

EFFECT OF SURFACTANTS IN SIMULTANEOUS ELECTROANALYTICAL DETERMINATION OF BIOLOGICALLY ACTIVE NITROGEN-CONTAINING HETEROCYCLES

VLIV TENZIDŮ NA SIMULTÁNNÍ STANOVENÍ BIOLOGICKY AKTIVNÍCH HETEROCYKLŮ OBSAHUJÍCÍCH DUSÍK

Amir S. Farag^{1,2}, Milan Sýs¹ and Karel Vytřas¹

¹*Department of Analytical Chemistry, Faculty of Chemical Technology, University of
Pardubice, Studentská 573, Pardubice, CZ-53210 Czech Republic*

²*Department of Analytical Chemistry, Faculty of Pharmacy,
University of Helwan, 11795 Cairo, Egypt*

E-mail st56093@student.upce.cz

Abstract

This electrochemical study is focused on selection of suitable surfactant for simultaneous voltammetric determination of biologically active nitrogen-containing heterocycles. Herein, xanthine alkaloid caffeine (CA) and pyridoxine (vitamin B6; VB6) were chosen as typical illustrative analytes. This work represents an initial step in the development of sophisticated electroanalytical method. Glassy carbon electrode and two of its modifications were tested in model samples of the Britton-Robinson pH 4.0 buffer, which contained always 100 μ M CA and 100 μ M VB6 and one of the surfactants tested, either nonionic Triton X-100, anionic sodium dodecyl sulfate, or cationic cetylpyridinium chloride or 1,3-didecyl-2-methylimidazolium chloride. The results show that the presence of surfactants contributes to improving the reproducibility of voltammetric measurements, but unfortunately does not cause any peak position differentiation.

Souhrn

Tato elektrochemická studie je zaměřena na výběr vhodné povrchově aktivní látky pro simultánní stanovení biologicky aktivních dusíkatých heterocyklů. V tomto případě byly jako typické ilustrativní analyty vybrány xantinový alkaloid kofein (CA) a pyridoxin též známý jako vitamin B6; (VB6). Tato práce je úvodní studií při vývoji sofistikované elektroanalytické metody. Elektroda ze skelného uhlíku a dvě její modifikované verze byly testovány na modelových vzorcích Brittonova-Robinsonova pufru o pH 4,0, které obsyhovaly vždy 100 μ M CA a 100 μ M VB6 a jeden z vybraných tenzidů, a to buď neiontový Triton X-100, aniontový dodecylsírant sodný, kationtový chlorid cetylpyridinia či chlorid 1,3-didecyl-2-methylimidazolia. Získané výsledky ukazují, že přítomnost tenzidů sice přispívá ke zlepšení reprodukovatelnosti voltamtrických měření, ale bohužel nezpůsobuje žádné rozlišení polohy píků.

1. Introduction

Nitrogen-containing heterocycles represent the board group of biologically active compounds such as alkaloids (caffeine, ricinine, nicotine, etc.), vitamins (pyridoxine, thiamin, riboflavin, folic acid, etc.), bases of nucleic acid (guanine, adenine, cytosine, thymine, etc.)

and drugs (minoxidil, esomeprazole, thiabendazole, etc.). It is known that many of them usually occur together in different clinical or food samples and can be classified as electroactive species which can be sensitively determined by specific electroanalytical methods utilizing a pulse voltammetric technique using different types of working electrodes and using surfactants as surface modifiers [1-4]. Nevertheless, it is necessary to mention that many of these methods have been developed only for their separate determination [5,6]. Only a few scientific articles dealing with using surfactants in the simultaneous voltammetric determination of nitrogen-containing heterocycles have been published [1]. The main aim of this work was to verify the effect of surfactant, when caffeine (CA) and pyridoxine (vitamin B6) were selected as illustrative examples of analytes.

Vitamin B6 (VB6), an essential water-soluble vitamin, is commonly added to multivitamin tablets and many energy drinks in the form of pyridoxine hydrochloride (Fig. 1a). VB6 is a key cofactor in transamination and other biochemical reactions and plays several important roles in human health [7]. Unlike this, CA is one of the naturally occurring alkaloids widely found in various foodstuffs (Fig. 1b) and is used for treatment of many diseases such as asthma, nasal congestion, and headache and even for improving athletic endurance and facilitating weight loss [8,9].

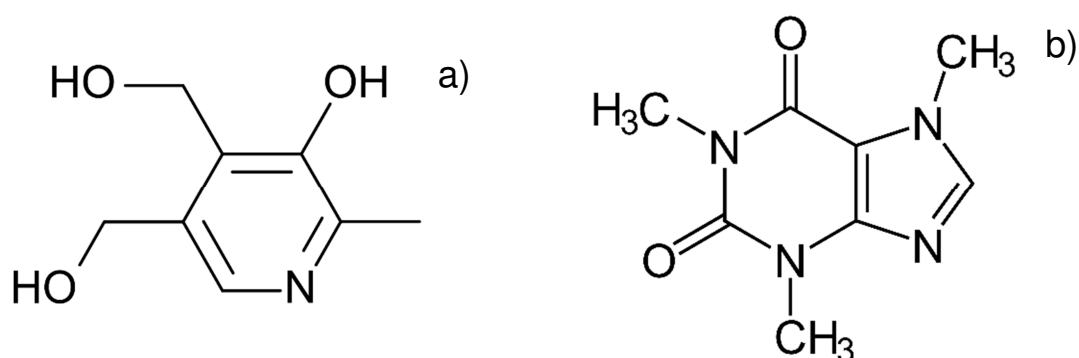


Figure 1. Chemical structures of pyridoxine (a) and caffeine (b).

2. Experimental

2.1. Reagents and Chemicals

Analytical standards of pyridoxine and caffeine, Nafion[®], surfactants such as sodium dodecyl sulfate (SDS), cetylpyridinium chloride (CPC), Triton X-100, 1,3-didecyl-2-methylimidazolium chloride (TEGO[®]trant A 100) were purchased from Sigma-Aldrich (Prague, Czech Republic). Multi-wall carbon nanotubes (MWCNTs) of diameter 10-30 nm; length 5-15 μm ; specific surface area 40 300 $\text{m}^2 \text{g}^{-1}$ from Shenzhen Nanotech Port Co., Ltd.

(Shenzhen, China) were used as surface modifier. Chemicals needed for preparation of 0.1 M Britton-Robinson buffer (BRB) pH 4.0 were obtained from Lach-Ner (Neratovice, Czech Republic). Ultrapure water ($\rho = 18.3 \text{ M}\Omega \text{ cm}$) obtained by passing of the already deionized water again through a purification unit (Milli Q system, Millipore) was used throughout the experimental work.

2.2. Preparation of Working Electrode

Three different types of working electrodes were tested, namely bare glassy carbon electrode (GCE), GCE modified with thin layer of Nafion[®] (Nafion[®]/GCE), and GCE covered by composite material of MWCNTs with Nafion[®] (Nafion[®]/MWCNTs/GCE). Surface of solid GCE with diameter 3 mm from Metrohm (Prague, Czech Republic) was renovated on polishing pad with water suspension of Al₂O₃ powder (particle size 1.0 μm) for 30 s. Dispersions (2 mg mL⁻¹) of MWCNTs in 1% Nafion[®] neutralized by 8% ammonia solution were prepared using ultrasonic bath for 30 min. The modification of GCE surface was made by dropping of corresponding 20 μL dispersion and left to dry at laboratory conditions for minimally one hour.

2.3. Electrochemical Instrumentation

All electrochemical measurements were performed on conventional three-electrode arrangements, each containing one of the working electrodes tested, the reference (Ag/AgCl/3.0 M KCl) and the auxiliary electrodes (Pt-wire). Mentioned setup was connected to a potentiostat PGSTAT101 from Metrohm (Prague, Czech Republic) operating with Nova software version 1.11.

2.4. Procedures

All electrochemical experiments were performed at room temperature using 10 mL of 0.1 M BRB pH 4.0 as a supporting electrolyte containing always 100 μM CA, 100 μM VB₆, and different portions of tested surfactant. As electrochemical technique, differential pulse voltammetry (DPV) from 0 to +1.6 V at potential step 5 mV, potential amplitude 70 mV and scan rate 30 mV s⁻¹ was used.

3. Results and Discussion

3.1. Selection of Suitable Surfactant

Four different types of surfactants such as anionic sodium dodecyl sulphate (SDS), 1,3-didecyl-2-methylimidazolium chloride (TEGO[®]trant A 100), cationic cetylpyridinium chloride (CPC), and nonionic Triton X-100, were tested within optimization. At first glance, it was evident that no one of them had any significant effect on resolution of obtained anodic peaks. However, presence of surfactant, especially Triton X-100, caused an improvement in peak current reproducibility. Results obtained at bare GCE are shown in Table 1.

Table 1. Comparison of different tested surfactants.

Surfactant	Pyridoxine		Caffeine	
	E_p / V	I_p / μ A	E_p / V	I_p / μ A
CPC	1.26	0.94 \pm 0.2	1.05	5.43 \pm 1.2
SDS	1.27	1.29 \pm 0.2	1.05	5.34 \pm 0.9
Triton X-100	1.31	13.15 \pm 1.5	1.04	7.19 \pm 0.4
TEGO [®] trant A 100	1.25	0.38 \pm 0.1	1.05	2.23 \pm 0.5

3.2. Effect of Triton X-100

Different amounts of Triton X-100 (0-200 μ L) were added. The effect of Triton X-100 presence is shown in Fig. 2. It was evident that, the highest current signal was obtained with addition of 120 μ L of Triton X-100 for VB6 and 80 μ L of 0.01 M Triton X-100 for CA.

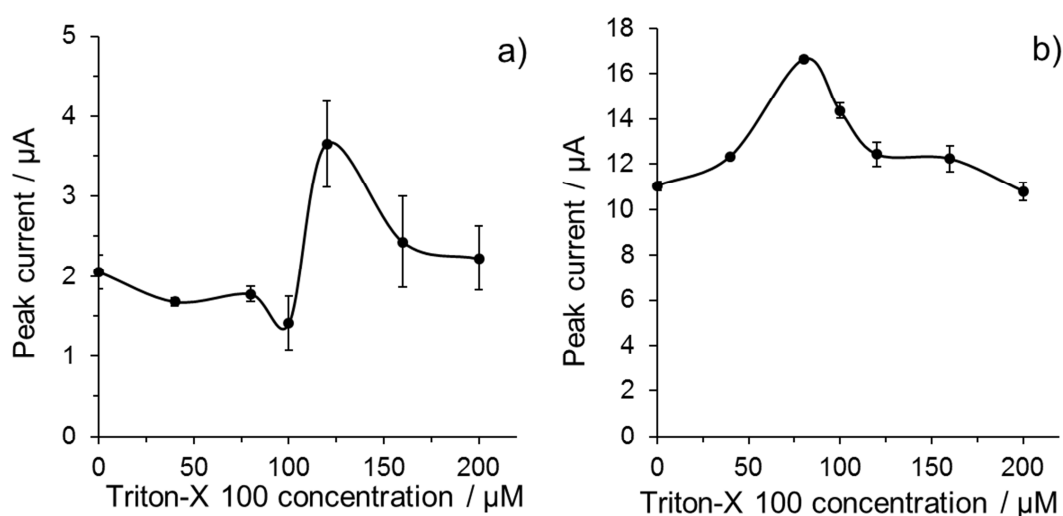


Figure 2. Effect of Triton X-100 on current response of VB6 (a) and CA (b).

3.3. Comparison of Different Working Electrodes

Nitrogen-containing heterocycles are involved in the protonation reactions and therefore they are represented as positively charged molecules in aqueous electrolytes. No wonder, solid electrode materials covered by conductive polymers with negatively charged functional groups, especially in the case of Nafion[®] with HSO₃⁻ groups, are the most often used sensors in their electroanalysis [10,11]. An explanation can be found in electrostatic interaction between positive target molecules and negative electrode surface which causes significant improvement in the sensitivity.

Bare GCE, Nafion[®]/GCE, and Nafion[®]/MWCNTs/GCE were tested. It was observed that sensor based on MWCNTs provided the highest peak current response (see Fig. 3). However, Nafion[®]/GCE represents sufficient electroanalytical device for upcoming monitoring of chosen model analytes.

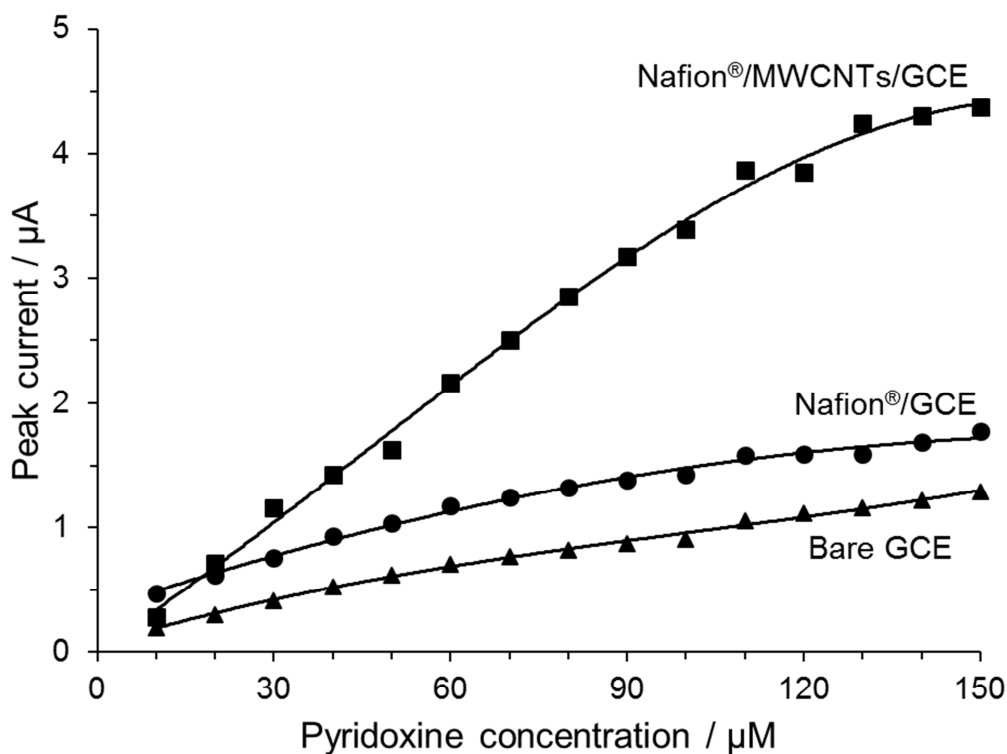


Figure 3. Calibration curves obtained with corresponding working electrodes.

4. Conclusion

On the basis of the results obtained, it can be stated that the simultaneous determination of vitamin B6 and caffeine can be carried out using anodic differential pulse voltammetry at Nafion[®] modified glassy carbon electrode without addition of any surfactant.

It seems that it is enough to find the optimal conditions of the aforementioned pulse voltammetric technique. Developed simple electroanalytical method could be probably used in the real sample analysis. This study lets the door open for further studies on using surfactants for the determination of other biologically active nitrogen containing heterocycles.

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