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Determination of the isomeric forms proportion of fluorogenic naphthalene-2,3-dicarboxaldehyde in a binary mixture of water: methanol using electrochemical methods

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ABSTRACT

The electrochemical response of the fluorogenic label naphthalene-2,3-dicarboxaldehyde (NDA) in a binary mixture of water/methanol was characterized with cyclic voltammetry (CV) and differential pulse voltammetry (DPV) electrochemical techniques. Naphthalene-2,3-dicarboxaldehyde does exist in three isomeric forms in aqueous solution: the unhydrated dialdehyde (DA), the acyclic monohydrated (MA) and the cyclic hemiacetal (HAC). The study underlines that the proportion of each of them varies according to the working pH. At low and high pH, the dialdehyde form is in larger proportion than the acyclic monohydrated form. Conversely at intermediate pH, the concentration of the acyclic form is in greater proportion than the dialdehyde form. These results allowed us to determine the optimal pH of 9 for which the labeling of biomolecules could be more efficient due to the base catalyzed regeneration of the unhydrated form. At this pH, the data processing from the analysis of measured currents and estimation of diffusion coefficients of each form according to the semi-empirical models of Wilke–Chang, Scheibel, Reddy–Doraiswamy and Lusi–Ratcliff allowed us to obtain the concentration of dialdehyde (0.28 mM), acyclic monohydrated (0.57 mM) and cyclic hemiacetal monohydrated (0.15 mM) forms starting from 1 mM naphthalene-2,3-dicarboxaldehyde.

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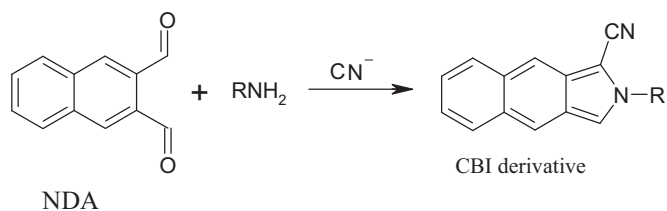
1. Introduction

Detection of peptides or amino acids is generally done after a derivatization step. The compound labeled is generally fluorescent, electrochemically active or both, depending on the detection method implemented. One of the fluorogenic reagent commonly used for the derivatization of RNH₂ group is the naphthalene-2,3-dicarboxaldehyde, NDA (see Scheme 1) which forms the N-2-substituted-1-cyanobenz-[f]-isoindole derivative (CBI) that is known as being electroactive and fluorescent [1–20]. Most derivatization steps using NDA were made in borate or phosphate buffered solution in the presence of acetonitrile (ACN) or methanol (MeOH) mainly used in order to increase its solubility [18–20]. However, excepted Zuman et al. [21–28] few studies have been focused on the electrochemical response of NDA alone. They investigated on the orthophthalaldehyde (OPA) and NDA

polarographic current–voltage curves and have shown the importance of taking into account the hydrated forms [25,26]. They first mentioned that NDA was present under three isomeric forms in solution: the unhydrated dialdehyde (DA), the acyclic monohydrated (MA) and the cyclic hemiacetal (HAC) (see Scheme 2). However, in the water/ACN mixture, NDA was mostly under the cyclic hemiacetal form while the DA form (useful for the labeling step) was in low concentration level [26]. This study is focused on the electrochemical response of the NDA in a binary water/methanol mixture, traditionally used for capillary electrophoresis coupled to fluorescence detection (CE-LIF) of proteins [18,20] by the use of two electrochemical techniques that are cyclic voltammetry (CV) and differential pulse voltammetry (DPV). The data processing from the analysis of measured peak current and estimation of diffusion coefficients of each isomeric form following the semi-empirical models of Wilke–Chang [29], Scheibel [30], Reddy–Doraiswamy [31] and Lusi–Ratcliff [32] allowed us to measure the concentration of each NDA isomeric form.

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Scheme 1. Derivatization reaction of primary amine by NDA in presence of KCN.

2. Experimental

2.1. Chemicals and reagents

NDA and boric acid were purchased from Sigma Aldrich (Saint-Quentin Fallavier, France). Methanol and sodium hydroxide were obtained from VWR (Fontenay-sous-Bois, France).

Preparation 0.1 M Borate buffer was performed by mixing boric acid solution and sodium hydroxide solution. The desired pH 9 was adjusted with HCl addition. NDA was dissolved in a binary mixture 0.1 M borate/methanol (50/50 v/v). The pH range was corrected according to the pH correlation for water/methanol mixtures established by Bosch et al. [33].

2.2. Instrumentation

Electrochemical measurements were performed using a Biologic SP-300 electrochemical analysis system with EC-lab software. Experiments were done with a three-electrode cell configuration. The reference and the counter electrodes were a saturated calomel electrode (SCE, $E = +0.241$ V/NHE at 25 °C) and a platinum grid (Pt), respectively. The working electrode was a glassy carbon disk with an area of 0.071 cm². DPV parameters were modulation time (100 ms), modulation amplitude (7.5 mV) and scan rate (25 mV s⁻¹). Baselines were recorded after DPV response with a blank solution.

3. Results and discussion

3.1. Scan rate and concentration dependences

The preliminary measurement displayed in Fig. 1A is performed using CV in a binary mixture 0.1 M borate/methanol buffer at pH 9. On the voltammogram of Fig. 1A, NDA highlights two electrochemically irreversible reduction waves named 1 and 2 that are located at -1.1 V/SCE and -1.4 V/SCE for a scan rate of 100 mV s⁻¹, respectively. The DPV electrochemical response in the same solution buffer is given on Fig. 1B. The first peak potential is located at -1.11 V/SCE, and that of the second peak at -1.34 V/SCE for a scan rate of 25 mV s⁻¹. The advantages and usefulness of DPV technique will be discussed below.

By analogy with OPA reduction in water/acetonitrile mixtures described in the literature by using polarographic technique, the two reduction waves can be ascribed to the successive reduction of the aldehyde groups [25,26]. Indeed, each peak was the result of the two electrons two protons reduction of an aldehyde group. On

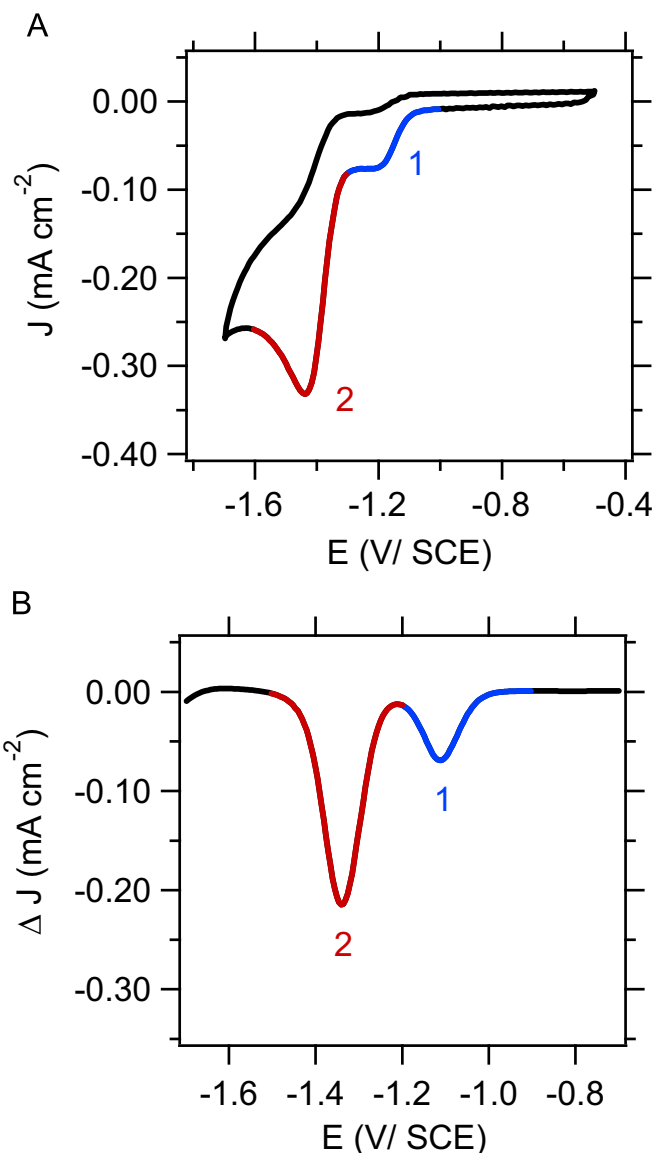
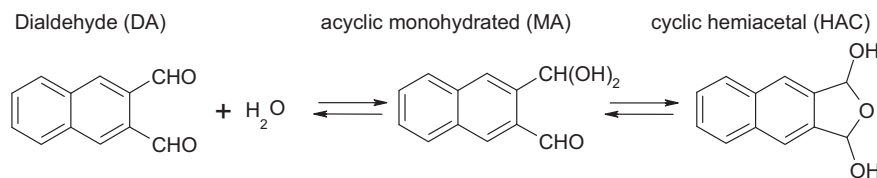


Fig. 1. Electrochemical response for 1 mM NDA in a binary mixture 0.1 M borate/methanol buffer at pH 9 on a glassy carbon electrode ($S = 0.071$ cm²) at 100 mV s⁻¹. A. Cyclic voltammetry. B. Differential pulse voltammetry (see Section 2).

the other hand, the obtained ratio of the current densities for peaks 1 and 2 (J_2/J_1) was higher than 1. It can not therefore be only a subsequent 2 electrons reduction occurring at more negative potentials of the product formed during the first reduction. Indeed, the J_2/J_1 ratio was found equal to 4.0 for a scan rate of 100 mV s⁻¹. The observed high current density for peak 2 is probably due to two reactions occurring at -1.4 V/SCE. We therefore suggest that the reduction of the second aldehyde group on the DA form occurs concomitantly with the second reduction of the former MA, following the mechanism displayed in Scheme 3.

In the following, we present the study of the variation of peak



Scheme 2. Hydration scheme reaction and equilibrium hydration of NDA in aqueous solution.

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