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Electrochemical Behavior of 2-(p-isobutylphenyl)propionic Acid at Platinum Electrode

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The electrochemical behavior of 2-(p-isobutylphenyl)propionic acid (IB) - both pure and contained in pharmaceutical products (ibuprom, modafen and nurofen), was investigated at platinum electrode using voltammetric methods. Cyclic voltammograms of IB oxidation and reduction were recorded and the following parameters were determined: peak potential (E_p), half-peak potential ($E_{p/2}$), half-wave potential ($E_{1/2}$), anodic and cathodic peak currents (i_{pa}, i_{pc}). The parameters were used in calculations of transfer coefficients (βn_β, αn_α) and electrode reaction rate constants (k_f, k_{fh}). IB is irreversibly oxidized in at least two electrode steps. Its electroreduction proceeds quasi-reversibly or irreversibly in at least one electrode step. Voltammetric investigations proved the effect of the excipients on antioxidative and antireductive properties of the tested pharmaceuticals.

Keywords: ibuprofen; electrooxidation; electroreduction; ibuprom; modafen; nurofen

1. INTRODUCTION

2-(p-isobutylphenyl)propionic acid (ibuprofen, IB) is a non-steroidal anti-inflammatory drug (NSAID). IB is a propionic acid derivative that is effectively used in the treatment of muscle and head pain, inflammation in rheumatic disease and other muscular-skeletal disorders [1, 2]. This compound is a component of various pharmaceuticals, belonging to the most commonly used over-the-counter drugs (OTC). Average content of IB in pharmaceuticals is 200-400 mg. IB shows a strong analgesic and antipyretic action [3, 4]. The most recent epidemiological studies have indicated that chronic intake of ibuprofen is associated with lower risk of Alzheimer's disease (AD). This beneficial effect is attributed to the reduction of the inflammation response in brain in the AD and hence delays the cognitive decline [2, 5].

Taking into consideration that IB is commonly applied, it is important to develop efficient, sensitive and simple analytical techniques used in its determination in aqueous solutions and human

body fluids. Up to now, many methods such as spectrophotometry [6], gas chromatography coupled with mass spectrometry [7], high-performance chromatography (HPLC) [8], capillary electrophoresis [9] and potentiometry [10], have been developed in the IB determination. Last years, determinations and studies of IB by electroanalytical methods have drawn attention due to their precision and simplicity [11-13]. Moreover, electroanalytical methods, especially voltammetry, are characterized also by high sensitivity, selectivity, low detection limit and reproducibility of the results, what is very important in identification and quantification of various components in pharmaceuticals [14, 15]. Active substances present in pharmaceuticals, such as IB, have often antioxidative properties and are electrochemically active what means that they easily participate in electron transfer reactions resulting in formation of their oxidized forms [14]. Various excipients used in pharmaceuticals are generally electrochemically inactive. Certain similarity in electrochemical and biological reactions which take place at the electrode and in the human body, makes electroanalytical methods very attractive and important tool in investigation of pharmaceuticals effect on processes in human body [14-17]. Electroanalytical measurements are helpful in determination of physicochemical parameters for studied compounds (*e.g.*, redox potential, the number of transferred electrons, rate constants of electrode reactions, *etc.*) [18-24]. These investigations are important in estimation of antioxidative and antireductive properties of IB.

The aim of the investigations described in this paper was to determine electrochemical behaviour of IB at platinum electrode. Moreover, electrooxidation and electroreduction of IB in selected pharmaceuticals was compared.

2. EXPERIMENTAL

2.1. Chemicals and solutions

The subject of the investigation were 2-(p-isobutylphenyl)propionic acid (ibuprofen, IB) purchased in Sigma-Aldrich (Germany) and pharmaceutical products (ibuprom, modafen, nurofen) containing IB - the active substance. Pharmaceuticals were purchased in pharmacies in Lodz (Poland). The concentration of IB solutions was in the range from 0.2 to 5.0 mmol L^{-1}. The aqueous solutions of IB were prepared by its dissolution in 0.1 mol L^{-1} $NaClO_4$ (Fluka, France). The solutions of the pharmaceuticals were prepared in the same way by dissolution of one pill in $NaClO_4$ (0.5 L). Each pill contained 200 mg IB which corresponds to IB concentration of 1.94 mmol L^{-1}.

2.2. Apparatus

Electroanalytical measurements of IB and pharmaceuticals were carried out using an Autolab PGSTA30 Electrochemical Analyzer (EcoChemie, The Netherlands) controlled by GPES 4.9 electrochemical software. A three-electrode electrochemical cell employed in measurements consisted of a reference electrode, an auxiliary electrode (platinum wire) and a working electrode (platinum) with geometric surface area of 0.5 cm^2. A potential of the working electrode was measured vs. saturated calomel electrode (SCE).

2.3. Measurement methods

Measurements were carried out using a method of cyclic (CV) and differential pulse (DPV) voltammetry. CV curves were recorded for electrooxidation of IB and the pharmaceuticals in the potential range from 0 to 1.25 V with various scan rates (0.01 to 0.5 V s^{-1}). Electroreduction of IB was investigated in the potential range from 0 to -0.8 V with the same scan rates. DPV curves were recorded in the same potential ranges as CV curves in the case of electrorooxidation and elctroreduction. Modulation amplitude was 25 mV, pulse width was 50 ms (scan rate - 0.01 V s^{-1}).

Volume of the solutions used in the measurements was 20 ml. Prior to the measurements, the solutions were purged with argon in order to remove dissolved oxygen. During measurements, argon blanket was kept over the solutions. All voltammetric experiments were performed at room temperature.

3. RESULTS AND DISCUSSION

3.1. Electrooxidation and electroreduction of 2-(p-isobutylphenyl)propionic acid

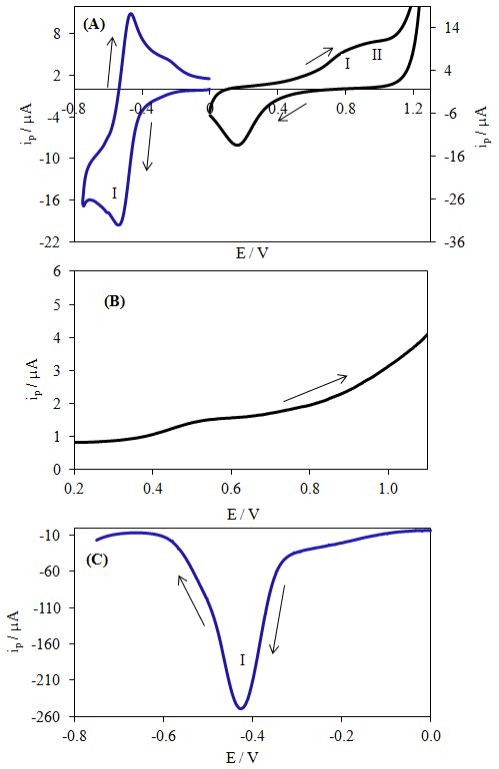

Figure 1. CV curves of IB electrooxidation (left axis) and electroreduction (right axis) at Pt electrode (A), DPV curves recorded in electrooxidation (B) and electroreduction (C) of IB at different concentrations at Pt electrode; c = 5.0 × 10^{-3} mol L^{-1} in 0.1 mol L^{-1} $NaClO_4$, v = 0.01 V s^{-1}.

Voltammetric methods are frequently used for the characterisation of compounds which play important role in pharmaceutical industry [25-27]. These compounds include also ibuprofen. IB electrooxidation and electroreduction at platinum electrode is described in this paper. According to our best knowledge,

electroreduction of ibuprofen is poorly described in literature in contrary to its electrooxidation. Ibufrofen electrooxidation was investigated at various electrode materials but not at platinum electrode. Electrooxidation of IB (5 mmol L^{-1} in 0.1 mol L^{-1} H_2SO_4) at BDD electrode proceeded in at least one electrode step (a peak at ca. 1.65 V) before the potential at which oxygen evolution started [28]. However, CV curves recorded at Ti/TiO_2-RuO_2, Ti/IrO_2-RuO_2, Ti/RuO_2/SnO_2-Sb_2O_5, Ti/RuO_2/SnO_2-Sb_2O_5-RuO_2 and BDD electrode in the solution of IB (50 ppm in 0.1 mol L^{-1} Na_2SO_4) proved no presence of IB electrooxidation peaks but changes in oxidation current were observed if IB concentration varied [29, 30]. Two steps of IB electrooxidation were observed at EG-Z-Ag-Epoxi electrode in the potential range from -0.5 to 1.25 V [29].

Electrochemical oxidation and reduction of IB at the platinum electrode was studied by cyclic voltammetry (CV). Exemplary voltammogram of IB electrooxidation presented in Fig. 1A (right axis) shows that this process proceeds probably irreversibly in at least two electrode steps at potentials lower than the potential at which oxygen evolution starts. The first peak at 0.83 V corresponds to the first step of IB elecrooxidation while the second peak at 0.92 V can be attributed to the second step of this process. In the reverse scan, a peak at the potential of 0.16 V can be ascribed to the reduction of IB oxidation products. In the case of IB electroreduction, the cathodic peak at -0.522 V was followed by the anodic peak at -0.468 V in the reverse scan (Fig. 1A - left axis). Taking into consideration cathodic (E_{pc}) and anodic (E_{pa}) peak potentials, it can be stated that IB electroreduction proceeds quasi-reversibly in at least one step at potentials higher than the potential at which hydrogen evolution starts. An increase in the scan rate results in higher difference between E_{pc} and E_{pa}, and the IB electroreduction becomes more irreversible. In the reverse scan, the anodic peak can be ascribed to oxidation of IB reduced form.

3.2. The effect of the scan rate and IB concentration on its electrode reactions

Useful information about the character of electrode reactions can usually be acquired from the relationship between a peak current and scan rate. However, it is necessary to determine a character of an observed peak.

Adsorptive or diffusive character of peaks observed in IB electrooxidation and electroreduction can be stated by determination of $\ln i_p = f(\ln v)$ dependences obtained on the base of CV curves (Fig. 2). Moreover, DPV curves prove the presence of one reduction peak and no oxidation peaks. The lack of oxidation peaks can suggest an adsorptive character of two oxidation peaks visible in CV curve (Fig. 1A). The reduction peak observed in DPV curve (Fig. 1C) is well shaped and probably has diffusive character. Dependences of $\ln i_p = f(\ln v)$ for the oxidation (I step) and reduction of IB are linear but with various slopes. If the slope is close to 1, this indicates adsorptive character of the process. Otherwise, if the slope is close to 0.5 that means diffusion-controlled process [31-35]. In the case of IB electrooxidation, the slope is 0.73 and indicates mixed (adsorption-diffusion) character of the current. The dependence for IB electroreduction is characterized by the slope of 0.31 indicating its diffusive character.

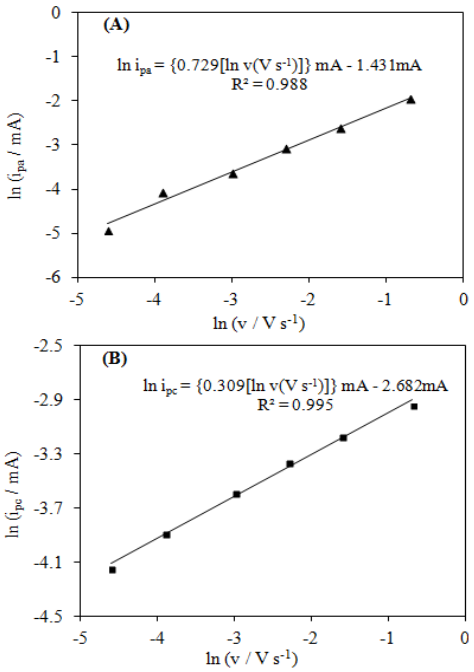

Figure 2. A dependence of ln i_p = f (ln v) determined for the anodic (A) and cathodic (B) peak currents recorded in IB electrooxidation and electroreduction, respectively.

The effect of IB concentration on its electrooxidation and electroreduction was studied in voltammetric experiments. Cyclic voltammograms were used in determination of anodic (i_{pa}) and cathodic (i_{pc}) peak currents.

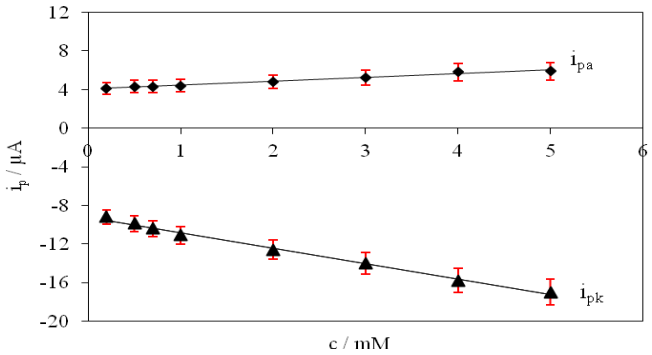

Figure 3. Dependences of the anodic and cathodic peak currents on IB concentration (c) in its electrooxidation and electroreduction at Pt electrode, respectively; v = 0.01 V s^{-1}.

Dependences of i_{pa} and i_{pc} on IB concentration are presented in Figure 3 and described by the following equations:

i_{pa} = {0.395[c (mmol L^{-1})]} µA + 4.042 µA, R^2 = 0.985 (1)

i_{pc} = {-1.605[c (m mol L^{-1})]} µA – 9.209 µA, R^2 = 0.994 (2)

Although, both dependences are linear at Pt electrode, only the dependence for IB electroreduction can be potentially applied in determination of IB content in pharmaceuticals, due to diffusive character of the electroreduction peak.

3.3. Kinetic parameters of IB electrode reactions

The rate constant of electrode reactions (k_f, k_{fh}) determined for a specified potential characterizes the transfer rate of an electron through the electrode-solution interface. The electron transition coefficient characterizes the symmetry of the energy barrier of an electrode reaction. In order to calculate these parameters, peak potentials (E_p), half-peak potentials ($E_{p/2}$), half-wave potentials ($E_{1/2}$) and peak currents (i_{pa}, i_{pc}) were calculated for the first step of IB electrooxidation and electroreduction from the recorded cyclic voltammograms.

As it was proved and described in the previous section, the peak of IB electrooxidation had an adsorptive character and the peak of IB electroreduction revealed an diffusion character. For an adsorption-controlled and irreversible electrode process, according to Laviron [36], E_{pa} is defined by the following equation:

$$E_{pa} = E^o + \frac{RT}{\beta n_\beta F}\ln\frac{RTk^o}{\beta n_\beta F} + \frac{RT}{\beta n_\beta F}\ln v \quad (3)$$

where β is the transfer coefficient, k^o - the standard heterogeneous rate constant of the reaction, n - the number of electrons transferred during the oxidation, v - the scan rate and E^o - the formal redox potential, R - universal gas constant (8.314 J K^{-1} mol^{-1}), F - Faraday constant (96,487 C mol^{-1}) and T - Kelvin temperature. This dependence was used in the case of the IB electrooxidation reaction which is irreversible and controlled by adsorption. The value of the overall electron transfer coefficient (βn_β) calculated according to the equation (3) was 0.57. According to Bard and Faulkner [37], β can be calculated from the following equation:

$$\beta = \frac{47.7}{E_p - E_{p/2}} mV \quad (4)$$

where $E_{p/2}$ is the potential determined at half peak height. The calculated value of β was 0.52. Based on values of βn_β and β, the number of exchanged electrons (n) is equal to 1. The equation for the formal rate constant (k_f) for the surface reaction of an irreversible system [38-40] is given by the following equation:

$$E_p = E_{1/2} - (\frac{RT}{nF})[0.78 - \ln(\frac{k_f}{\beta})^{1/2}] \quad (5)$$

Substituting the value of β (0.52) in Eq. (5), the formal rate constant for the irreversible surface reaction, k_f, is calculated to be 55.79±0.50 s^{-1} (Table 1).

Table 1. Peak potentials (E_p), half-peak potentials ($E_{p/2}$), half-wave potential ($E_{1/2}$), transition coefficients (βn_β, αn_α) and rate constants (k_f, k_{fh}) determined for electrooxidation and electroreduction of IB, c = 5.0 mmol L^{-1} in 0.1 mol L^{-1} $NaClO_4$.

Parameter	Electrooxidation	Electroreduction
E_p / V	0.83	-0.522
$E_{p/2}$ / V	0.72	-0.472
$E_{1/2}$ / V	0.79	-0.502
βn_β or αn_α	0.57	0.88
k_f / s^{-1} or k_{fh} / cm s^{-1}	55.79	6.52×10^{-4}

If the electrode process proceeds under linear diffusion conditions, as it was stated in the case of IB reduction peak, then transition coefficient (αn_α) and heterogeneous rate constant (k_{fh}) for the irreversible electrode process can be calculated from the following equations [37, 41-42]:

$$\alpha n_\alpha = \frac{1.857RT}{F\left(E_{pc/2} - E_{pc}\right)} \quad (6)$$

$$E_{pc} = -1.14\frac{RT}{\alpha n_\alpha F} + \frac{RT}{\beta n_\beta F}\ln\frac{k^o_{fh}}{D^{1/2}_{0x}} - \frac{RT}{2\alpha n_\alpha F}\ln \alpha n_\alpha v \quad (7)$$

$$k_{fh} = k^o_{fh}\exp\left(\frac{-\alpha n_\alpha FE}{RT}\right) \quad (8)$$

where D_{ox} - diffusion coefficient of an oxidized form, $k_{fh}{}^o$ - heterogeneous rate constant for IB reduction at a peak potential, k_{fh} - heterogeneous rate constant for IB reduction at specified potential. The heterogeneous rate constants calculated at the half-wave potentials. The value of k_{fh} for IB electroreduction is 6.52×10^{-4} cm s^{-1} (Table 1).

3.3. IB electrochemical behaviour in pharmaceutical products

Electroanalytical method as the cyclic voltammetry (CV) has many advantages in pharmaceutical analysis [43-51]. CV curves were recorded in solutions of the pharmaceuticals containing the same amount of IB (Fig. 4).

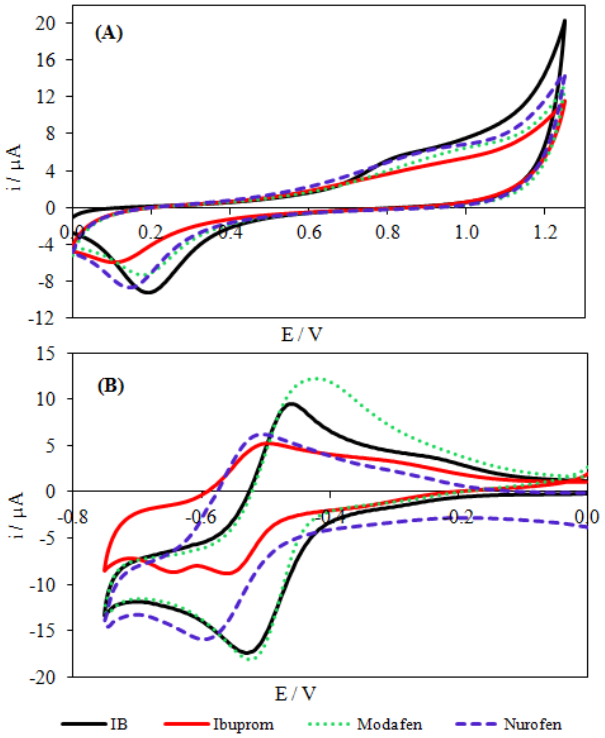

Figure 4. CV curves recorded at Pt electrode for the electrooxidation (A) and electroreduction (B) of IB and the pharmaceuticals containing IB; $c_{IB} = 1.94 \times 10^{-3}$ mol L^{-1} in 0.1 mol L^{-1} $NaClO_4$, v = 0.01 V s^{-1}.

Electrochemical oxidation and reduction of the tested pharmaceuticals at Pt electrode proceeds in at least two and one electrode step, respectively before the potential reaches a value at which oxygen or hydrogen evolution starts. However, currents of oxidation and reduction observed for the pharmaceuticals are different than those observed for IB (Table 2).

Table 2. Comparison of E_p and i_p observed in the electrooxidation and electroreduction of IB and tested pharmaceuticals.

Compound	Parameters	
	E_p / V	i_p / μA
Electrooxidation		
IB	0.830	4.8
Ibuprom	0.866	3.5
Modafen	0.871	4.5
Nurofen	0.891	5.1
Electroreduction		
IB	-0.522	-12.6
Ibuprom	-0.557	-5.7
Modafen	-0.520	-14.3
Nurofen	-0.590	-10.0

Differences in currents can be attributed to the presence of excipients in drugs. Comparison of peak potentials observed in the electrooxidation and electroreduction of the pharmaceuticals with IB shows that they are more difficult oxidized and reduced than IB. Although, there is one exception - susceptibility of modafen to electroreduction is comparable with IB. Comparison of peak currents observed in the electrooxidation of the tested compounds leads to a conclusion that the presence of excipients results in a decrease in oxidation current except for nurofen. Similarly, electroreduction currents of the pharmaceuticals are lower than for IB except for modafen. Higher effect of the excipients is observed in the case of the electroreduction process.

4. CONCLUSIONS

The electrooxidation and electroreduction of 2-(p-isobutylphenyl)propionic acid (IB) was investigated at Pt electrode. IB is electrochemically oxidized (irreversibly) in at least two electrode steps and reduced quasi-reversibly or irreversibly at higher scan rates in at least one electrode step. Its electrooxidation has adsorptive whereas the electroreduction reveals diffusive character. Both dependences of the anodic and cathodic peak current on IB concentration are linear but only the dependence for the reduction peak can be applied in quantitative determination of IB due to its diffusive character.

Taking into consideration that the lower oxidation potential results in the better antioxidative properties, it can be concluded that all tested pharmaceuticals show worse antioxidative abilities in comparison with the tested active substance - IB. On the other hand, the antireductive abilities of the pharmaceuticals were also worse than in the case of IB with the exception of modafen. The presence of

excipients in the tested pharmaceuticals influences not only peak potentials in the electrooxidation and electroreduction of IB contained in these drugs but also observed peak currents.

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