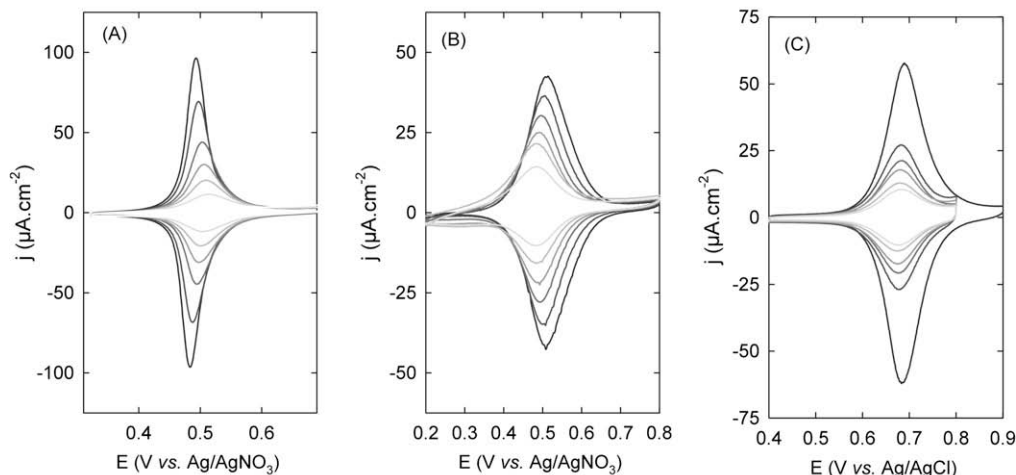


Fig. 1. (A) Experimental CVs of SAM in 0.1 M nBu₄NPF₆/CH₂Cl₂, prepared from different **1c**:decanethiol ratios, leading to 4.7, 3.7, 2.8, 2.1, 1.4 and 0.8 × 10⁻¹⁰ mol cm⁻². (B) Experimental CVs of SAM in 0.1 M nBu₄NPF₆/CH₃CN, prepared from different **1c**:decanethiol ratios, leading to 4.6, 3.3, 2.7, 2.3, 1.8 and 1.4 × 10⁻¹⁰ mol cm⁻². (C) Experimental CVs of SAM in 0.1 M NaPF₆/H₂O, prepared from different **1c**:decanethiol ratios, leading to 5.3, 2.7, 2.2, 1.9, 1.3 and 1.0 × 10⁻¹⁰ mol cm⁻². All CVs were performed at 0.1 V s⁻¹.

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