



Bidimensional Spectroelectrochemistry: application of a new device in the study of a *o*-vanillin-copper(II) complex



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ABSTRACT

A new bidimensional spectroelectrochemistry setup for UV-Vis absorption measurements has been developed. The new device has been used to follow electrochemical reactions using two different arrangements: 1) a near-normal configuration that supplies information about the processes taking place both on the electrode surface and in the solution adjacent to it, and 2) a long-optical-pathway configuration based on a mobile slit that controls the position of a light beam passing parallel and adjacent to the electrode surface providing information only about the processes taking place in solution during the electrochemical reaction. The new setup has been validated using *o*-tolidine, a typical reference system for spectroelectrochemistry. The electrochemical mechanism of oxidation/reduction of Cu(*o*-Va)₂(H₂O)₂ complex (*o*-Va = *o*-Vanillin = 2-hydroxy-3-methoxybenzaldehyde) has been studied using bidimensional UV-Vis absorption spectroelectrochemistry. This Cu(II) complex exhibits antimutagenic, anticarcinogenic and superoxide dismutase mimic properties.

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1. Introduction

Spectroelectrochemistry (SEC) is a powerful instrumental technique that combines two classical analytical techniques, such as electrochemistry and spectroscopy, to obtain *in situ* chemical information [1–6] about the reactions taking place during an electrochemical experiment. Usually, the electrochemical technique controls the chemical process, while spectroscopy provides molecular information about chemical compounds involved in the process, being complementary to the electrochemical information. Since 1964, when Kuwana proposed this technique [7], many approaches using different experimental setups [8–14] have been proposed to improve the quality and significance of the spectroelectrochemical experiments, trying to shed more light on the processes involved in the electrochemical reactions.

UV-Vis absorption spectroelectrochemistry can be performed in two different optical configurations, taking into account the position of the light beam with respect to the working electrode: normal [15,16] and parallel [17–19] arrangement. On the one hand, in normal configuration the light beam goes through the diffusion

layer perpendicularly to the working electrode surface. In this case, a transmission [20,21] or a reflectance [22,23] experimental setup can be used. On the other hand, in parallel configuration, also known as long-optical-pathway configuration, the light beam passes parallel to the electrode surface, with the light beam sampling the adjacent solution to the electrode surface [19,24,25]. Each configuration provides different type of information about the processes occurring at the electrode surface. Normal configuration mainly supplies information about the whole diffusion layer, including the compounds adsorbed or crystallized on the electrode surface, but also a small contribution of species in the solution near the electrode can be obtained. However, parallel configuration only provides information about the processes occurring in the solution close to the electrode. Besides, this second arrangement guarantees a longer optical pathway than in normal configuration. The main drawback of parallel configuration is the lack of sensitivity to adsorption/crystallization phenomena taking place on the electrode surface.

Usually, only one of these configurations is chosen depending on the chemical problem, but in many cases both kind of information are necessary to fully understand the studied chemical system. In this respect, bidimensional spectroelectrochemistry (BSEC) [26] allows us to perform simultaneously measurements in the two configurations, obtaining in only one experiment a more

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complete picture on the electrode processes. The main disadvantage of BSEC is the complexity of the spectroelectrochemical cells to get reproducible and good enough experimental results. Recently this problem has been minimized using optical fibers, simplifying the correct alignment of the light beam and improving the reproducibility of the experiment [27]. In this work, another setup with specific improvements is proposed for BSEC. On one hand we use a simple three electrode system placed in a spectrophotometric cuvette together with a reflection probe for normal configuration measurements. On the other, we use piezoelectric positioners to control the position of a slit that allows us to place the light beam adjacent to the electrode at controlled distances. Thus, although parallel beam alignment is usually very complex and troublesome, by using this new approach, previously tested with liquid/liquid interfaces [20], the experiments can be performed in a very simple and easy way.

Firstly, *o*-tolidine has been selected as reference system to prove the good performance of this new spectroelectrochemical setup [26,28,29]. Finally, BSEC has been used to study the electrochemical mechanism of reaction of, $[\text{Cu}(o\text{-Va})_2(\text{H}_2\text{O})_2]$ complex (*o*-Va = *o*-vanillin = 2-hydroxy-3-methoxybenzaldehyde).

Copper can be coordinated by ligands with therapeutic properties, often with a synergic effect on the activity, as the metal center improves the mobility and bio availability of the agent. The studied compound, Cu-*o*-Va is an antimutagenic, anticarcinogenic agent and exhibits superoxide dismutase (SOD) mimic properties. In particular, the ligand *o*-vanillin, as other related hydroxyaldehydes, has demonstrated antimutagenic and carcinogenesis inhibitory activities and is also an antioxidant agent and scavenger of free radicals. It has been employed in the syntheses of many active poly-functional ligands, including those belonging to the Schiff Bases family, that form many active copper complexes, among other metals.

In this work we report the usefulness of the new BSEC spectroelectrochemical setup proposed to understand the complex electrochemistry of $[\text{Cu}(o\text{-Va})_2(\text{H}_2\text{O})_2]$ in dimethylsulfoxide solution.

2. Experimental

2.1. Chemicals and Materials

o-Tolidine (Sigma-Aldrich), *o*-vanillin (*o*-Va, Sigma-Aldrich), tetrabutylammonium hexafluorophosphate (TBAPF₆, Merck), dimethylsulfoxide (DMSO, Sigma-Aldrich), acetic acid (HAc, Acros) and perchloric acid (HClO₄, Acros) are analytical grade and used as received without further purification. $[\text{Cu}(o\text{-Va})_2(\text{H}_2\text{O})_2]$ was prepared according to a reported synthesis procedure [30,31] from equimolar amounts of *o*-Va and $\text{Cu}(\text{CH}_3\text{COO})_2$. *o*-Va was dissolved in methanol and dropwise added, under continuous stirring to a 2:1 methanol:water solution of $\text{Cu}(\text{CH}_3\text{COO})_2$. The mixture was stirred for 30 min, and the left to stand at room temperature until bright yellowish green monocrystals were obtained. Deionized water with a resistivity of 18 MΩ cm (Milli-Q purification system, Millipore), is used to prepare aqueous solutions. Analytical grade DMSO (Fisher Chemical) was used for prepared nonaqueous solutions. For safety considerations, all handling and processing were performed carefully particularly when *o*-tolidine and DMSO was used.

2.2. Instrumentation

A new experimental setup (Fig. 1 and Figure S11) has been developed to perform BSEC experiments using a mobile slit to locate the desired position of the light beam in the parallel arrangement. The experimental setup used for BSEC measurements to control the

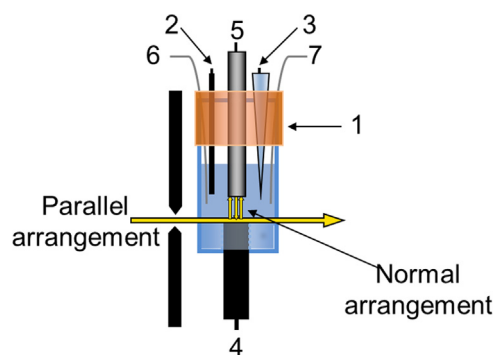


Fig. 1. Scheme of the spectroelectrochemical cell. (1) Suba-Seal septa, (2) auxiliary electrode, (3) reference electrode, (4) working electrode, (5) reflection probe, (6) N₂ inlet, (7) N₂ outlet.

motion of the slit are based on previous works [18], where a detailed description of the device can be found. In the present work, the previous liquid/liquid interface is replaced by a solid electrode. The mobile slit device consists of a rigid block supporting the slit and the lenses, attached to the positioner in order to transmit the motorized actuator movement to the whole block. The slit is located between two collimating lenses with fitted optical fibers. Normal arrangement is based on a near-normal incident reflection spectroelectrochemical configuration (NNIRS) [32,33]. Spectroelectrochemical experiments were carried out using a PGSTAT 302N potentiostat (Eco Chemie B.V) coupled to two QE65000 Spectrometers (Ocean Optics) one for each configuration. The potentiostat and the two spectrometers were exactly synchronized with an external trigger. The common end of a 200-μm bifurcated fiber (Ocean Optics) was connected to a DH-2000 Deuterium-halogen light source (Ocean Optics). One of the fibers end of the bifurcated fiber is attached to a 450-μm diameter optical fiber (Ocean Optics) and used for parallel configuration measurements, while the other fiber end is connected to a reflection probe (FCR-7UV200-2-1.5 × 1SR, Avantes) to perform normal configuration measurements. The reflection probe is connected to the other spectrometer. The 450-μm diameter optical fiber in parallel configuration leads the light beam from the light source to a collimating lens that is fixed to the holder before crossing the solution. The light beam after sampling the solution in parallel configuration is collected by a collimating lens and is conducted to the spectrometer using a 450-μm diameter optical fiber (Ocean Optics).

The last and central part of this setup is the spectroelectrochemical cell (Fig. 1). It consists of a three-electrode system with a glassy carbon disk as working electrode (WE), a platinum wire as auxiliary electrode (AE) and a home-made Ag/AgCl/3 M KCl reference electrode (RE). The three-electrode system is placed in a modified commercial quartz spectrophotometric cuvette 110-QS (Hellma) to properly perform simultaneously the experiment in the two spectroscopic configurations. Thus, the bottom part of the quartz cuvette was cut to fill it with the corresponding solution and to place the reflection probe and the reference and auxiliary electrodes. The WE was placed in the cuvette hole usually used to fill the cuvette, sealing the electrode with Teflon tape to avoid any leakage of the solution when the cuvette is placed in an inverted position during a BSEC experiment. Next, a Suba-Seal septa with five drilled holes is used to close the upper part of cuvette and to properly fix the reference and the auxiliary electrode, the reflection probe, the nitrogen inlet and outlet, and to avoid any interference with the light beam in parallel configuration.

All the experiments were performed in a semiinfinite diffusion regime. Actually, this is the most used diffusion regime in electrochemistry. Although thin-layer cells are commonly used in spectroelectrochemistry to obtain formal potentials and number

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