

VOLTAMMETRIC DETERMINATION OF 6-NITROBENZIMIDAZOLE IN THE PRESENCE OF SURFACTANTS

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Dedicated to the Dr. Michael Heyrovský on the occasion of his 80th birthday.

Determination of 6-nitrobenzimidazole by differential pulse voltammetry at a hanging mercury drop electrode, a polished silver solid amalgam electrode and a mercury meniscus modified silver solid amalgam electrode was studied in the presence of the surfactants Triton X-100, cetyltrimethylammonium bromide and sodium dodecyl sulfate. It was found that only cetyltrimethylammonium bromide at polished silver solid amalgam electrode increases the voltammetric signal. This fact was used for the determination of 6-nitrobenzimidazole in the concentration range from 1×10^{-7} to 1×10^{-4} mol l⁻¹ by differential pulse voltammetry at polished silver solid amalgam electrode in the presence of cetyltrimethylammonium bromide (concentration 1×10^{-4} mol l⁻¹).

Keywords: 6-Nitrobenzimidazole; Triton X-100; Cetyltrimethylammonium bromide; Sodium dodecyl sulfate; Differential pulse voltammetry; Hanging mercury drop electrode; Polished silver solid amalgam electrode; Mercury meniscus modified silver solid amalgam electrode.

6-Nitrobenzimidazole (6-NBIA; Fig. 1) belongs to the group of genotoxic nitrated heterocyclic aromatic compounds. It can damage natural biological functions of living organisms. 6-NBIA was determined as a part of photographic processing solutions using DC and AC polarography¹ and its adsorptive and inhibitive properties have been studied in the area of metal corrosion protection². It is proven carcinogen and mutagen³. The occur-

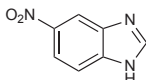


FIG. 1

Structural formula of 6-nitrobenzimidazole

rence of 6-NBIA in the environment is connected with fossil fuels combustion⁴.

6-NBIA can be determined spectrophotometrically in the ultraviolet and visible region⁵, by chromatographic techniques (high performance liquid chromatography⁶, thin-layer chromatography⁷) and by potentiometric titration⁸.

The easy electrochemical reduction of nitro groups at the aromatic or heteroaromatic ring, whose mechanism is discussed in ref.⁹, permits very sensitive determinations of a number of genotoxic and ecotoxic nitro compounds using modern voltammetric techniques such as differential pulse voltammetry (DPV) at a hanging mercury drop electrode (HMDE)¹⁰ and adsorptive stripping voltammetry (AdSV) at HMDE¹¹. Nevertheless, due to increasing fears of liquid mercury toxicity during the last decades¹², which has resulted in somewhat unreasonable "mercury phobia"¹³, attention is paid to the development of solid electrodes (e.g., solid amalgam electrodes^{14,15}, solid composite electrodes¹⁶, carbon paste electrodes¹⁷ or boron-doped diamond film electrodes¹⁸), which can also be used for determination of various nitro compounds. From this point of view, working electrodes based on silver solid amalgam (p-AgSAE)¹⁹ and modified by a mercury meniscus (m-AgSAE) represent a suitable non-toxic alternative to the traditional mercury electrodes. A good mechanical stability, simple handling and regeneration including an electrochemical pretreatment of the electrode surface are among the main advantages of these electrodes. The wide field of analytical applications of these electrodes has been reviewed^{14,20}. The purpose of this work was to investigate how the presence of surfactants influences an electroanalytical response of 6-NBIA at HMDE, p-AgSAE and m-AgSAE and, possibly, to utilize any signal enhancement to increase the sensitivity of the determination.

According to the ionic character of the molecules dissolved in water, ionic surfactants are classified as anionactive, cationactive and ampholytic. Anionactive ions have a negative charge in aqueous solution, cationactive ions have a positive charge and the charge of ampholytic ions depends on the pH of the solution. Non-ionic surfactants do not have a charge in the molecule and their solubility in water is given by the presence of a hydrophilic group²¹.

Good solubility, high conductivity, low toxicity and good chemical and electroanalytical stability of ionic surfactants make these substances useful for many electroanalytical applications. The presence of surfactants influences the parameters of measurement which often leads to the design of new procedures and methods for the determination. Traditional applica-

tion of the surfactants in electrochemistry is the suppression of maxima on polarographic curves²². They may change the shape of the polarographic wave and the reversibility of the electrode reaction which is reflected in the change of DPV peak height. The character of changes depends on the structure and concentration of the surfactant. By suitable choice, the limiting diffusion current might be increased, although under some circumstances, the decrease may also occur.

For this work, three surfactants were selected: Cationactive cetyltrimethylammonium bromide (CTMAB) (Fig. 2A), non-ionic Triton X-100 (Fig. 2B) and anionactive sodium dodecyl sulfate (SDS) (Fig. 2C). These surfactants might be used as modifiers for a variety of paste electrodes²³ and electro-analytical sensors²⁴. Therefore, we have investigated their influence on voltammetric determination of genotoxic nitro compounds using 6-NBIA as a model substance.

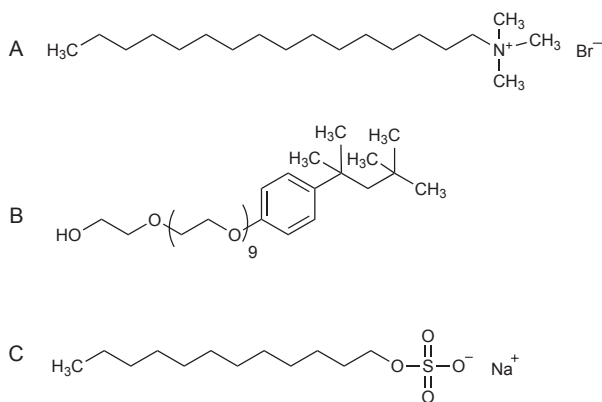


FIG. 2

Structural formulae of cetyltrimethylammonium bromide (A) Triton X-100 (B) and sodium dodecyl sulfate (C)

EXPERIMENTAL

Reagents

6-NBIA (98%, CAS Registry Number 94-52-0) was supplied by Sigma-Aldrich, Prague, Czech Republic in the form of nitrate. $1 \times 10^{-3} \text{ mol l}^{-1}$ stock solution was prepared by dissolving an exactly weighed amount of the substance in deionized water. A spectrophotometric study demonstrated that the stock solution is stable for at least three months⁵. The stock solution

of surfactants – CTMAB (98%, Sigma–Aldrich), Triton X-100 (laboratory grade, Sigma–Aldrich) and SDS (98%, Sigma–Aldrich) – were prepared in deionized water at the concentration $1 \times 10^{-2} \text{ mol l}^{-1}$. The solutions were stored in refrigerator. Diluted solutions were prepared freshly every day by exact dilution of the stock solution.

The Britton–Robinson buffer solutions (BR-buffer) were prepared in a usual way by mixing a 0.04 mol l^{-1} solution of phosphoric acid, acetic acid and boric acid with an appropriate volume of 0.2 mol l^{-1} sodium hydroxide, using analytical-reagent grade chemicals obtained from Merck, Prague, Czech Republic. Deionized water was produced by Milli-Q Plus system, Millipore, Billerica, USA.

Apparatus

Voltammetric measurements were carried out using Eco-Tribo Polarograph driven by Polar Pro 2.0 software (all Polaro-Sensors, Prague, Czech Republic). The software worked under the operational system Microsoft Windows 98 Plus (Microsoft Corporation, Redmond, USA). All measurements were carried out in a three-electrode system using platinum electrode PPE as an auxiliary electrode and silver|silver chloride electrode RAE 113 ($3 \text{ mol l}^{-1} \text{ KCl}$) (both Monokrystaly, Turnov, Czech Republic) as a reference electrode. The following working electrodes were used: (i) Pen type hanging mercury drop electrode UM μ E (Polaro-Sensors), the valve opening time 100 ms, the mercury drop surface 1.37 mm^2 , (ii) laboratory-made p-AgSAE (the disc diameter 2.64 mm) prepared according ref.¹⁹ and (iii) laboratory-made m-AgSAE (the disc diameter 2.64 mm) prepared according the same ref.¹⁹. The scan rate, 20 mV s^{-1} , the pulse amplitude, -50 mV , and the pulse width, 100 ms, with current sampling for last 20 ms were used for DPV. The p-AgSAE consisted of a drawn-out glass tube, whose tip was packed with a fine silver powder ($2.0\text{--}3.5 \mu\text{m}$, 99.9%, Sigma–Aldrich), amalgamated by liquid mercury (99.999%, Polarografie, Prague, Czech Republic) and connected to an electric contact. The m-AgSAE was prepared from p-AgSAE by immersing this electrode into a small volume of liquid mercury and agitating for 15 s (ref.¹⁴). The m-AgSAE could be used for several weeks, only its covering by mercury was usually repeated every week.

The solution pH was measured by Conductivity & pH meter 4330 (Jenway, Chelmsford, UK) with a combined glass electrode (type 924 005) of the same producer.

Procedures

Before starting the work with p-AgSAE and m-AgSAE, as well as after electrodes passivation or every break in the voltammetric measurements longer than 1 h, the electrochemical activation was carried out in $0.2 \text{ mol l}^{-1} \text{ KCl}$ (Lachema, Brno, Czech Republic) at -2200 mV under stirring for 300 s followed by rinsing with deionized water.

Regeneration of p-AgSAE and m-AgSAE lasting about 30 s preceded each measurement. It was based on application of 300 polarizing cycles (switching the electrode potential from $E_{1,\text{reg}}$ to $E_{2,\text{reg}}$ for 50 ms). For p-AgSAE, $E_{1,\text{reg}} = 0 \text{ mV}$ and $E_{2,\text{reg}} = -1200 \text{ mV}$, and for m-AgSAE, $E_{1,\text{reg}} = -100 \text{ mV}$ and $E_{2,\text{reg}} = -900 \text{ mV}$. Under these conditions, eventual oxides of mercury or silver are reduced and adsorbed molecules are desorbed²⁵. The appropriate values of the potential and time of the regeneration were inset in the software of the computer-controlled instrument used and the regeneration of electrodes was thus carried out automatically.

The general voltammetric procedure was as follows: An appropriate volume of the stock solutions of 6-NBIA and selected surfactant was diluted with BR-buffer of the appropriate pH

in a 10.0 ml volumetric flask and transferred into the voltammetric cell. Oxygen was removed by bubbling with nitrogen (purity class 4.0, Linde, Prague, Czech Republic) for 5 min and the voltammogram at HMDE, p-AgSAE or m-AgSAE was recorded.

All curves were measured 3 times and all the measurements were carried out at laboratory temperature. DPV peaks were evaluated from the straight line connecting the minima before and after the peak. The parameters of calibration curves (such as slope, intercept, correlation coefficient (R) and limit of quantification (L_Q)) were calculated with statistic software Adstat 2.0 (TriloByte, Pardubice, Czech Republic)²⁶.

RESULTS AND DISCUSSION

As optimal pH for DPV measurement, pH 4.0 was selected for HMDE (on the basis of the ref.²⁷) and pH 8.0 for p-AgSAE and m-AgSAE (on the basis of the ref.²⁸).

The next step was to find out if surfactants have any influence on the DPV peak of 6-NBIA (Figs 3, 4 and 5). The concentration of studied surfactants varied from zero to 1.0 mmol l⁻¹. At all three electrodes, the decrease of the signal (or non-significant change in voltammetric signal) of 6-NBIA with addition of SDS and Triton X-100 was observed. Different behavior was observed only with CTMAB at p-AgSAE and m-AgSAE (at lower concentrations of CTMAB), where the signal increased (it decreased at HMDE). The maximum enhancement of DPV signal of 6-NBIA was higher using p-AgSAE (increase by about 130%) in comparison with m-AgSAE (increase by about 50%). Therefore, the combination of p-AgSAE and CTMAB was selected for further investigation.

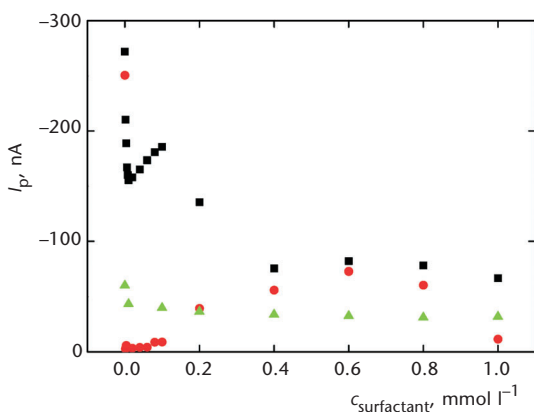


FIG. 3

The dependence of the DPV peak height of 6-NBIA ($c = 1 \times 10^{-5}$ mol l⁻¹) measured at HMDE in BR-buffer pH 4.0 on the surfactant concentration (SDS (■), Triton X-100 (●) and CTMAB (▲))

The addition of CTMAB can effectively enhance the signals of 6-NBIA at p-AgSAE even for a trace amount of CTMAB. With the increase of CTMAB concentration, the peak current initially increases and then remains constant up to 0.8 mmol l⁻¹ of CTMAB. CTMAB might form a monolayer in this concentration range and hence there is an increase in the signal²⁹. Above 0.8 mmol l⁻¹, addition of CTMAB surfactant results in the shift of peak potential of 6-NBIA towards more negative potential with decrease in

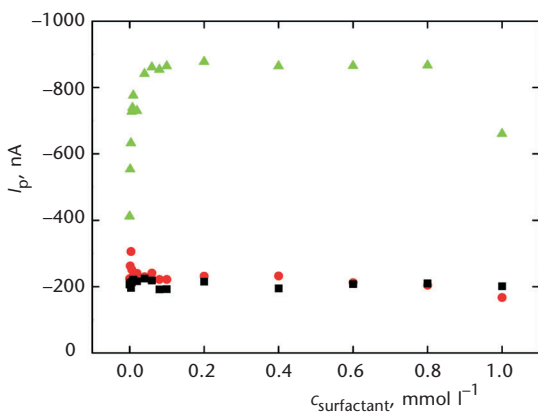


FIG. 4

The dependence of the DPV peak height of 6-NBIA ($c = 1 \times 10^{-5}$ mol l⁻¹) measured at p-AgSAE in BR-buffer pH 8.0 on the surfactant concentration (SDS (■), Triton X-100 (●) and CTMAB (▲))

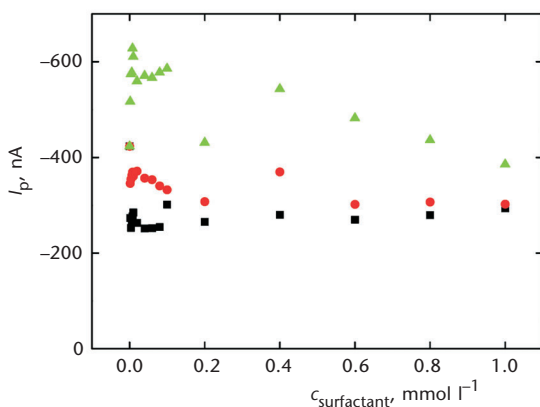


FIG. 5

The dependence of the DPV peak height of 6-NBIA ($c = 1 \times 10^{-5}$ mol l⁻¹) measured at m-AgSAE in BR-buffer pH 8.0 on the surfactant concentration (SDS (■), Triton X-100 (●) and CTMAB (▲))

peak current. This may be attributed to the direct adsorption of the surfactant at the p-AgSAE surface. Decrease in the availability of electroactive sites due to solubilization of the substrate may also contribute to this effect³⁰. The results showed that CTMAB exhibited different types of adsorptive behavior at p-AgSAE at different CTMAB concentrations.

The concentration $1 \times 10^{-4} \text{ mol l}^{-1}$ of CTMAB was chosen as optimal for the measurement of calibration curves at p-AgSAE. Calibration curves were measured in the concentration range of 6-NBIA from 2×10^{-7} to $1 \times 10^{-4} \text{ mol l}^{-1}$ with and without addition of CTMAB ($c = 1 \times 10^{-4} \text{ mol l}^{-1}$) (Fig. 6). The peaks in the presence of the surfactant are up to four times higher than peaks without the surfactant. This trend can be seen in the whole concentration range. Parameters of calibration curves are summarized in Table I,

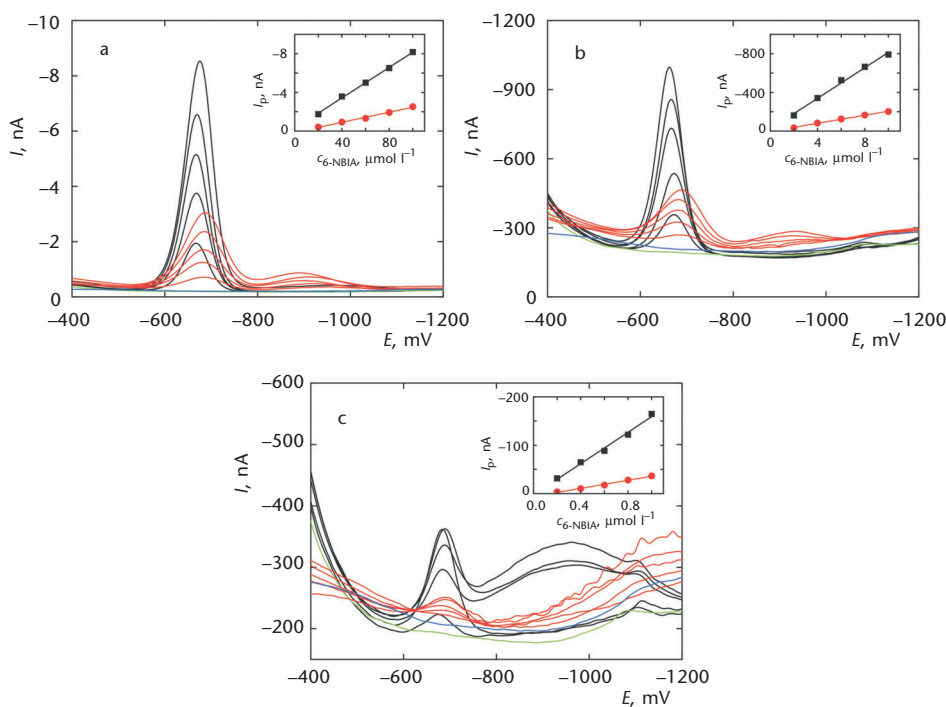


FIG. 6

Calibration curves for DPV determination of 6-NBIA ($c_{6\text{-NBIA}} = (2-10) \times 10^{-5} \text{ mol l}^{-1}$ (a), $(2-10) \times 10^{-6} \text{ mol l}^{-1}$ (b) and $(2-10) \times 10^{-7} \text{ mol l}^{-1}$ (c)) with CTMAB ($c_{\text{CTMAB}} = 1 \times 10^{-4} \text{ mol l}^{-1}$; black lines) and without CTMAB (red lines) in BR-buffer pH 8.0 at p-AgSAE (green and blue lines represent the supporting electrolytes with and without CTMAB, respectively)

from which the linearity in the whole concentration range is obvious, as well as a decrease of the L_Q of 6-NBIA and a higher slope of calibration dependences in the presence of CTMAB.

TABLE I

Parameters of the calibration dependences for DPV of 6-NBIA at p-AgSAE with and without CTMAB in BR-buffer pH 8.0

$c_{6\text{-NBIA}}$ mol l ⁻¹	c_{CTMAB} mol l ⁻¹	Slope nA mol ⁻¹ l	Intercept nA	R	L_Q mol l ⁻¹
$(2-10) \times 10^{-5}$	0	-2.60×10^7	132.6	-0.9971	-
	1×10^{-4}	-7.87×10^7	-280.5	-0.9992	-
$(2-10) \times 10^{-6}$	0	-2.90×10^7	3.1	-0.9981	-
	1×10^{-4}	-7.91×10^7	-22.6	-0.9964	-
$(2-10) \times 10^{-7}$	0	-4.18×10^6	5.9	-0.9969	4.3×10^{-7}
	1×10^{-4}	-1.62×10^7	2.9	-0.9953	2.5×10^{-7}

CONCLUSIONS

It has been proven that the addition of SDS and Triton X-100 does not significantly influence the DPV determination of 6-NBIA at HMDE, p-AgSAE and m-AgSAE. However, the addition of CTMAB significantly increases the height of DPV peak of 6-NBIA at p-AgSAE resulting in lower limit of quantification. The mechanism of this enhancement is not wholly clear at the moment and it will require further investigation. Most probably, cetyltrimethylammonium cation is adsorbed at the surface of negatively charged p-AgSAE. Silver obviously plays a certain role in this process³¹ which can explain that no or low enhancement is observable with HMDE or m-AgSAE. Long cetyl chain then enables the adsorption of low polar 6-NBIA at the electrode surface thus increasing the height of DPV peak. Under the optimal conditions, the limit of quantification for DPV of 6-NBIA at p-AgSAE decreased about twice by addition of CTMAB in comparison with measurement in the absence of the surfactant with keeping good accuracy.

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