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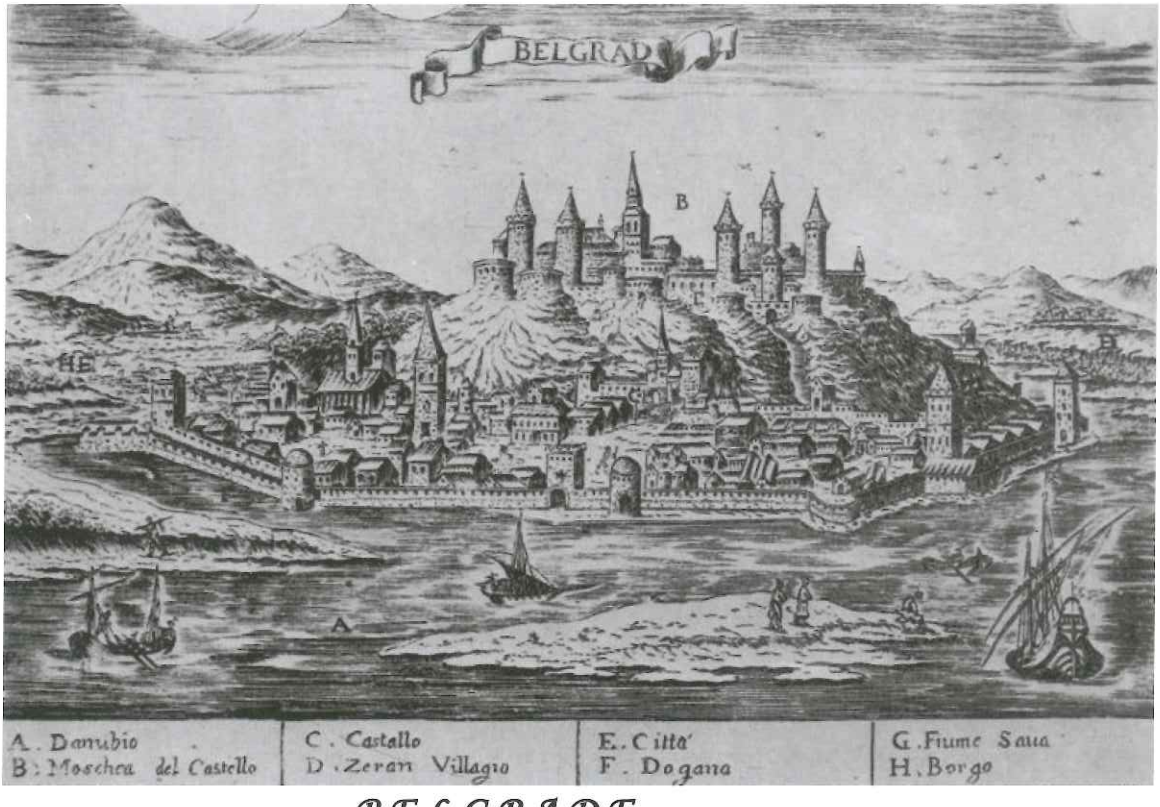

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ELECTROCHEMICAL BEHAVIOR AND DETERMINATION OF SULFAQUINOXALINE AT GLASSY CARBON ELECTRODE

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ABSTRACT

Electrochemical behavior of sulfaquinoxaline (SQN) was investigated using cyclic (CV) and differential pulse voltammetry (DPV) at glassy carbon electrode (GCE). CV was applied to investigate the effect of the supporting electrolyte pH on the SQN oxidation. In the pH range 2.0 – 10.0, the best current response was obtained at pH 7.0 in phosphate buffer. Results indicated that SQN is oxidized in irreversible process. DPV method was optimized, and the linear dependence of peak current *vs.* SQN concentration was obtained in the range 3×10^{-6}–5×10^{-5} molL^{-1}, with limits of detection and quantification of 1.53×10^{-6} molL^{-1} and 5.10×10^{-6} molL^{-1}, respectively.

INTRODUCTION

The sulfonamide drugs ("sulfas") had been discovered primarily as antibacterial agents and later on, their efficacy had been shown to extend to protozoan parasites. Sulfaquinoxaline was found to be a superior agent against sporozoan parasite, *Eimeria* spp., the causative agent of coccidiosis in domestic chickens [1]. Different methods such as liquid chromatography with ultraviolet detection [2], high performance liquid chromatography (HPLC) coupled to a mass spectrometer (MS) [3], and a new HPLC method that is based on zwitterionic hydrophilic interaction liquid chromatography (ZIC-HILIC) coupled with ultraviolet detection [4] were used to determine SQN. Electrochemical reduction of SQN at mercury electrode was reported [5] and used for its determination in veterinary preparations. There is no literature report about the oxidation of SQN. The aim of this work was to investigate SQN oxidation properties at GCE and to optimize DPV method for its determination.

EXPERIMENTAL

The voltammetric measurements were performed with μAutolab analyzer (EcoChemie, Utrecht, TheNederlands). Three-electrode system was employed with GCE working electrode, Ag/AgCl reference and Pt-auxiliary electrode. Before each experiment the GCE was manually polished using the aqueous slurry of Al_2O_3 powder (particle size 0.05μm) on a smooth polishing pad and sonicated in absolute ethanol. Chloride, acetate, phosphate and ammonia buffers were used as supporting electrolytes. An appropriate volume of supporting electrolyte of different pHs was placed in electrochemical cell, de-aerated for 15 minutes with high purity nitrogen and SQN stock solution ($c_0=2\times10^{-3}$ molL^{-1}) was added to make its final concentration of 1×10^{-4} molL^{-1} for CV and 1×10^{-5} molL^{-1} for DPV. The cyclic voltammograms were recorded at scan rate of 100 mVs^{-1}. Parameters for DPV were: potential pulse width 50ms, pulse amplitude 75mV and step potential 5mVs^{-1}. All experiments were performed at 24 ± 1 ^{o}C.

RESULTS AND DISCUSSION

The oxidation of 1×10^{-4} molL^{-1} solution of SQN at GCE was preliminary studied in acetate buffer pH 3.5 by cyclic voltammetry.Cyclic voltammograms were obtained in repeated scans starting from 0 V towards +1.25 V and reversing to negative potential limit -1.2 V at a scan rate 100 mVs^{-1}. On the first positive-going scan (Fig. 1, grey line) one anodic peak (I) was obtained at E_{pI} = 0.98 V and on the second scan (Fig. 1, black line) another anodic peak (II) was obtained at E_{pII} = 0.5 V. Changing the scan direction both anodic peaks were obtained (Fig. 2.) in the first scan. Peak II is probably due to oxidation of the SQN reduction product formed at the surface of GCE at negative potential values.

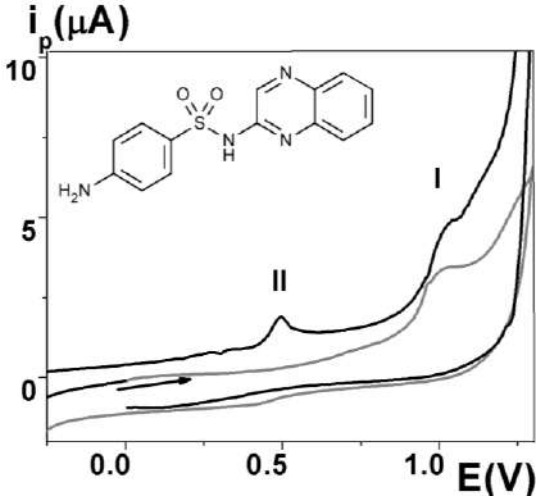

Figure 1. CVof 1×10^{-4}molL^{-1} SQN in two successive scans: —— first scan, ——second scan (v = 100mVs^{-1})
Attached: SQN structure

These results correspond to already established redox mechanism of C=N quinoxaline core group [6]. There are no peaks at

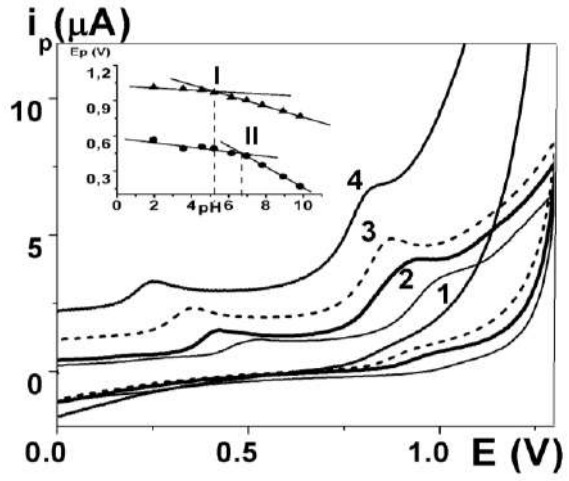

Figure 2. CVof 1×10^{-4} molL^{-1} SQN at different pH values:1 − pH 4.6;2− pH 6.1; 3 − pH 7.8; 4 − pH 8.9; (scan rate 100 mVs^{-1})
Attached: Influence of the pH on SQN CV peaks potential, I (▲) and II (●)

reverse part of scan indicating that processes corresponding to peaks I and II are irreversible.

Anodic peaks I i II are present in the pH range from 2.0 up to10.0 at positive potentials. The influence of the pH on these peaks potential resulted in the shift to the less positive potentials with increasing of pH and that H^+ ions areincluded in the electron transfer process. Observing E_p*vs*. pH dependence, both peaks show two linear segments. According to their intersection, experimental pKa values were determined: pKa(I) ~ 5.2 and pKa(II) ~6.7. First value corresponds to literature data (pKa = 5.1 for sulfonamide nitrogen [7]).

This result indicates that oxidation of nitrogen in sulfonamide group is responsible for peak I and that it could be used for further research and SQN determination. Another pKa value corresponds to pKa of nitrogen in dihydro derivate of quinoxaline. It is assumed that this derivative is result of the oxidation of SQN reduction product [6].

For peak I the best current response was obtained at pH 7.0 in phosphate buffer. DPV method was optimized by varying important operation parameters, and the best obtained values were: potential pulse width 50ms, pulse amplitude 75mV and scan rate 5mVs^{-1}.

The linear dependence of peak current *vs*. SQN concentration was obtained in the range 3×10^{-6}–5×10^{-5} molL^{-1}, under optimal conditions, and expressed by the equationi_p (μA) = 0.510 × c (10^{-5}molL^{-1}) - 0.139 (r = 0.9984, SD = 0.026 μA), with LOD = 1.53×10^{-6} molL^{-1} and LOQ = 5.10×10^{-6}molL^{-1}.

SQN represents one of two active components in veterinary medicine NEOCOCCYN WSP. According to our preliminary results another active component,amprolium hydrochloride,is not electrochemically active under

the conditions used for SQN determination, and therefore the proposed DPV method at GCE can be used to determine SQN in this veterinary medicine.

CONCLUSION

An extensive study of SQN electrochemical behavior at GCE was done by applying CV and DPV. It is confirmed that oxidation of nitrogen from sulfonamide group is irreversible, pH dependent process. From E_p*vs.* pH relation, experimental pKa values were obtained. The selective/specific DPV method at GCE without pretreatment will be optimized for SQN determination in veterinary medicine NEOCOCCYN WSP, which contains amprolium hydrochloride, as active component too.

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