ENVIRONMENTAL FRIENDLY ELECTROCHEMICAL DETERMINATION OF ASPIRIN FROM ALKALINE AQUEOUS SOLUTION

A. Remes, F. Manea, G. Burtica, R. Pode

„Politehnica" University of Timisoara, P-ta Victoriei Nr.2, 300006, Timisoara, Romania,
e-mails: adriana.remes@chim.upt.ro; florica.manea@chim.upt..ro

ABSTRACT

The electrochemical determination of acetylsalicylic acid (ASA) on multi-walled carbon nanotube- epoxy composite electrode (MWCNTs-EP) in aqueous solution was investigated using electrochemical techniques, *e.g.* cyclic voltammetry (CV), differential-pulsed voltammetry (DPV) and square-wave voltammetry (SWV). SWV applying allowed to reach the best performance in relation with the sensitivity for ASA determination in alkaline medium.

Keywords: multi-walled carbon nanotube, aspirin, electrochemical determination

INTRODUCTION

Acetylsalicylic acid (ASA) or aspirin has been used to treat a variety of imflammatory conditions such as headache (including migraine), muscle aches, menstrual cramps, colds and sinus infections. Several studies have shown that administrated in specific dosages, aspirin has the ability to prevent cardiovascular events and different types of cancer and to reduce even the incidence of Altzheimer's disease occurence [1-3].

Carbon nanotubes are novel materials with remarkable mechanical and electrical properties. These properties have attracted attention from researchers worldwide because of the superior physical and electrical potential. They are also capable of becoming good electrochemical sensors because of their low cost, high conductivity, good mechanical properties and many other advantages.

Therefore, the paper presents the cyclic voltammetry (CV) investigation and the determination of ASA by differential-pulsed voltammetry (DPV) and square wave woltammetry (SWV), using a multi-walled carbon nanotube- epoxy composite electrode (MWCNTs- EP).

MATERIALS and METHODS

Commercially available multi-walled carbon nanotubes (MWCNTs)(NC7000, Nanocyl S.A., Belgium) synthesized by catalytic carbon vapor deposition, having an average diameter of 9.5 nm and an average length of 1.5 μm were used. Araldite®LY5052-type epoxy resin and its corresponding hardener Aradur®5052 was obtained from the Huntsman Advanced Materials, Switzerland. Two gram of unmodified MWCNTs were initially dispersed in 200 ml of tetrahydrofuran (THF), and then mixed with epoxy resin under sonication. Finally the solvent was removed at 80°C for about 12 hours.

The batch was three-roll milled for several times on a laboratory scale three-roll mill (EXAKT 80E, EXAKT Technologies Inc.) at different shear intensities. Next, the mixture was placed into cylindrical PVC tubes and cured in vacuum oven at 80°C for 24 hours.

Samples for electrical conductivity (plates with a thickness ~ 1cm and length ~ 4 cm) were pressed/moulded into a Fontijne, TP 200 hydraulic press (pressing conditions: 1 h at 80°C) followed by immediate cooling at room temperature, to ensure a smooth surface.

Electrochemical measurements were carried out using an Autolab potentiostat/galvanostat PGSTAT 12 (Eco Chemie, The Netherlands) controlled with GPES 4.9 software and a three-electrode cell, with a saturated calomel (SCE) as reference electrode, platinum counter electrode and MWCNTs-EP working electrode. Before starting each electrochemical measurements, the working electrode was first polished with abrasive paper and then on a felt-polishing pad by using 0.03 μm alumina powder (Metrohm, Switzerland) in distilled water for 5 minutes. The alumina powder on the electrode was removed and carefully washed with double distilled water.

The optimum working parameters for differential-pulsed voltammetry (DPV) applying was modulation amplitude (MA) of 100 mV and step potential (SP) of 10 mV, and frequency (f) of 50 Hz, MA of 50 mV and SP of 5 mV for square-wave voltammetry (SWV) technique.

The samples from pharmaceutical formulations were aqueous solutions freshly prepared by dissolution of ASA tablets (OZONE)

RESULTS

Cyclic voltammograms (CVs) obtained with the MWCNTs-EP composite electrode and various concentrations of ASA in 0.1 M NaOH are shown in Fig. 1, and it can be noticed that the anodic limiting current recorded at +0.5 V vs. SCE depends linearly on the ASA concentration in the range 0.02-0.2 mM, with a correlation coefficient better that 0.998 (inset of Figure 1). The CV successive scans were collected in the potential range between -0.2 V versus SCE and +0.8 V versus SCE, starting in the positive direction from 0 V versus SCE, at a scan rate of $0.05 Vs^{-1}$. Calibration plot data of I_{pa} versus concentration of ASA exhibited good linearity and sensitivity (see Table 1).

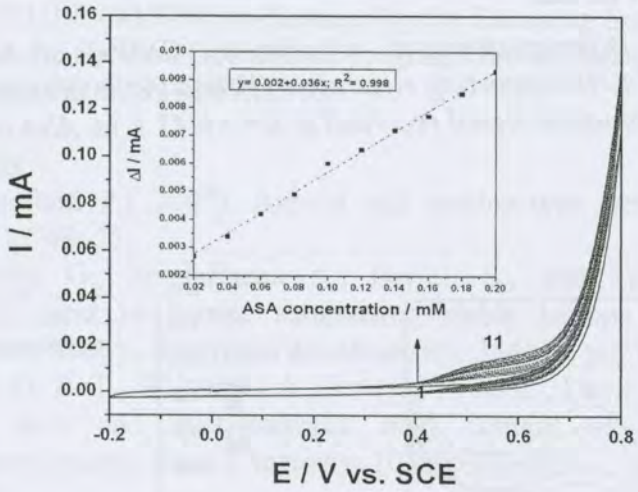

Figure 1. Cyclic voltammograms of MWCNTs-EP composite electrode in 0.1 M NaOH (1) and in the presence of 0.02 mM- 0.2 mM ASA (2-11); potential range: -0.2 V → +0.8 V; scan rate: 0.05 V/s

Other investigations with electroanalytical application purposes were conducted using two other different voltammetric techniques, differential- pulsed voltammetry (DPV) and square-wave voltammetry (SWV). Differential-pulsed and square-wave voltammetric techniques are widely used to improve the electroanalytical parameters for the direct

measurements of concentrations, e.g., the lowest limit of detection and the sensitivities. Also, they provide information about mechanistic aspects.

The optimum working conditions for both techniques were determined by varying all characetristics parameters. Thus, modulation amplitude (MA) of 100 mV and step potential (SP) of 10 mV were used for DPV applying and frequency (f) of 50 Hz, MA of 50 mV and SP of 5 mV for square-wave voltammetry (SWV) technique.

Figure 2 shows as example a DPVs series of MWCNTs-EP composite electrode in the presence of 0.1 M NaOH supporting electrolyte over the concentration range of 0.2-1.2 mM ASA. Calibration plot (for calibration data, see Table 1) of anodic current peak, I, versus ASA concentration showed a satisfactory high sensitivity of 0.063 $m\text{AmM}^{-1}$ respectively 0.076 $m\text{AmM}^{-1}$ and a very good linearity with a determination coefficient, $R^2 = 0.996$/ $R^2 = 0.999$. For comparison the SWV series corresponding to the same ASA concentration range is shown in Figure 3a. Also, a very good correlation coefficient was reached for linear dependence between anodic currents and ASA concentration (see Figure 3b and Table 1)

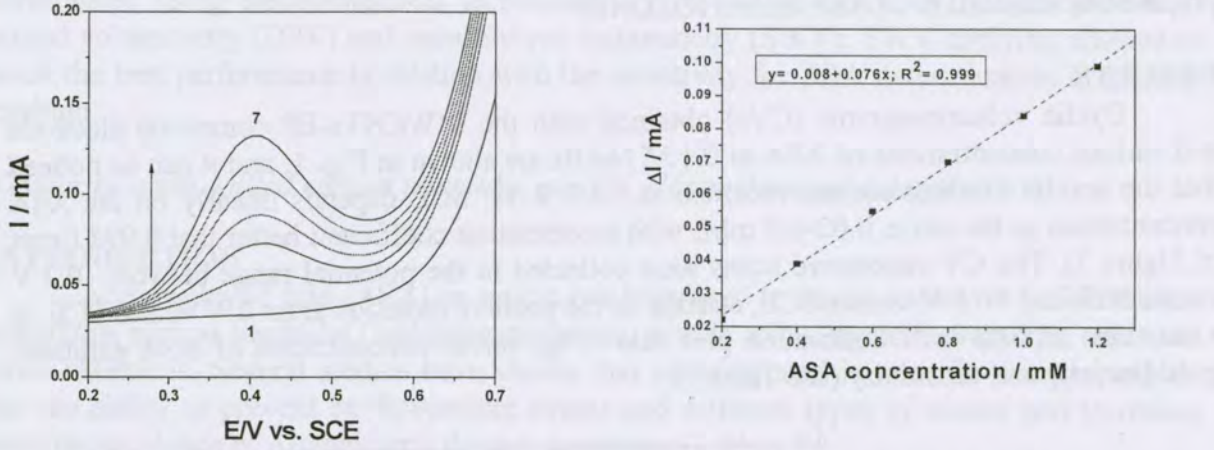

Figure 2.a) Differential-pulsed voltammetry (DPVs) of MWCNTs-EP composite electrode in 0.1 M NaOH supporting electrolyte (1) and in the presence of 0. 2-1.2 mM ASA; b) Calibration plots of useful signal recorded at E= +0.41 V vs. ASA concentrations

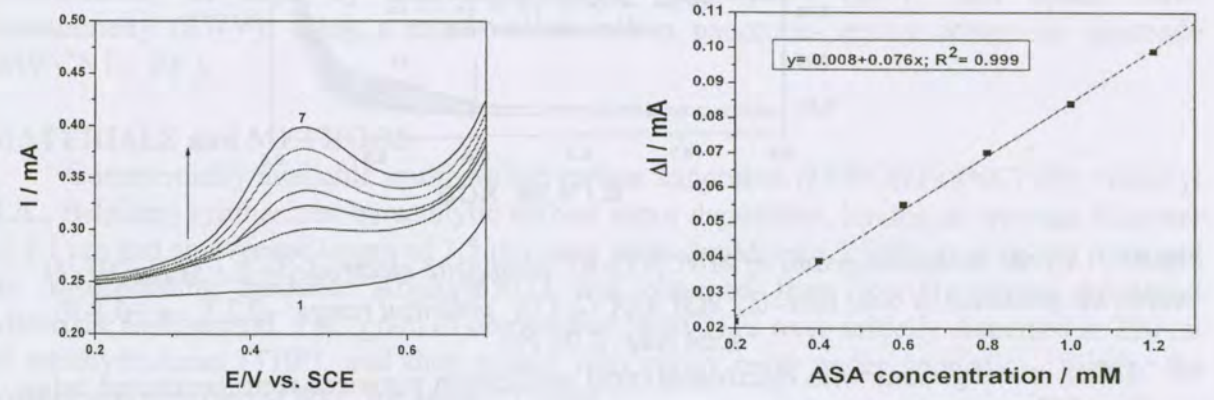

Figure 3. a) Square-wave voltammetry (SWVs) of MWCNTs-EP composite electrode in 0.1 M NaOH supporting electrolyte (1) and in the presence of: 0. 2-1.2 mM ASA; Calibration plots of useful signal recorded at E= +0.46 V vs. ASA concentrations

As can be seen form Table 1, which gathered the electroanalytical parameters for ASA determination in alkaline medium with MWCNTs-EP composite electrode, the best sensitivity was achieved by SWV technique at the potential value of +0.46 V/SCE.

Table 1. The electroanalytical parameters for the determination of aspirin in alkaline medium using MWCNTs-EP composite electrode

Used technique	E [V]	Sensitivity [$mA*cm^{-2}*mM^{-1}$]	Concentration range [mM]	Correlation coefficient (R^2)
CV	+0.5	0.036	0.02-0.2	0.998
DPV	+0.4	0.063	0.02-0.2	0.996
DPV	+0.4	0.076	0.2-1.2	0.999
SWV	+0.46	0.247	0.02-0.2	0.995
SWV	+0.46	0.097	0.2-1.2	0.998

CONCLUSIONS

The results obtained by all used techniques, i.e., CV, DPV, and SWV proved the useful features for the oxidation and direct voltammetric determination of aspirin with the multi-walled carbon nanotube- epoxy composite electrode in 0.1 M NaOH aqueous solution.The highest electroanalytical sensitivity for the determination of aspirin with the the composite electrode was reached using SWV technique at the potential value of +0.46 V/SCE. The newly developed electrode material presents attractive features for environmentally friendly voltammetric determination of ASA from alkaline medium and exhibited high sensitivity, stability and fast response.

ACKNOLEDGEMENTS

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LIST OF REFERENCES

[1] Farinelli I. and Martelletti P.(2007). Aspirin and tension-type headache, *Journal of Headache and Pain*, 8 (1)p. 49–55,.

[2] Battezzati A., Fiorillo G., Spadafranca A., Bertoli S., and Testolin G. (2006). Measurement of salicylic acid in human serumusing stable isotope dilution and gas chromatography-mass spectrometry, *Analytical Biochemistry*, 354(2), p. 274–278,.

[3] Scotter M. J., Roberts D. P. T., Wilson L. A., Howard F. A. C., Davis J., and Mansell N. (2007). Free salicylic acid and acetylsalicylic acid content of foods using gas chromatography-mass spectrometry, *Food Chemistry*, 105, p. 273-279.