



# Voltammetric studies of acetylsalicylic acid electrooxidation at platinum electrode

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## ABSTRACT

The electrooxidation of acetylsalicylic acid (ASA) has been investigated at a platinum electrode in aqueous solutions. The process of oxidation and its kinetics has been investigated using cyclic and differential pulse voltammetry. The rate constant, electron transfer coefficient and diffusion coefficients were determined for ASA electrochemical oxidation. The ASA electrooxidation involves an irreversible transfer of one electron and two protons in the first step in solutions with pH up to 8, in agreement with the one step one-electron mechanism. If solution pH is higher than 8, then one electron without protons is involved in the electrooxidation. The process is diffusion controlled in the whole pH range studied.

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## 1. Introduction

Synthetic substances as well naturally originated substances which show high antioxidative activity, draw great attention. They are components of commonly used medicines, but they can also negatively influence human health.

Unhealthy life style and environment pollution are the main factors which accelerate formation of free radicals in human body. These radicals are responsible for many diseases and accelerate ageing. One of the methods to prevent their harmful impact is application of medicines with antioxidative activity which can scavenge these radicals. Acetylsalicylic acid, which is a component of a common medicine—*aspirin*, belongs to the group of phenolic compounds with antioxidative ability [1,2]. This compound can neutralize free radical molecules by supplying electrons and can limit negative influence to human body due to tissue damage prevention.

Acetylsalicylic acid (ASA), shown in Fig. 1, is one of the oldest and most popular pharmaceuticals with anti-inflammatory, antipyretic and analgesic action [3,4]. It is often applied in curing such diseases as Alzheimer's [5], cardiovascular disease [6,7] and cancer [8]. Taking into consideration its structure, ASA belongs to non-steroid anti-inflammatory medicines. Long lasting application of *aspirin* can be harmful to a man because it can cause damage of mucous

membrane in stomach and ulcers. After swallowing, ASA quickly hydrolyses resulting in formation of salicylic acid (SA) which is responsible for pharmacological action. Consumption of ASA in the world is significant. Taking into consideration its therapeutic action and possible toxic effects, this compound is a subject of many investigations [9].

Electrochemical characteristic of ASA as well as its determination is very important due to its common application in drugs. Many techniques including spectrophotometry [10,11], spectrofluorimetry [12–14], high-performance chromatography (HPLC) [15–17], Raman spectroscopy [18] and gas chromatography [19] is involved in its determination. Recently, electroanalytical methods have been often employed in ASA determination due to their sensitivity and simplicity [3,20–23]. Electrochemical methods can be successfully applied also in determination of physicochemical parameters of antioxidants, such as redox potential, number of exchanged electrons, electrode reaction rate constants [24–28]. These parameters are important in the evaluation of antioxidative abilities of ASA and useful in determination of electrooxidation and electroreduction process mechanisms. Especially, it is important to determine half-wave potentials of an antioxidant because the lower value of this parameter the better abilities to scavenge free radicals, an investigated compound shows [29–31].

The aim of the investigations described in this paper was determination of ASA electrochemical behaviour in the process of its electrooxidation at platinum electrode. Experiments were carried out in aqueous media with various pH values in order to reflect ASA behaviour in human body.

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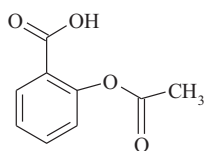


Fig. 1. Chemical structure of acetylsalicylic acid (ASA).

## 2. Experimental

### 2.1. Chemicals

Acetylsalicylic acid (ASA) purchased in Sigma–Aldrich was of analytical pure grade. ASA solutions were prepared by dissolving the substrate in 0.1 M NaClO<sub>4</sub> (Fluka). The concentration of ASA solutions was in the range from  $0.2 \times 10^{-3}$  to  $5 \times 10^{-3}$  M. Solutions used in the determination of pH effect on ASA oxidation, were prepared by dissolving the substrate in buffers. Phosphate buffer solutions with different pH values were prepared from stock solutions (0.1 M) of H<sub>3</sub>PO<sub>4</sub>, NaH<sub>2</sub>PO<sub>4</sub>, Na<sub>2</sub>HPO<sub>4</sub>, and NaOH. All reagents used were of analytical grade. Solutions were prepared using doubly distilled water.

### 2.2. Measurement methods

Cyclic voltammetry (CV) and differential pulse voltammetry (DPV) methods were used in electrochemical measurements carried out in an Autolab PGSTAT30 Electrochemical Analyser (EcoChemie, Netherlands). A three-electrode cell system with a saturated calomel electrode (SCE) as a reference electrode, a platinum wire as an auxiliary electrode, and the platinum (geometric surface area of 0.5 cm<sup>2</sup>) as the working electrode, was applied in electroanalytical studies. Before measurements, the solutions were purged with argon in order to remove dissolved oxygen. During measurements argon blanket was kept over solutions. All experiments were carried out at room temperature.

The pH of buffer solutions was measured using digital pH meter (Elmetron, Model CPC-401, Poland).

## 3. Results and discussion

### 3.1. Electrochemical behaviour of ASA

The electrode reactions characterizing electrochemical oxidation of ASA at the platinum electrode were studied by cyclic and differential pulse voltammetry. Exemplary cyclic and differential pulse (with higher resolution) voltammograms of ASA electrooxidation are presented in Fig. 2.

If peaks observed at voltammograms correspond to diffusion controlled process, then half-wave potential of electrode reaction determined from cyclic voltammograms, is in accordance with a peak potential determined from differential pulse voltammograms. Within the potential range where the compound oxidation peaks appear, the supporting electrolyte (0.1 M NaClO<sub>4</sub>) shows no characteristic peaks, (Fig. 2, curve 3).

Voltammograms presented in Fig. 2 (curve 1 and 2) show that ASA is oxidized probably irreversibly at potentials lower than the potential at which oxygen evolution starts. Irreversibility of this electrode reaction needs to be proved. Two peaks (I at 0.69 V and II at 1.02 V) visible in the differential pulse voltammogram correspond to ASA electrooxidation. The cyclic voltammogram shows one well shaped peak at 1.04 V which is preceded by slightly visible pre-wave. This pre-wave has adsorptive character and corresponds to electrooxidation of an ASA adsorbed form.

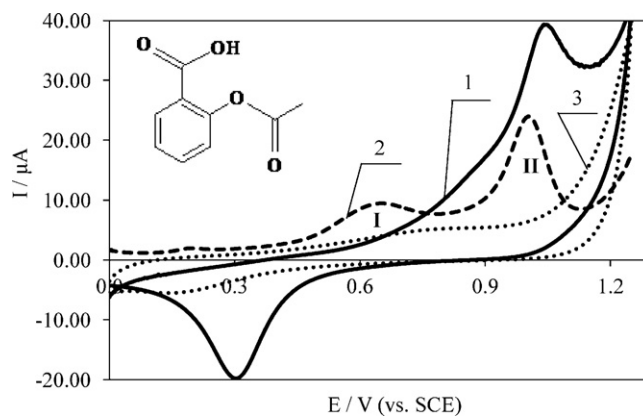


Fig. 2. Voltammograms of ASA electrooxidation at Pt electrode; curve 1—cyclic voltammogram, curve 2—differential pulse voltammogram, and curve 3—cyclic voltammogram recorded in the supporting electrolyte;  $c = 5.0 \times 10^{-3}$  M in 0.1 M NaClO<sub>4</sub>,  $\nu = 0.01$  V s<sup>-1</sup>.

### 3.2. Influence of scan rate

Scan rate is one of parameters significantly affecting electrooxidation of various compounds. Thus, an effect of the scan rate on ASA electrooxidation was investigated in the range from 0.01 to 0.5 V s<sup>-1</sup> using cyclic voltammetry method (Fig. 3).

Cyclic voltammograms were used in determination of peak current and potential for the ASA electrooxidation. Two approaches widely used to study the reversibility of reactions and to determine whether a reaction is adsorption or diffusion controlled consist of the analyses of dependences:  $i_p$  on  $\nu^{1/2}$  and  $\ln i_p$  on  $\ln \nu$ . Fig. 4 shows these plots for the oxidation peak of ASA in NaClO<sub>4</sub>. For reversible or irreversible systems without kinetic complications,  $i_p$  varies linearly with  $\nu^{1/2}$ , intercepting the origin. Although, the plot of  $i_p$  on  $\nu^{1/2}$  presented in Fig. 4 is linear ( $R^2 = 0.9996$ ), it does not cross the origin of the axes. This is characteristic for the electroodic process preceded or followed by a homogenous chemical reaction.

In the scan rate range from 0.01 to 0.5 V s<sup>-1</sup>, peak current ( $i_p$ ) of ASA electrooxidation depends linearly on square root of the scan rate ( $\nu$ ) and is described by the following equation:

$$i_p = \{0.4437 [\nu(\text{V s}^{-1})]^{1/2}\} \text{ mA} - 0.0207 \text{ mA} \quad (R^2 = 0.9996)$$

This dependence does not cross the origin (Fig. 4A). This fact can suggest that the electrode process of ASA electrooxidation is controlled by diffusion and can be preceded by chemical reaction. On

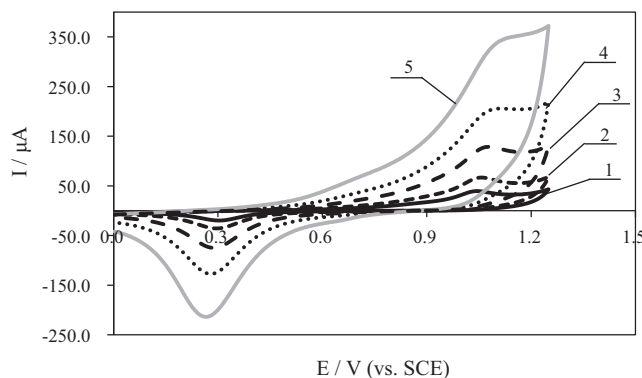


Fig. 3. Cyclic voltammograms of ASA oxidation at Pt electrode, recorded at various scan rates; curve 1—0.01 V s<sup>-1</sup>, curve 2—0.02 V s<sup>-1</sup>, curve 3—0.05 V s<sup>-1</sup>, curve 4—0.2 V s<sup>-1</sup>;  $c = 5.0 \times 10^{-3}$  M in 0.1 M NaClO<sub>4</sub>.

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