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## pH- and temperature-responsive redox behavior of hydroxyanthracenediones



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### ABSTRACT

The redox response of three anthracenediones; 4,8-dihydroxy-9,10-dioxo-9,10-dihydroanthracen-1-yl acetate (HACAD), 1,4,5-trihydroxyanthracene-9,10-dione (HAD) and 1,4,5-trihydroxy-2-methyl-3-(3-oxobutyl)anthracene-9,10-dione (HOAD) was probed at the surface of a glassy carbon electrode (GCE) over a wide pH range from pH 3 to pH 12 using voltammetric techniques. Cyclic voltammetry (CV) allowed us to evaluate the redox processes in general. Temperature-dependent sweep rate experiments allowed us to obtain kinetic parameters like the diffusion coefficient and the electron transfer rate constant, which were further used to evaluate the thermodynamics of the processes. Differential pulse voltammetry (DPV) allowed the determination of the number of electrons and protons involved in the Faradaic processes. In addition, square-wave voltammetry (SWV) allowed us to assess the reversible/irreversible nature of the electrode processes and allowed the determination of analytical parameters, such as the limit of detection and the limit of quantification. A thorough UV–vis spectroscopy, in a wide pH range, allowed the determination of the acid-base dissociation constant,  $pK_a$ , and of the molar extinction coefficient. The  $pK_a$  values determined by different methods were found to be in very good agreement.

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## 1. Introduction

Anthracenediones (ACDs) have a broad range of applications and properties. Depending upon the position of the keto groups, ACDs have various isomers, but the most studied and common representative of this class is

9,10-anthracenedione. Natural ACDs are structurally diverse and their diversity is related to the existence of different substituents that include alkyl substituents, as well as reduced systems including hydro-anthracenediones. Anthracenedione derivatives are used as colorants and 9,10-anthracenedione is the constituent of several dyes [1]. Solvent violet 13, a synthetic anthracenedione dye, is used to dye hydrocarbon products, including thermoplastics, polystyrenes and synthetic fibers [2]. It is also used in hair and skin care products [3]. ACDs are used as useful nucleotide-specific ligands for the purification of proteins

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[4]. The enzyme encoded by *UGT1A8* gene has glucuronidase activity with many substrates, including anthracenediones [5]. Anthracenedione sulfonate is used to catalyze cyclic photophosphorylation reactions [6], which are employed for labeling purposes in biological systems. Modification of deoxynucleosides or deoxynucleoside triphosphates by linking the anthracenedione molecule at 5-position in pyrimidine or 7-position in 7-deazaadenosine yields suitable substrates for polymerases and incorporation of a label in DNA [7]. ACDs are also used for labeling the N-terminus of peptides [8]. Some of these compounds are inhibitors of topoisomerase and are pharmacological targets for cancer prevention [9]. The use of anthracene-9,10-dione as a bird repellent has been reported, being a post-ingestional irritant that produces a conditioned taste aversion after the consumption of treated seeds [10].

Due to the ability of ACDs to act as carriers of electrons and hydrogens, the electrochemical behavior of this class of compounds has been the main focus of researchers. Allietta et al. reported the electro-polymerization of pyrrole-substituted anthracenedione at an indium-tin oxide electrode [11]. These are also potentially useful semiconductors due to their intriguing properties for low-cost organic electronics [12,13].

One of the major focal points are the biological activities of ACDs that are associated with their redox behavior [14,15]. To gain insights into their biological action, mode of reaction, and determine their physicochemical parameters, several researchers have studied the reduction of these molecules under different conditions [16]. The quinones and anthracenediones undergo two successive one-electron reduction steps to produce the corresponding semiquinone and dianion, generating two separate cathodic waves in which the first step is fully electrochemically reversible and the second step is either reversible or quasi-reversible, depending on the experimental conditions [17–21]. Anthracenediones containing hydroxyl groups are interesting from an electrochemical point of view, and their position alters the redox behavior of the quinonoid moiety [18,22–24] due to the formation of intramolecular hydrogen bonds. In addition, these moieties are related to the biological activity of ACDs [25,26].

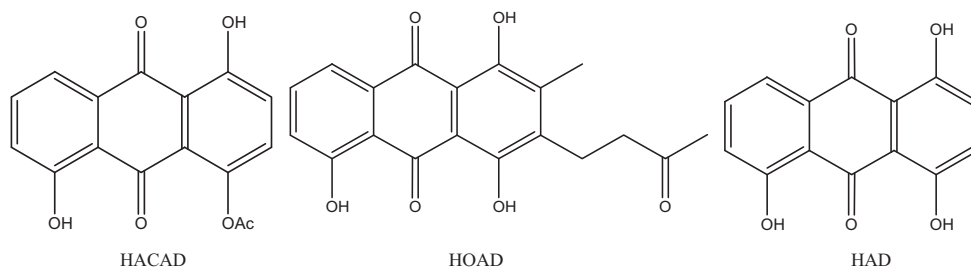
Though anthracenediones have a broad spectrum of applications and their reduction is widely studied [17–24], the literature about their electro-oxidation is limited and thus deserves further investigations. In the present work, we focus on the pH-dependent and temperature-dependent

electro-oxidation of 4,8-dihydroxy-9,10-dioxo-9,10-dihydroanthracen-1-yl acetate (HACAD), 1,4,5-trihydroxyanthracene-9,10-dione (HAD) and 1,4,5-trihydroxy-2-methyl-3-(3-oxobutyl)anthracene-9,10-dione (HOAD), with the hope of providing useful insights into their electron transfer reactions.

### 1.1. Instrumentations and chemicals

An Autolab potentiostat/galvanostat equipped with GPES 4.9 software, Eco-Chemie, imported from the Netherlands, was used for carrying out all voltammetric experiments. The electrochemical cell (Model K64 PARC) was connected to a thermostat LAUDA, Model K-4R for holding a constant temperature during the electrochemical experiments. The three-electrode system consisted of a glassy carbon (GC) working electrode, an Ag/AgCl reference electrode (saturated with 3 M KCl) and a Pt wire as a counter electrode. The surface of the GCE was polished with diamond slurry (1- $\mu\text{m}$  particle size) before each experiment, followed by thorough rinsing of the electrode with distilled water. All voltammetric experiments were conducted in a high-purity  $\text{N}_2$  atmosphere. The experimental conditions for DPV were a pulse amplitude of 50 mV, a pulse width of 70 ms, and a scan rate of 5  $\text{mV}\cdot\text{s}^{-1}$ . For the SWV experiment, a 50 Hz frequency was used and stepped in 2 mV potential increments corresponding to an effective scan rate of 100  $\text{mV}\cdot\text{s}^{-1}$ .

An UV-visible spectrophotometer (UV-1601 Shimadzu spectrophotometer) with a wavelength range of 200–800 nm and a quartz cuvette of path length 1 cm was used for electronic spectroscopic studies. All experiments were carried out using bidistilled water and analytical-grade chemicals. The compounds 4,8-dihydroxy-9,10-dioxo-9,10-dihydroanthracen-1-yl acetate (HACAD), 1,4,5-trihydroxyanthracene-9,10-dione (HAD), and 1,4,5-trihydroxy-2-methyl-3-(3-oxobutyl)anthracene-9,10-dione (HOAD), shown in Scheme 1, were kindly provided by Prof. Dr. Amin Badshah. The solubility problem of the analytes in aqueous system was avoided by preparing 2 mM stock solutions of the analytes in analytical-grade ethanol. Fresh working solutions were prepared in a 1:1 aqueous ethanol solvent by mixing 5 mL of the stock solution with 5 mL of a Britton-Robinson (BR) buffer of ionic strength 0.2 M. Thus, working solutions of 0.1 M ionic strength were prepared in the pH range from 3 to 12. The residual liquid potential of the water:organic solvent mixture was included in the pH



**Scheme 1.** Chemical structures of the selected hydroxyanthracenediones, 4,8-dihydroxy-9,10-dioxo-9,10-dihydroanthracen-1-yl acetate (HACAD), 1,4,5-trihydroxyanthracene-9,10-dione (HAD), and 1,4,5-trihydroxy-2-methyl-3-(3-oxobutyl)anthracene-9,10-dione (HOAD).

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