Electrochimica Acta 59 (2012) 150–155

Contents lists available at SciVerse ScienceDirect

Electrochimica Acta

journal homepage: www.elsevier.com/locate/electacta

Electrochemical characterization of tenoxicam using a bare carbon paste electrode under stagnant and forced convection conditions

D.S. Guzmán-Hernández[a], M.T. Ramírez-Silva[a,*], M. Palomar-Pardavé[b,**], S. Corona-Avendaño[b], Annia Galano[a], A. Rojas-Hernández[a], M. Romero-Romo[b]

[a] Universidad Autónoma Metropolitana Iztapalapa, Departamento de Química, Av. San Rafael Atlixco #186, Col. Vicentina, C.P. 09340 México, D.F, Mexico
[b] Universidad Autónoma Metropolitana Azcapotzalco, Departamento de Materiales, Av. San Pablo #180, Col. Reynosa-Tamaulipas, C.P. 02200 México, D.F., Mexico

ARTICLE INFO

Article history:
Received 28 May 2011
Received in revised form 15 October 2011
Accepted 15 October 2011
Available online 22 October 2011

Keywords:
Tenoxicam
Electrooxidation
Carbon paste electrode
Diffusion coefficient
Hydrodynamic conditions

ABSTRACT

From potentiostatic current transients and voltammetry studies, carried out under both stagnant and forced convection conditions, the tenoxicam electrochemical behavior on a bare carbon paste rotating disk electrode was assessed in an aqueous solution (pH = 0.403). It was found that tenoxicam's electrochemical oxidation is a mass transfer-controlled process where a current peak is clearly formed at around 0.74 V when the potential scan was varied in the positive direction. However, when the potential was switched to the negative direction, up to the initial potential value, no reduction peak was formed. Tenoxicam's electrochemical oxidation follows an EC mechanism where the electrodic and chemical kinetics are fast. From sample-current voltammetry both the number of electrons, n, that tenoxicam losses during its electro-oxidation and its half-wave potential, $E_{1/2}$, were determined to be 2 and 0.770 V *vs.* Ag/AgCl, respectively. Moreover, from differential pulse voltammetry plots it was confirmed that effectively in this case $n = 2$. Considering 2 electrons and both the Randles-Sevcik and Cotrell equations, the tenoxicam's diffusion coefficient, D, was determined to be $(3.745 \pm 0.077) \times 10^{-6}$ and $(4.116 \pm 0.086) \times 10^{-6}$ cm^2 s^{-1}, respectively. From linear sweep voltammetry plots recorded under forced convection conditions, it was found that Levich's equation describes adequately the limiting current recorded as a function of the electrode rotation rate, from where the D value was also found to be $(4.396 \pm 0.058) \times 10^{-6}$ cm^2 s^{-1}. Therefore, the average D value was $(4.09 \pm 0.33) \times 10^{-6}$ cm^2 s^{-1}. Furthermore, from the radius of the tenoxicam molecule, previously optimized at M052X/6-31 + G(d,p) level of theory, and using the Stokes–Einstein approach, D was also estimated to be 4.54×10^{-6} cm^2 s^{-1} which is similar to the experimentally estimated values, under both stagnant and forced convection hydrodynamic conditions.

1. Introduction

Tenoxicam (Tenox) is a non-steroidal anti-inflammatory drug that belongs to a class of compounds called oxicams [1]. The structure of this drug is illustrated in Fig. 1. Tenox is used to relieve inflammation, swelling, stiffness, and pain associated with rheumatoid arthritis, osteoarthritis, ankylosing spondylitis (a sort of arthritis involving the spine), tendinitis (inflammation of a tendon), bursitis (inflammation of a bursa, a fluid-filled sac located around joints and near the bones), and periarthritis of the shoulders or hips (inflammation of tissues surrounding these joints). The drug is counter indicated to senior patients or to those who have been given anesthesia or surgery, because they are at risk of increased bleeding or kidney failure, have an active inflammatory disease involving the stomach or intestine (e.g., ulcerative colitis), have an active stomach or intestinal ulcer, have had an acute asthmatic attack, hives, rhinitis (inflammation of the inner lining of the nasal passage), or other allergic reactions caused by Aspirin or other nonsteroidal anti-inflammatory drugs (e.g. Diclofenac, Ibuprofen, Indomethacin, Naproxen).

In spite of Tenox's inherent importance there are but a few studies involving electrochemical methods [2–6]. Özaltin [6] reported the differential pulse polarographic determination of tenoxicam in pharmaceuticals and in blood, using a static mercury drop electrode. El-Maali and Hassan [4] reported an investigation on the oxidation behavior of the anti-inflammatory drug Piroxicam and Tenox at the carbon paste electrode (CPE), found out that these compounds showed a relatively similar voltammetric behavior and degree of accumulation at the CPE surface. Hitherto, a deeper electrochemical characterization of Tenox has not been reported, that could give account, for instance, of how many electrons does Tenox lose during its oxidation? Or what is the value of its diffusion

---

* Corresponding author.
** Corresponding author. Tel.: +52 55 53 18 94 72; fax: +52 55 53 18 90 87.
E-mail addresses: mtrs218@xanum.uam.mx (M.T. Ramírez-Silva), mepp@correo.azc.uam.mx, mpalomar@hotmail.com (M. Palomar-Pardavé).

0013-4686/$ – see front matter © 2011 Elsevier Ltd. All rights reserved.
doi:10.1016/j.electacta.2011.10.046

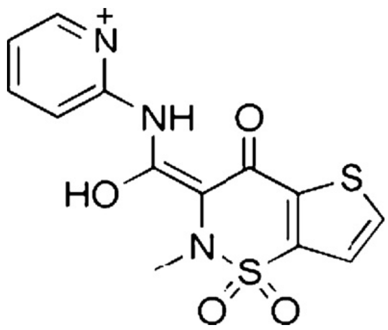

Fig. 1. Chemical structure for the tenoxicam (4-hydroxy-*N*-(2-pyridyl)-2-methyl-2*H*thieno-[2,3e]-1,2-thiazine-3-carboxamide-1,1-dioxide) reduced form, fully protonated, ($H_2Tenox^+{}_R$).

coefficient in aqueous media? Considering that this electrochemical knowledge is important for a number of reasons, namely: the development of electrochemical methods for tenoxicam quantification and to construe an insight on tenoxicam's degradation products. Therefore, in this work we study the electrochemical oxidation behavior of Tenox in aqueous solution using a bare CPE in both stagnant and forced convection conditions.

2. Experimental

2.1. Reagents and chemicals

An aqueous Tenox solution (153 ± 1) μM, HCl 1 M (pH = 0.403 adjusted with NaOH) was made from Merck's analytical grade reagents and deionized water type 1 with 18.2 MΩ cm resistivity, free from organic matter, obtained from a US Filter PURE-LAB Plus UV. The resulting solution was deaerated with nitrogen and freshly prepared prior to each determination.

2.2. Instrumentation

The electrochemical determinations were carried out with the aid of an EPSILON potentiostat–galvanostat coupled to a PC running the BASi-Epsilon-EC software to allow experimental control and data acquisition. A typical three electrode cell was used where a carbon paste electrode, CPE, was the working electrode. The CPE was prepared as usual, by mixing the Johnson Matthey 1 mm, 99.9% graphite powder with nujol as indicated elsewhere, Ramírez-Silva et al. [7,8]. A platinum wire (BAS MW- 1032) was the counter electrode, while saturated Ag/AgCl (BAS MF-2052) was the reference electrode, against which all potentials (E) reported in this work were measured. The pH monitoring was done with a TACUSSEL potentiometer LPH 430T pH-METER coupled to a CORNING combined glass electrode. For the electrochemical experiments under forced convection conditions, a CPE (3 mm diameter) coupled to a rotating disk electrode controller (BAS-RDE-2) was used as working electrode.

2.3. Procedure

The electrochemical behavior of Tenox was studied in the system CPE/HCl 0.1 M, Tenox (153 ± 1) μM (pH = 0.403) by chronoamperometry and voltammetric studies (cyclic voltammetry, CV, and differential pulse voltammetry, DPV). As stated above, these experiments were carried out under stagnant and forced convection conditions, maintaining a nitrogen atmosphere and controlled temperature (25 °C) in the cell. The CVs were recorded in the 0 mV to 1000 mV potential range applying different potential scan rates (ν), namely: $20\,\mathrm{mV\,s^{-1}} \leq \nu \leq 180\,\mathrm{mV\,s^{-1}}$ and/or varying the CPE-RDE angular speed, ω, in the $50\,\mathrm{rpm} \leq \omega \leq 600\,\mathrm{rpm}$ range.

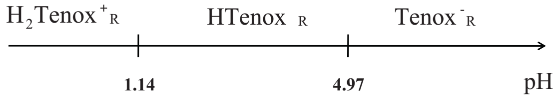

Fig. 2. Predominance zone diagram for tenoxicam constructed following the methodology proposed by Rojas-Hernández et al. [9–13], and the acidity constants reported by Moya-Hernández et al. [14].

In all cases, the potential sweeps started at the open circuit or nil current potential ($E_i = 0$).

3. Results and discussion

3.1. Tenox chemical speciation analysis

Fig. 2 shows the predominance zone diagram for Tenox constructed following the methodology proposed by Rojas-Hernández et al. [9–13], and the acidity constants reported by Moya-Hernández et al. [14], from spectrophotometric studies; the pK values found were pK_{a1} 1.14 and pK_{a2} 4.97. It is important to note that at the experimental conditions considered in this work, Tenox is present as the $H_2Tenox^+{}_R$ species where R indicates that is the reduced form of Tenox and that it is fully protonated, see Fig. 1.

3.2. Tenox electrochemical oxidation

3.2.1. Stagnant conditions

3.2.1.1. Cyclic voltammetry study. Fig. 3 shows a typical CV recorded in the system CPE/HCl 0.1 M (pH = 0.403) with and without Tenox present in solution. It is possible to note that the electrochemical response is only displayed when Tenox is present, during the positive scan rate: a current peak was clearly formed at around 0.74 V, with no reduction peak appearing when the scan was reversed in the negative direction, up to the initial potential value. Such voltammetry behavior could be due to the following reasons: the electrode kinetics of the Tenox's electrochemical oxidation (E) is sluggish or a rapid chemical reaction (C) is coupled to Tenox oxidation, giving rise to the so called EC mechanism. In accordance with Gosser [15], who describes a simplified two-dimensional "zone" diagram for the EC mechanism, see Figs. 2–15 in Ref. [15], our case would correspond to an EC mechanism where both, the electrode and chemical kinetics are fast. In order to support further the conclusion regarding the electrochemical reaction, the variation of the peaks' potential as a function of the scan rate was analyzed.

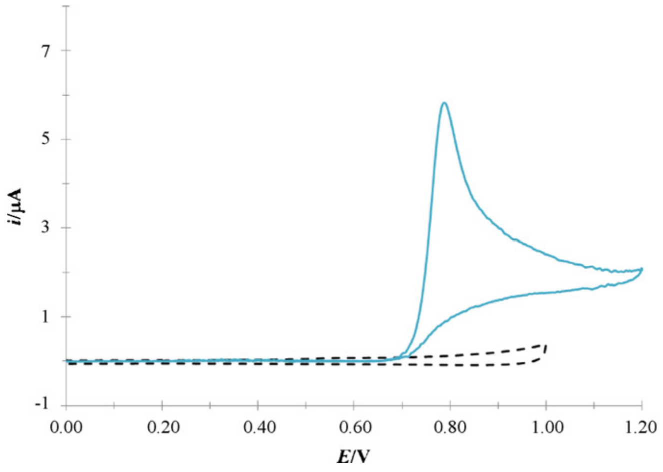

Fig. 3. Experimental cyclic voltammograms recorded, under stagnant conditions, in the system CPE/HCl 0.1 M (pH = 0.403) with different [Tenox]: 0, broken line, and (153 ± 1) μM, solid line; in both cases the potential scan rate was $100\,\mathrm{mV\,s^{-1}}$.