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Study of acetylsalicylic acid electroreduction behavior at platinum electrode

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ABSTRACT

Electroreduction behavior of acetylsalicylic acid (ASA) was investigated at platinum electrode using the cyclic voltammetry method. An effect of scan rate, ASA concentration and pH on electrode reaction was determined. The process is diffusion-controlled. Parameters of ASA electroreduction, i.e., rate constant, charge transfer coefficient and diffusion coefficient, were calculated. The ASA electroreduction is quasi-reversible and proceeds in two steps. This process is preceded by substrate hydrolysis resulting in the formation of salicylic (SA) and acetic (AA) acid. Hydrolysis products are electrochemically reduced. In the first and second step, electroreduction of SA and AA proceeds, respectively. Possible mechanism of ASA electroreduction was proposed.

1. Introduction

Acetylsalicylic acid (ASA), commonly known as aspirin, is one of the most important anti-inflammatory pharmaceuticals. Aspirin is applied to cure pain and decrease fever [1,2]. Last years, investigations on pharmaceuticals show that aspirin has been also applied in antithrombotic curing [3–6], coronary heart [7–9] and Alzheimer's diseases [10,11] as well as in cancer prevention [12,13]. Application of ASA in small doses has positive effect in the case of patients suffering from atherosclerosis [14]. Common applications of aspirin result in the possibility of its overdosage [15]. After swallowing, ASA quickly hydrolyses and, as a result, forms salicylic (SA) and acetic (AA) acid. Salicylic acid is responsible for pharmacological features of aspirin. Under physiological conditions (pH = 7.4), it reacts with hydroxyl radicals giving three products: 2,3-dihydroxybenzoic (49%) and 2,5-dihydroxybenzoic (40%) acids as well as o-catechol (11%). The trapping of hydroxyl radicals by salicylic acid was described in [16–20].

Although, ASA shows high antioxidative activity [10,21,22], it can also have a negative effect on human health. This medicine should not be applied by people suffering from stomach and duodenum peptic ulcers, because it blocks evolution of protective mucus by stomach septum. Moreover, it has an irritative action on the mucosa of the gastrointestinal tract [23–25]. ASA should not be applied by pregnant women – studies proved correlation between its application and appearance of palate split and heart defects as well as lower birth mass of neonates [26]. Moreover, salicylates applied during pregnancy increase the risk of perinatal complications due to their ability of disorder in the synthesis of arachidonic acid derivatives. Acetylsalicylic acid should not be applied by small children and young people during symptomatic treatment of flu and chill as well as virus diseases due to the possibility of Reye's syndrome appearance [27–29]. This acid reduces blood coagulability [30].

ASA is applied in great amounts and that is why its therapeutic action as well as side and toxic effects are still of interest [31–33]. Last years, determination and studies of ASA by electrochemical methods have drawn attention due to their precision and simplicity [21,34–37]. Electrochemical measurements are fundamental in the determination of physico-chemical parameters of studied compounds (e.g. redox potential, the number of electrons transferred, rate constants of electrode reactions, etc.) [38–41]. These investigations are important in the estimation of antioxidative and antireductive properties of organic compounds and in understanding mechanisms of their oxidation and reduction [42–47].

The aim of the investigations described in this paper was determining ASA electrochemical behavior in the process of its electroreduction at platinum electrode. According to our best knowledge, electroreduction of ASA is poorly described in literature in contrary to its electrooxidation. Experiments were carried out in aqueous media with various pH values in order to reflect ASA behavior in human body. The studies presented in this paper are a continuation of our investigations concerning electrochemical (oxidative) behavior of ASA described in [48].

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2. Experimental

2.1. Reagents

The pure acetylsalicylic acid (ASA) was purchased from Sigma–Aldrich and used as received. The aqueous solutions of ASA were prepared by dissolving the substrate in 0.1 M $NaClO_4$ (Fluka). The concentration of ASA solutions was in the range from 0.2×10^{-3} to 5×10^{-3} mol L^{-1}. Solutions used in the determination of pH effect on ASA reduction were prepared by dissolving the substrate in buffers. Phosphate buffer solutions (0.1 mol L^{-1}) with different pH values were prepared from stock solutions of 0.1 mol L^{-1} H_3PO_4, NaH_2PO_4, Na_2HPO_4 and NaOH. Doubly distilled water was used throughout the experiments. All the reagents used were of analytical grade. The experiments were carried out at room temperature.

2.2. Measurement methods

Methods of cyclic (CV) and differential pulse (DPV) voltammetry were used in electrochemical measurements with an Autolab PGSTAT30 Electrochemical Analyser (EcoChemie, Netherlands). A three-electrode cell system including 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^2) as the working electrode, was applied in the electrochemical studies. Before measurements, the solutions were purged with argon in order to remove dissolved oxygen. During measurements, argon blanket was kept over the solutions.

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

3. Results and discussion

3.1. Voltammetric behavior of ASA

Voltammetric methods are frequently used for the characterization of electroactive systems. The electrode reactions of reduction and oxidation of ASA at the platinum electrode were studied by cyclic and differential pulse voltammetry. Fig. 1 shows the exemplary CV and DPV (with higher resolution) voltammograms recorded in ASA solution. Within the potential range, where the compound oxidation peaks appear, the supporting electrolyte (0.1 mol L^{-1} $NaClO_4$) shows no peaks (Fig. 1, curve 3).

Voltammograms presented in Fig. 1 (curves 1 and 2) prove that ASA is oxidized in at least two steps at potentials lower than the potential at which oxygen evolution starts [46]. Similarly, the ASA electroreduction proceeds in at least two steps at potentials lower than the potential at which hydrogen evolution starts. The electroreduction is quasi-reversible while the electrooxidation is irreversible. Peak potential (E_{pc}) of the first and second step in the electroreduction is −0.50 and −0.57 V, respectively. In the reverse scan, a peak at −0.41 V ascribed to oxidation of ASA reduced form is observed. ASA electroreduction is preceded by its hydrolysis resulting in the formation of salicylic (SA) and acetic (AA) acid. Thus, SA and AA electroreductions were also studied in order to compare them with ASA electroreduction (Fig. 2). Potential of the first peak of ASA electroreduction (Fig. 2, curve 1) corresponds to the potential of SA electroreduction peak (Fig. 2, curve 2). On the other hand, potential of the second peak of ASA electroreduction (Fig. 2, curve 1) corresponds to the potential of AA electroreduction (Fig. 2, curve 3). Probably, the electroreduction of SA is followed by AA electroreduction. Both these compounds are formed by ASA hydrolysis preceding the electrode reaction.

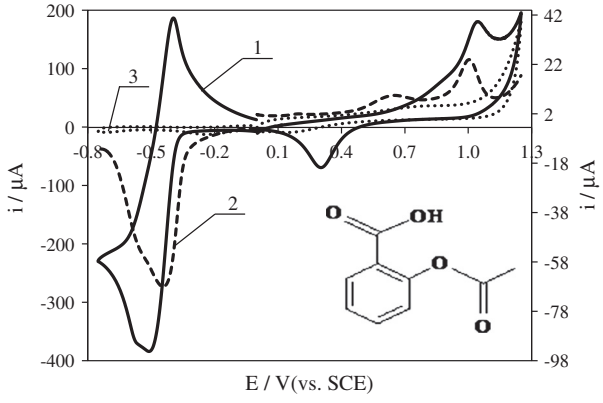

Fig. 1. Voltammograms of ASA electroreduction (left axis) and electrooxidation (right axis) at Pt electrode; curve 1 – cyclic voltammogram, 2 – differential pulse voltammogram, 3 – cyclic voltammogram recorded in the supporting electrolyte; $c = 5.0 \times 10^{-3}$ mol L^{-1} in 0.1 mol L^{-1} $NaClO_4$, $v = 0.01$ V s^{-1}.

3.2. Scan rate effect

Scan rate has an effect on the electroreduction of the studied compound. Thus, cyclic voltammogramms of ASA electroreduction were recorded in the scan rate range from 0.01 to 0.5 V s^{-1}. These voltammograms were used in determination of peak potential (E_p) and current (i_p).

Two approaches widely used to study the reversibility of reactions and to determine whether a reaction rate is adsorption or diffusion controlled, are the analyses of the $i_p = f(v^{1/2})$ and $\log i_p = f(\log v)$ curves [49]. Fig. 3 shows these plots for the first reduction peak of ASA in $NaClO_4$. For reversible or irreversible systems without kinetic complications, i_p varies linearly with $v^{1/2}$, intercepting the origin [49]. The plot of i_p on $v^{1/2}$ presented in Fig. 3A is linear and it does not cross the origin of the axes. This proves that the process can be diffusion controlled. A dependence of i_p on $v^{1/2}$ for cathodic and anodic peak can be described by the following equations:

$$i_{pc} = \left\{-2.258\left[v\ (\mathrm{V\ s^{-1}})\right]^{1/2}\right\}\ \mathrm{mA} - 0.206\ \mathrm{mA}, \quad R^2 = 0.996$$

$$i_{pa} = \left\{1.782\left[v\ (\mathrm{V\ s^{-1}})\right]^{1/2}\right\}\ \mathrm{mA} + 0.062\ \mathrm{mA}, \quad R^2 = 0.999$$

Diffusion character of ASA electroreduction was confirmed by a dependence of ln i_p on ln v which is linear (Fig. 3B). This dependence is described by the equation:

$$\ln i_{pc} = \left\{0.384 \ln v\ (\mathrm{V\ s^{-1}})\right\}\mathrm{mA} + 0.837\ \mathrm{mA}, \quad R^2 = 0.999$$

Similarly, this dependence for the anodic peak in the reverse scan is as follows:

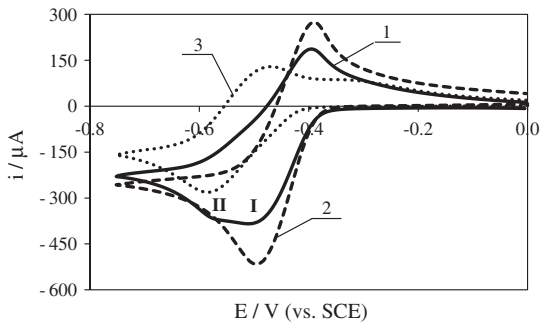

Fig. 2. Cyclic voltammograms of electroreduction at Pt electrode; curve 1 – ASA, 2 – SA, 3 – AA; $c = 5.0 \times 10^{-3}$ mol L^{-1} in 0.1 mol L^{-1} $NaClO_4$, $v = 0.01$ V s^{-1}.