



*Dedicated to the memory of
Professor Ioan Silaghi-Dumitrescu (1950 – 2009)*

NEW COMPOSITE MATERIALS USED IN THE PHENOL ELECTROANALYSIS. ¹ PART II. POLY(2-[(E)-2-AZULENE-1-YL]VINYL] THIOPHENE – PRUSSIAN BLUE

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New electrochemical sensors for phenol detection have been constructed using inorganic-organic composite materials based on poly(2-[(E)-2-azulene-1-yl]vinyl] thiophene) (PAVT) and Prussian Blue (PB). The PAVT films were generated by electrochemical polymerisation within two different potential ranges, *i.e.* from -0.6 to 1.2 V and from -0.6 to 1.8 V, respectively. PAVT and PB films were combined in order to obtain new composite materials with peculiar properties in phenol detection, the architecture of these materials being PAVT/PB or PB/PAVT. The electrochemical determination of phenol has been carried out in phosphate buffer solution with a pH of 6.0 by using square wave voltammetry (SWV). Under the optimal experimental conditions, the peak currents were proportional to the concentrations of phenol in the range from 30-100nM with a correlation coefficient $r^2=0.9900$ and sensitivity of 55 nA/nM.

INTRODUCTION

Phenols are involved in a lot of industrial processes and for this reason these compounds appear widespread in industrial waste.² Analytical techniques such as liquid chromatography,³ GC-MS,⁴ fluorimetric methods,⁵ titrimetric methods⁶ are very sensitive and reliable but they are time consuming, expensive and not for field use. The electrochemical sensors represent a promising alternative to the classical methods due to their relatively low-cost of operation, the potential of miniaturisation and rapid and simple detection procedures. Therefore, the determination of phenolic compounds in environmental, industrial,

food and clinical matrices has attracted a lot of attention in the modified electrodes field. Chemically modified electrodes using composite materials provide strategies for improving the performance of solid electrodes by incorporating catalytic sites at the interface electrode/solution.^{7,8} The motivations behind the modifications of the electrode surface are: i) improved electrocatalysis, ii) freedom from surface fouling and iii) prevention of undesirable reactions competing kinetically with the desired electrode process.⁹ The study of phenols electrooxidation using voltammetric and amperometric techniques for their monitoring has received a considerable attention. The recent activity in this field has been focused on the study of polymeric films.¹⁰⁻¹⁵ Conducting polymers such as polyaniline,⁷

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polypyrrole,⁶ and electroactive coatings such as poly(vinylferrocene),¹⁶ poly-nickel hydroxy tetraphenoxypyrrrolephthalocyanine (poly-Ni(OH)TphPyPc)¹⁷ or poly(methyleneblue)¹⁸ were used in order to clarify processes as doping/dedoping, charge transport or ion-exchange reactions.

In this paper, we report the results of a systematic study focusing on the preparation and characterization of new inorganic-organic composite materials based on poly(2-[(E)-2-azulene-1-yl]vinyl] thiophene) (PAVT) and Prussian Blue (PB). Determination of the phenol was carried out using square wave voltammetry (SWV) for the optimized experimental conditions. The phenol detection limits obtained using these composite materials are comparable with those reported in literature.¹⁹⁻²¹

RESULTS AND DISCUSSION

1. Preparation and characterization of modified electrodes

The polymeric films of PAVT were obtained by the electrochemical oxidation of 2-[(E)-2-azulene-1-ylvinyl] thiophene in 0.1 M tetrabutylammonium toluene 4-sulfonate (TBAT4S)-ACN on different potential ranges, (-0.6) - 1.2 V and (-0.6) - 1.8 V, respectively. The electrodeposition of PAVT films obtained in both manners is depicted in Fig. 1a and Fig. 2a. The doping-dedoping processes of PAVT films were studied in 0.1 M TBAT4S -ACN solution and the CV response of the PAVT films is depicted in Fig. 1b and Fig. 2b.

A good electroactivity of PAVT films obtained on the short potential range during electrochemical oxidation (p-doping) was observed. This behaviour could be explained considering that a polymer with a high effective conjugation length was obtained and the delocalization of π - electrons in the system is high. Some differences can be observed in the cyclic voltammograms of PAVT films synthesized according to both procedures, extended and short potential range. The PAVT films obtained by cycling of the potential on the extended potential range, *i.e.* (-0.6) - 1.8V (see Fig. 2b), have a lower charging current comparing to PAVT films obtained by cycling of the potential on the short potential range (see Fig. 1b). From Fig. 1b it can be seen that the polymeric film produces an oxidation peak at 0.5 V and a reduction peak at 0.35 V on the reverse scan, respectively. The redox behaviour for the PAVT films obtained on the extended potential range is not good as can be seen in Fig. 2b, the electrooxidation of PAVT film is an irreversible process.

This response of the PAVT film in transfer solution might be due to the fact that the charge transfer during charging and discharging reactions is very slow.

The PB was electrodeposited onto platinum disk electrode by using the potentiodynamic method, *i.e.* cycling the electrode potential for 8 cycles from -0.2 to 1.0 V at a scan rate of 50 mV/s in a solution containing 1 mM FeCl₃, 1mM K₃Fe(CN)₆, 0.1 M KCl and 0.01 M HCl.

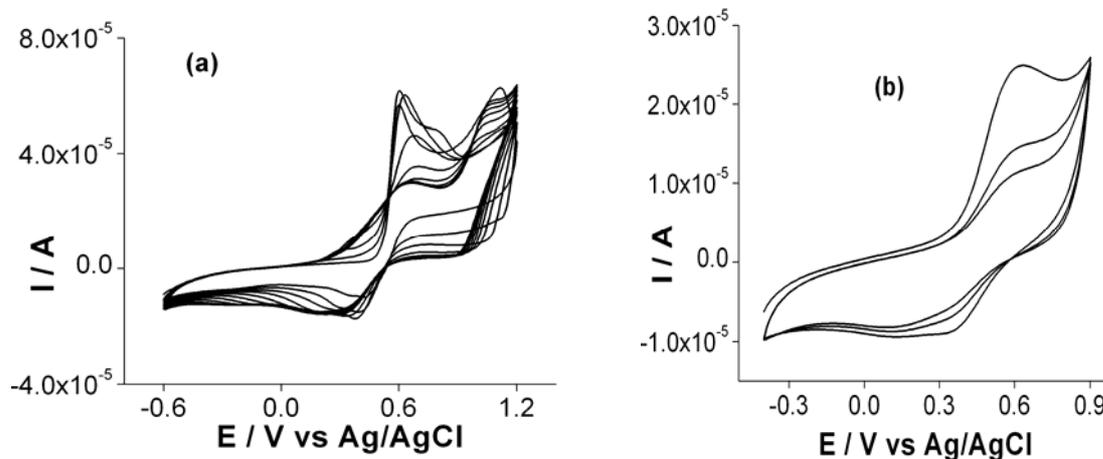


Fig. 1 – a) The cyclic voltammograms for electrodeposition of PAVT from 0.1 M TBAT4S-ACN solution containing 1mM AVT. The potential scan rate was 50 mV/s on the short potential range: -0.6 to 1.2V. b) The cyclic voltammograms of Pt/PAVT modified electrode (obtained on the short potential range, -0.6 to 1.2V) in 0.1 M TBAT4S-ACN monomer free electrolyte solution. Potential scan rate: 50 mV/s.

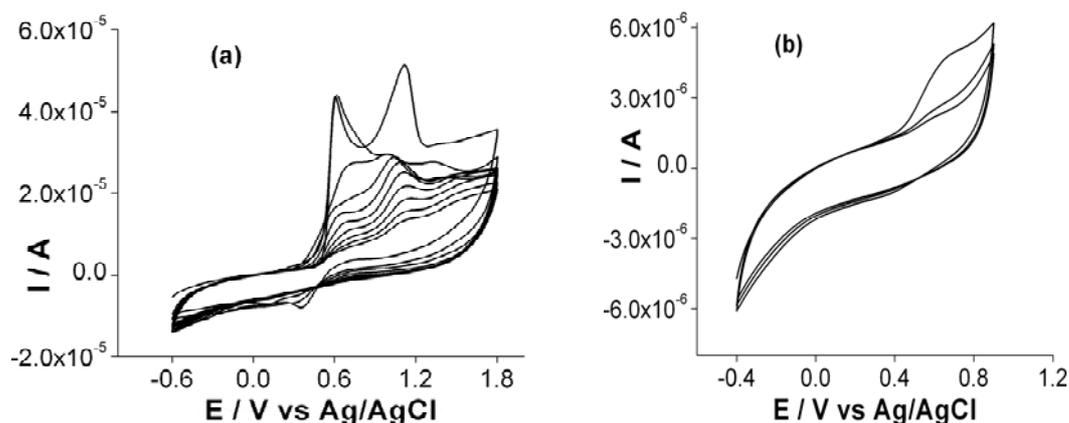


Fig. 2 – a) The cyclic voltammograms for electrodeposition of PAVT from 0.1M TBAT4S-ACN solution containing 1 mM AVT. The potential scan rate was 50 mV/s on the extended potential range, -0.6 to 1.8V. b) The cyclic voltammograms of Pt/PAVT modified electrode (obtained on the extended potential range, -0.6 to 1.8V) in 0.1 M TBAT4S-ACN monomer free electrolyte solution. Potential scan rate: 50 mV/s.

The bilayer coatings based on PB and poly(2-[(E)-2-azulen-1-ylvinyl] thiophene) films are obtained in a two steps preparation procedure and for different configurations. In the case of the PB/PAVT coating, a PB layer has been first electrodeposited onto the platinum electrode. In the second step, the electrochemical polymerization of 2-[(E)-2-azulen-1-ylvinyl] thiophene onto the Pt/PB modified electrode has been carried out. The cyclic voltammograms for electrodeposition of PB on Pt/PAVT modified electrode from an aqueous solution containing 1 mM FeCl_3 , 1 mM $\text{K}_3(\text{CN})_6$, 0.1 M KCl and 0.01 M HCl at potential scan rate=50 mV/s are presented in Fig.3a. The PAVT/PB coatings have been obtained and characterized under similar experimental conditions as those reported for PAZ/PB coatings. The redox behaviour of PAVT/PB coating was studied in the transfer solution of 0.1 M KCl and

0.01 M HCl at 20 and 50 mV/s. The corresponding voltammograms are depicted in Fig. 3b. Also in this case PAVT inner layer presents a similar electrochemical behaviour in respect with the absence of the PB redox waves, the organic PAVT film does not allow the free motion of potassium ions in order to maintain the electroneutrality.

The second geometry of the new composite material based on poly(2-[(E)-2-azulen-1-ylvinyl] thiophene and Prussian blue also has been obtained by two steps procedure, after electrodeposition of Prussian blue on platinum electrode, the poly 2-[(E)-2-azulen-1-ylvinyl] thiophene film was electrodeposited on Pt/PB modified electrode from 0.1 M TBAT4S-ACN solution that contains 1 mM AVT. The cyclic voltammograms for the obtaining of PAVT film on Pt/PB modified electrode and the characterization of the obtained composite material are presented in Fig. 4a and Fig. 4b, respectively.

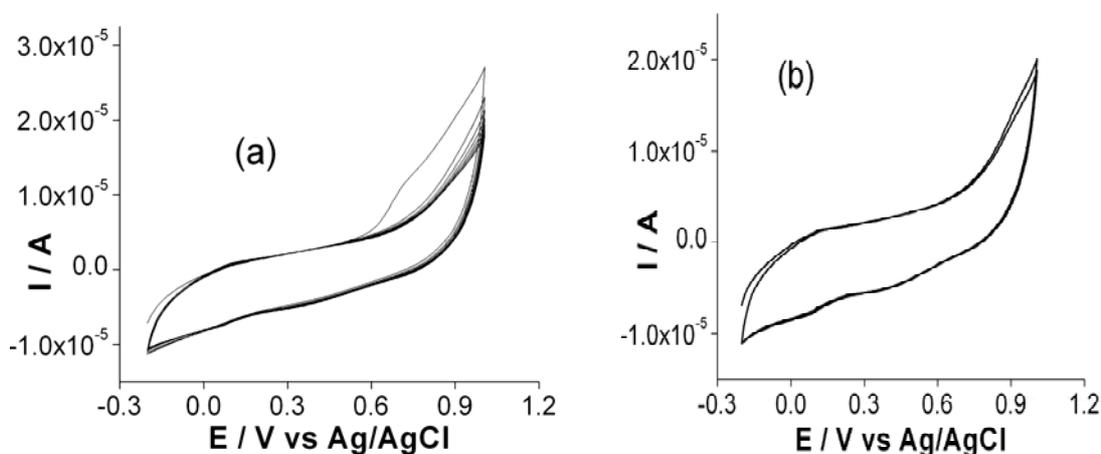


Fig. 3 – a) The cyclic voltammograms for electrodeposition of PB on Pt/PAVT modified electrode from an aqueous solution containing 1 mM FeCl_3 , 1 mM $\text{K}_3(\text{CN})_6$, 0.1 M KCl and 0.01 M HCl. Potential scan rate: 50 mV/s. b) The cyclic voltammograms of Pt/PAVT/PB modified electrode in the transfer solution containing 0.1 M KCl and 0.01 M HCl. Potential scan rate: 50 mV/s.

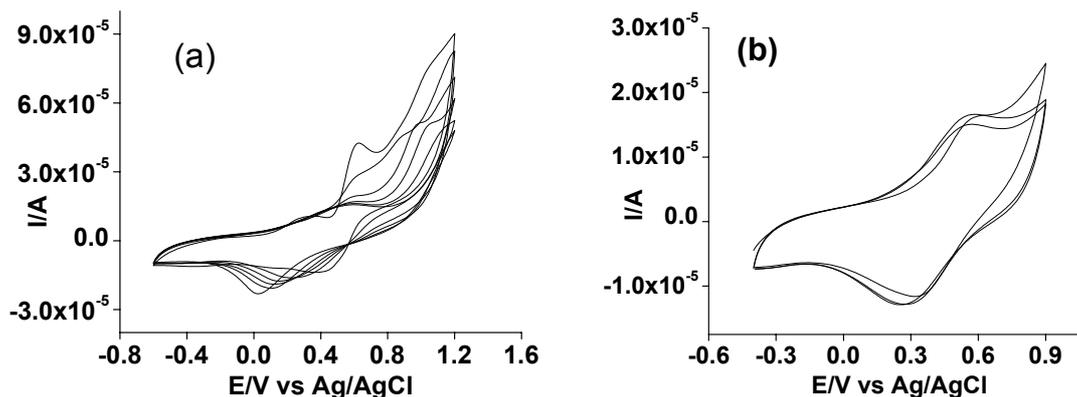


Fig. 4 – a) The cyclic voltammograms for electrodeposition of PAVT on Pt/ PB modified electrode from 0.1 M TBAT4S-ACN solution containing 1mM AVT. The potential scan rate was 50 mV/s on the short potential range: -0.6 to 1.2V. b) The cyclic voltammograms of Pt/ PB/PAVT modified electrode in the transfer solution. Potential scan rate: 50 mV/s.

2. Voltammetric determination of phenol at Pt/PAVT, Pt/PAVT/PB and Pt/PB/PAVT modified electrodes

The obtained modified electrodes, Pt/PAVT, Pt/PAVT/PB and Pt/PB/PAVT have been investigated by using square wave voltammetry (SWV) in order to establish the possibility of their application as electrochemical sensors for phenol determination. All voltammetric studies were performed in aqueous phosphate buffer solution with a pH of 6.

The phenol oxidation at Pt/PAVT modified electrode takes place at more negative values, 0.17 V versus 0.38 V for Pt/PAZ modified electrode.¹ The anodic peak current corresponding to the phenol oxidation at 0.17 V increases linearly with phenol concentration within range 30-100 nM. The

equation of the linear calibration graph is: $I_{pa} \text{ (A)} = 5.5 \times 10^{-8} C_{\text{phenol}} \text{ (nM)} - 3.1 \times 10^{-7}$, with a correlation coefficient $r^2 = 0.9900$ and a sensitivity value of 55 nA/nM, calculated from the slope of the I_{pa} versus phenol concentration plot. The linear range was better than that reported in the literature.^{22,23} The limit of detection for phenol, defined as the amount required to give a signal of three times the standard deviation of the noise signal is 9.8 nM at Pt/PAVT modified electrode, comparable with the literature.

Comparing the responses of Pt/PAVT and Pt/PAZ electrodes towards electrooxidation of phenol it could be observed a better sensitivity (55 nA/nM) when the electrode was modified with PAVT film.

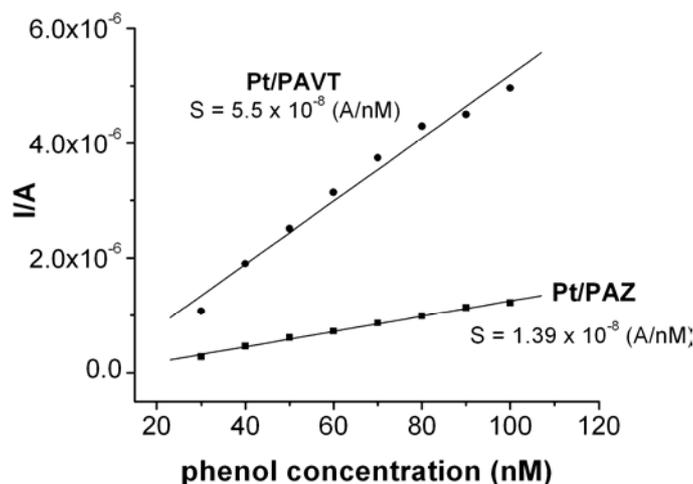
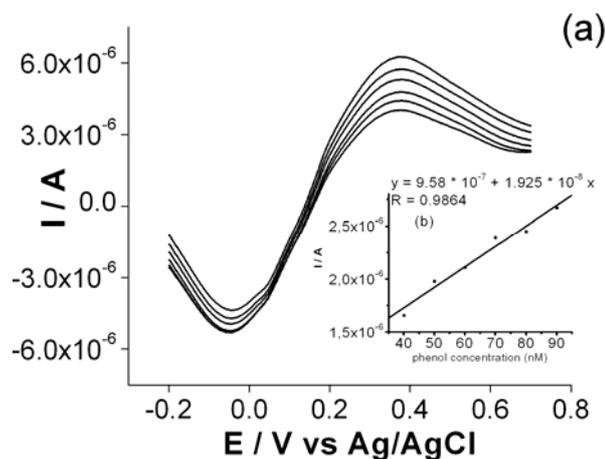


Fig. 5 – Calibration plots for the response of the Pt/PAVT and Pt/PAZ modified electrodes at different phenol concentrations.

In Fig. 6 it could be observed that at Pt/PAVT/PB modified electrode the oxidation of phenol occurs at 0.37 V, that is at a potential value shifted with 220 mV towards more positive potentials than the oxidation peak potential recorded at Pt/PAZ/PB modified electrode. For the

phenol concentration range between 40 and 90 nM, a linear dependence of the oxidation peak current with the concentration was obtained according with the equation: $I_{pa}(A) = 9.58 \times 10^{-7} + 1.925 \times 10^{-8} C_{phenol}(nM)$ (see inset of Fig. 6).

Fig. 6 – a) Square wave voltammograms recorded at Pt/PAVT/PB modified electrode in aqueous 0.1 M phosphate buffer solution of pH = 6 containing various phenol amounts in the range 40-100 nM. Pulse amplitude 70 mV, pulse step 2.5 mV, frequency 10 Hz. b) Inset: dependence of square wave anodic peak current on phenol concentration.



The Pt/PAVT/PB modified electrode has a good response for the determination of the phenol in aqueous solutions. The sensitivity of the electrochemical sensor based on PAVT/PB coating, calculated from the slope of the calibration graph, was 19.25 nA/nM. Comparing the analytical performances of Pt/PAVT, Pt/PAVT/PB and Pt/PB/PAVT electrodes it could be observed that the composite material based on PAVT and PB did not improve the analytical performances of the obtained electrochemical sensors for the determination of phenol. When the platinum electrode was modified with the PAVT/PB coating, the electrochemical response towards the oxidation of phenol for low concentration was worse than in the case of PB/PAZ or PAZ/PB coatings¹. Nevertheless the composite materials based on PAVT and PB have been successfully used to determine phenol, obtaining a good sensitivity and a good limit of detection.

The Pt/PB/PAVT modified electrode for higher concentration than 50 nM phenol does not respond in phosphate buffer solution, pH=6.

EXPERIMENTAL

All chemicals were purchased from Fluka and they were used without any further purification. The 2-[(E)-2-azulen-1-ylvinyl] thiophene (AVT) was synthesized and purified according to the method reported in the literature.²¹ The aqueous solutions were prepared with doubly distilled water.

All controlled-potential experiments were performed with an Autolab potentiostat/galvanostat 302N (Ecochemie BV, Utrecht, Netherlands) coupled to a PC running the GPES

software, using a single-compartment cell with three electrodes, at room temperature. Platinum wire served as the counter electrode, while a Ag/AgCl as a pseudo-reference electrode (calibrated against ferrocene/ferrocenium $E_{redox} = 0.48$ V) and a platinum disk (Metrohm, diameter 3mm) as working electrode. Before each electrochemical measurement the surface of the working electrode was mechanically polished with 1, 0.3, and 0.05 μ m alumina powders, and rinsed with doubly distilled water. The solutions were bubbled with high purity argon and a flow of argon was maintained over the solution during the measurements.

The polymerization of 2-[(E)-2-azulen-1-ylvinyl] thiophene was performed in acetonitrile (ACN) containing 0.1M tetrabutylammonium toluene 4-sulfonate (TBAT4S) and 1mM monomer by potentiodynamic cycling, in the potential ranges between -0.6 and 1.2V for 10 cycles or between -0.6 and 1.8V for 10 cycles, at a potential scan rate of 50 mV/s. The obtained polymeric films were characterized in monomer free solution of 0.1 M TBAT4S-ACN, at 50 mV/s and 20 mV/s potential scan rate. The thickness of the coatings was controlled by the number of potential cycles.

The inorganic-organic films have been obtained electrochemically by a two-step method in different configurations. In the case of the Pt/PB/PAVT coating, first a PB layer has been electrodeposited onto a Pt electrode. In the second step, the electrochemical polymerisation of 2-[(E)-2-azulen-1-ylvinyl] thiophene onto the Pt/PB modified electrode has been carried out. The outer layer of PAVT was obtained by scanning of the electrode potential between -0.6 and 1.8 V at scan rate of 50 mV/s from a solution of acetonitrile containing 0.1 M TBAT4S and 1 mM AVT.

CONCLUSIONS

In this work new electrochemical sensors based on PAVT and PB for determination of phenol were developed. New composite materials such as

Pt/PB/PAVT and Pt/PAVT/PB were prepared. The best sensitivity obtained in determination of the phenol was 55 nA/nM when platinum electrode was covered with PAVT film. The sensitivity of the composite material based on PAVT and PB is lower compared with Pt/PAVT electrode.

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