

Polyazulene based materials for heavy metal ions detection

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Abstract. Azulene is a special monomer used to functionalize electrodes, due to its spontaneous electron drift from the seven-membered ring to the five-membered ring. The seven-membered ring of the molecule may act as electron acceptor, while the five-membered ring – as electron donor. This leads to very attractive properties for the synthesis of functional advanced materials like: materials with nonlinear optical and photorefractive properties, cathode materials for lithium batteries, or light emitting diodes based on organic materials. Azulene derivatives have been used rarely to the metal ions electroanalysis. Our study concerns the synthesis and electrochemical characterization of a new azulene based monomer 4-(azulen-1-yl)-2,6-bis((E)-2-(thiophen-3-yl)vinyl)pyridine (**L**). **L** has been used to obtain modified electrodes by electrochemical polymerization. Poly**L** films modified electrodes have been characterized by cyclic voltammetry in ferrocene solutions. The complexing properties of poly**L** based functional materials have been investigated towards heavy metals (Pb, Cd Hg, Cu) by preconcentration – anodic stripping technique in order to analyze the content of these cations from water samples.

Keywords: Azulene derivatives; Chemically modified electrodes; Heavy metal ions detection; Electrochemical characterization

1. Introduction

Functionalized conducting polymer films have received considerable attention due to their great potential as analytical electrode materials [1-2]. Stable polymer film modified electrodes containing covalently attached dithiocarbamate [3] or EDTA [4] moieties, able to sense copper, cadmium or lead, have been produced by chemical derivatization of films previously coated by electropolymerization onto electrodes. Incorporation of complexing fragments into polymeric materials can alternatively be done by doping or ion exchange procedures [5]. However, the most efficient approach towards chelating-modified electrodes lies in the direct electropolymerization of complexing monomers, producing in one step stable functionalized polymers films with controlled sizes and sites concentrations. This straightforward approach has, however, seldom been applied to the determination of trace metals and only few examples can be found in literature [6-7].

Azulenes have a five-member (electron-rich) cyclic moiety connected with a seven-member (electron-poor) cyclic moiety. Azulene derivatives present an irreversible electrooxidation, and an



irreversible [8] or quasi-reversible reduction [9]. By electrooxidation polymeric films can be obtained in order to build electrochemical sensors, as shown in our recent works [10]. This research studies aimed to obtain modified electrodes for heavy metal ions detection.

There are different methods for determination of heavy metals from water samples based on iron oxide/graphene composite [10], bismuth nanoparticle-porous carbon paste [11], and zinc oxide-graphene composite [8]. The approach in our group is focused on complexing modified electrodes based on azulene derivatives [11]. In order to develop new sensors for heavy metals 4-(azulen-1-yl)-2,6-bis((E)-2-(thiophen-3-yl)vinyl)pyridine (**L**), with the formula shown in Figure 1, has been synthesized and electropolymerized to get poly**L** modified electrodes.

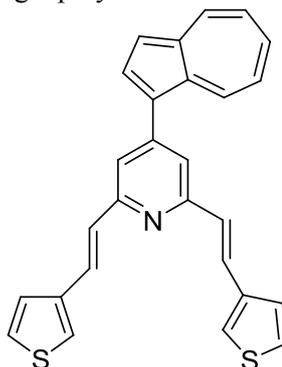


Figure 1. Structure of **L**.

The investigated compound has been characterized by electrochemical techniques, and the preparation of the modified electrodes has been studied. The heavy metals recognition based on poly**L** modified electrodes has been tested.

2. Experimental

Acetonitrile (CH_3CN) and tetrabutylammonium perchlorate (TBAP) from Fluka were used as received for solvent and supporting electrolyte, respectively. The azulene derivative (**L**) was synthesized according to previously described methods [7]. The metal salts used for recognition were commercial products: mercury (II) acetate, cadmium nitrate tetrahydrate, and lead (II) nitrate from Sigma Aldrich, copper (II) acetate monohydrate from Fluka. The electrochemical characterization of **L** was performed in 0.1M TBAP, CH_3CN .

The electrochemical experiments were carried out using a potentiostat PGSTAT 12 AUTOLAB connected to a three-electrode cell. The working electrode was a glassy carbon electrode from Metrohm (diameter of 3 mm). Its active surface was polished before each determination with diamond paste (1 μm) and cleaned with the solvent. A platinum wire was used as auxiliary electrode, and the reference electrode was dependent on the solvent: Ag/Ag^+ in acetonitrile ($\text{Ag}/10\text{mM AgNO}_3$, 0.1M TBAP, CH_3CN) or Ag/AgCl in water. The applied potential was finally referred to the potential of the ferrocene/ferricinium redox couple (Fc/Fc^+) which in our experimental conditions was 0.07 V.

Cyclic voltammetry (CV) curves were recorded at different scan rates (between 0.1 V/s and 1.0 V/s). Differential pulse voltammetry (DPV) curves were recorded at 0.01V/s with a pulse height of 0.025 V and a step time of 0.2 s. Rotating disk electrode (RDE) curves were recorded at 0.01 V/s. The anodic and cathodic CV, DPV and RDE scans have been recorded starting from the stationary potential.

The heavy metals ions detection was carried out in 0.1 M acetate buffer at $\text{pH} = 5.5$ which has been used as supporting electrolyte. The acetate buffer was prepared from 0.2 M acetic acid and 0.2 M sodium acetate solutions. The detection was studied using a glassy carbon disk (3 mm diameter) modified with poly**L** as working electrode, and Ag/AgCl , 3 M KCl from Metrohm as reference electrode. The heavy metals detection has been performed from synthetic heavy metals solutions with concentrations between 10^{-4} and 10^{-8} mol/L, prepared by successive dilutions from a stock solution containing all cations at the same concentration (10^{-2} M).

All electrochemical experiments have been conducted at 25°C under argon atmosphere.

3. Results and discussion

3.1. Electrochemical characterization of *L*

The electrochemical experiments were performed by differential pulse voltammetry (DPV), cyclic voltammetry (CV), and rotating disk electrode (RDE) in 0.1 M TBAP, CH₃CN in millimolar solutions of *L*.

DPV and CV curves at different concentrations (0 – 3.75mM) of *L* are presented in Figure 2. Three anodic and four cathodic main peaks are distinguished in DPV. They were denoted in the order of their apparition in anodic (a1 – a3) or cathodic (c1 – c4) scans. DPV peaks potentials are given in Table 1. In CV some peaks are not well distinguished, they appearing as shoulders (c2 and c4). The peak currents increase with concentrations in CV. In DPV curves this increase is valid for the first anodic and cathodic peaks, but for several peaks it is not valid (a2 and c4). Figure 3 shows the linear dependences of the peak currents on *L* concentration. Table 2 presents the equations and correlation coefficients for these CV and DPV dependences.

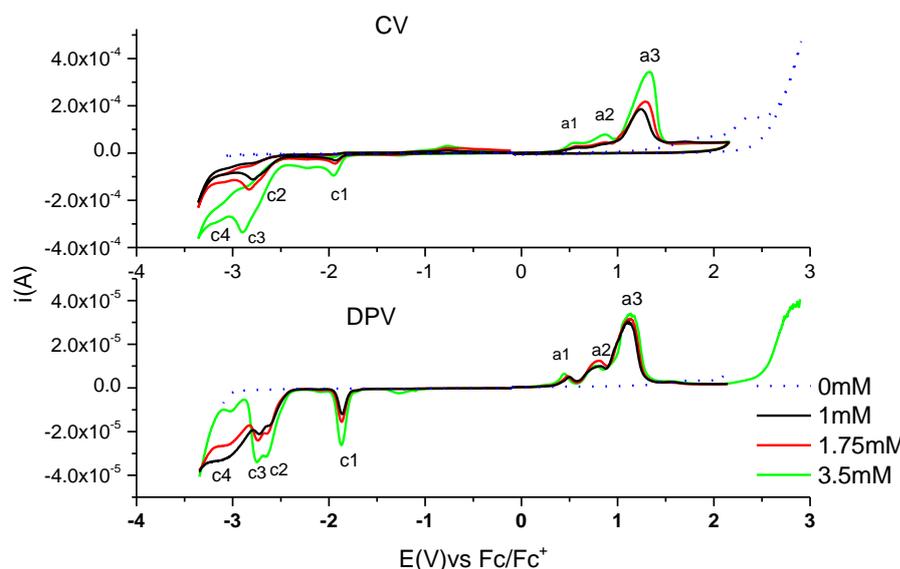


Figure 2. CV (up) and DPV (down) curves on glassy carbon (3 mm in diameter) for *L* at different concentrations in 0.1M TBAP, CH₃CN.

Table 1. Peak potentials (V) vs Fc/Fc⁺ from DPV and CV curves for *L* (1 mM).

Peak	Method	
	CV	DPV
a1	0.569 (i)*	0.501
a2	0.861 (i)*	0.800
a3	1.245 (i)*	1.118
c1	-1.930 (i)*	-1.865
c2	-	-2.624
c3	-2.789	-2.724
c4	-3.077	-3.09

*r - reversible process; q - quasi-reversible process; i - irreversible process

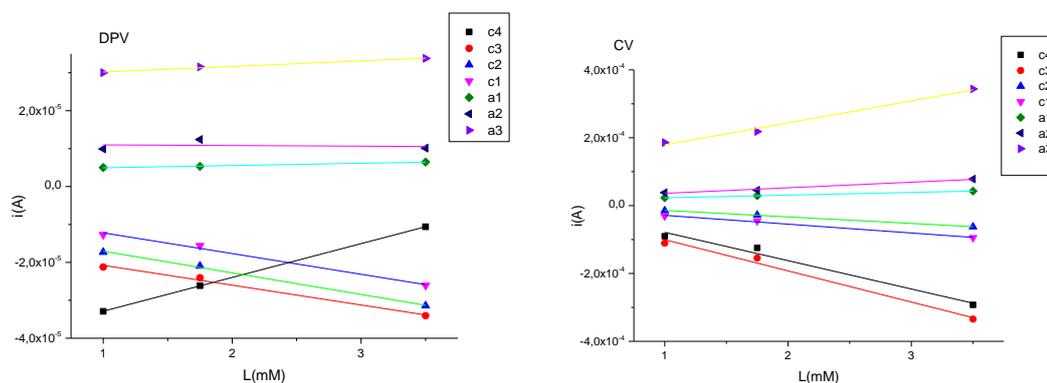


Figure 3. Dependences of the peak currents on **L** concentration in CV and DPV.

Table 2. Equations and correlation coefficients for CV and DPV peak currents.

Method	Equation*	Correlation coefficient
CV	$i_{\text{peak a1}} \text{ (A)} = 1.51\text{E-}5 + 7.91\text{E-}6 \cdot [\text{L}]$	0,999
	$i_{\text{peak a2}} \text{ (A)} = 1.96 \text{ E-}5 + 1.64\text{E-}5 \cdot [\text{L}]$	0,968
	$i_{\text{peak a3}} \text{ (A)} = 1.14\text{E-}4 + 6.47\text{E-}5 \cdot [\text{L}]$	0,979
	$i_{\text{peak c1}} \text{ (A)} = -2.64\text{E-}6 - 2.6\text{E-}5 \cdot [\text{L}]$	0,986
	$i_{\text{peak c2}} \text{ (A)} = 5.14\text{E-}6 - 1.92\text{E-}5 \cdot [\text{L}]$	0,997
	$i_{\text{peak c3}} \text{ (A)} = -8.57\text{E-}6 - 9.19\text{E-}5 \cdot [\text{L}]$	0,976
	$i_{\text{peak c4}} \text{ (A)} = 4.88\text{E-}6 - 8.36\text{E-}5 \cdot [\text{L}]$	0,963
DPV	$i_{\text{peak a1}} \text{ (A)} = 4,35\text{E-}6 + 5.95\text{E-}7 \cdot [\text{L}]$	0,985
	$i_{\text{peak a2}} \text{ (A)} = 1.115\text{-}5 -1,63\text{E-}7 \cdot [\text{L}]$	-0,954
	$i_{\text{peak a3}} \text{ (A)} = 2,87\text{E-}5 + 1,46\text{E-}6 \cdot [\text{L}]$	0,972
	$i_{\text{peak c1}} \text{ (A)} = -6.75\text{E-}6 - 5.46\text{E-}6 \cdot [\text{L}]$	0,984
	$i_{\text{peak c2}} \text{ (A)} = -1,14\text{E-}5 - 5.7\text{E-}6 \cdot [\text{L}]$	0,996
	$i_{\text{peak c3}} \text{ (A)} = -1,55\text{E-}5 - 5,23\text{E-}6 \cdot [\text{L}]$	0,985
	$i_{\text{peak c4}} \text{ (A)} = -4,18\text{E-}5 - 8,91\text{E-}6 \cdot [\text{L}]$	0,999

* i_{peak} is expressed in A, while $[\text{L}]$ is expressed in mmol/L (mM)

RDE curves have been recorded for different concentrations of **L**. In Figure 4 are shown the curves obtained at **L** concentration of 1,75mM at different rotation rates (500 – 1500 rpm). In the anodic scans the curves present 3 anodic processes a1, a2 and a3, denoted according to the corresponding peaks in DPV (shown below). RDE a1 peak currents increase with increasing the rotation rate, but this increase is stopped at potentials higher than a2, when the current drops suddenly to values closer to zero, and they are kept constant over a large scan range. This drop is characteristic for the electrode coverage with insulating films. Consequently, the aspect of RDE curves has confirmed the coverage of the electrode with an insulating layer, fact that has been noticed in DPV curves. The process a3 appears rather higher in RDE curves, but shows no variation with the rotation rate of **L**, being attributed to the accumulation of oxidation products from the supporting electrolyte.

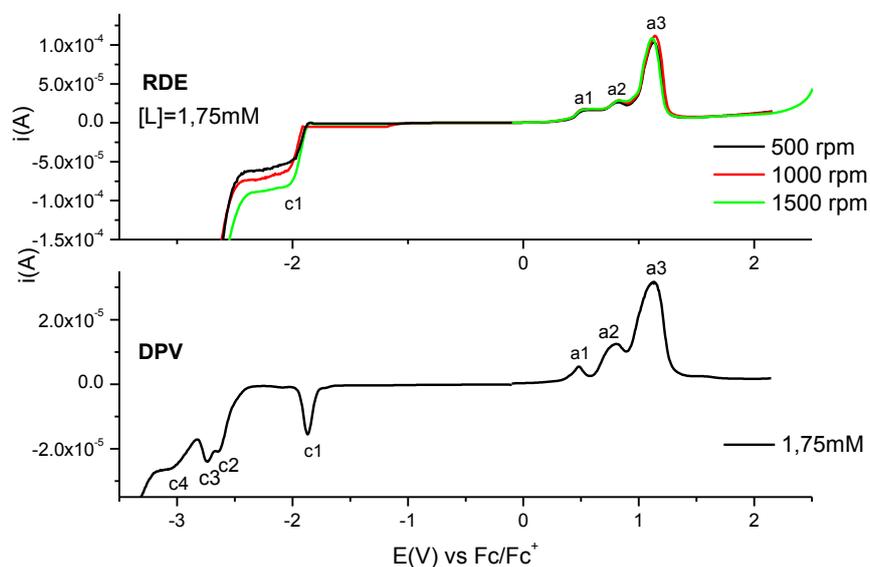


Figure 4. RDE and the corresponding DPV curves on glassy carbon (3mm in diameter) at different rotation rate (rpm) for L (1,75mM) in 0.1M TBAP, CH_3CN .

Figure 5 shows the CV curves for different scan rates (0.1 V/s – 1.0 V/s) in the domains of the first anodic and cathodic peaks, as well as on different scan domains (0.1 V/s), in comparison with the corresponding DPV curve recorded for the same concentration of L (1.75mM). They enable establishing the irreversible (i) or quasi-reversible (q) character of each process. Table 1 also shows their peak potentials from CV and DPV curves.

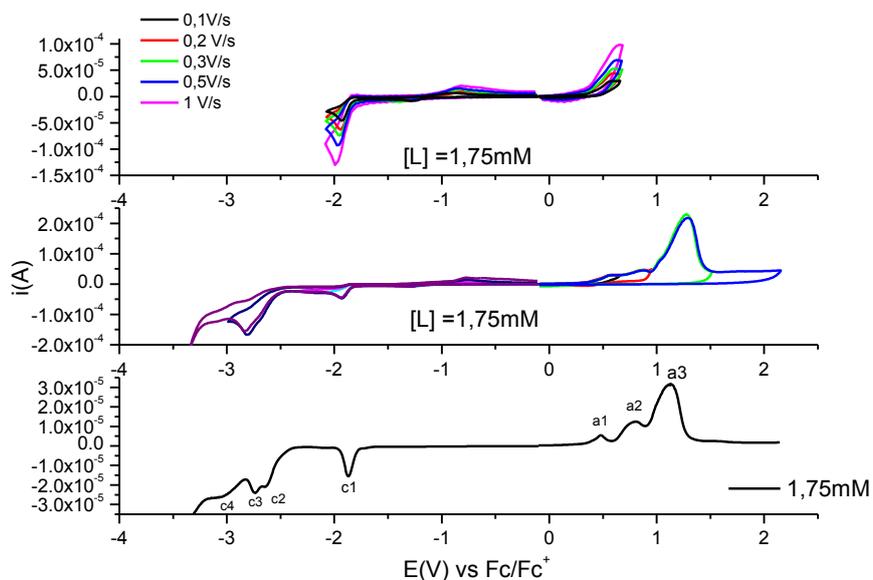


Figure 5. CV curves at different scan rates and scan domains and DPV curve at the concentration of 1.75mM for L in 0.1M TBAP, CH_3CN .

3.2. Modified electrodes based on polyL

PolyL film were obtained by successive scanning or by controlled potential electrolysis (CPE) in L solutions (1.75mM) in the domain of the anodic processes identified to lead to insulating films. Evidence on the films formation on the electrode surface was obtained by transferring the modified electrodes in a solution of ferrocene (0.5 mM) in 0.1M TBAP, CH₃CN. Figure 6 shows the CV curves obtained after the transfer of the modified electrode obtained by successive potential scanning in the domain of the first anodic peak. It can be seen that the signal for ferrocene couple on the modified electrode is not very different from that recorded on the bare electrode, indicating the formation of a thin layer film.

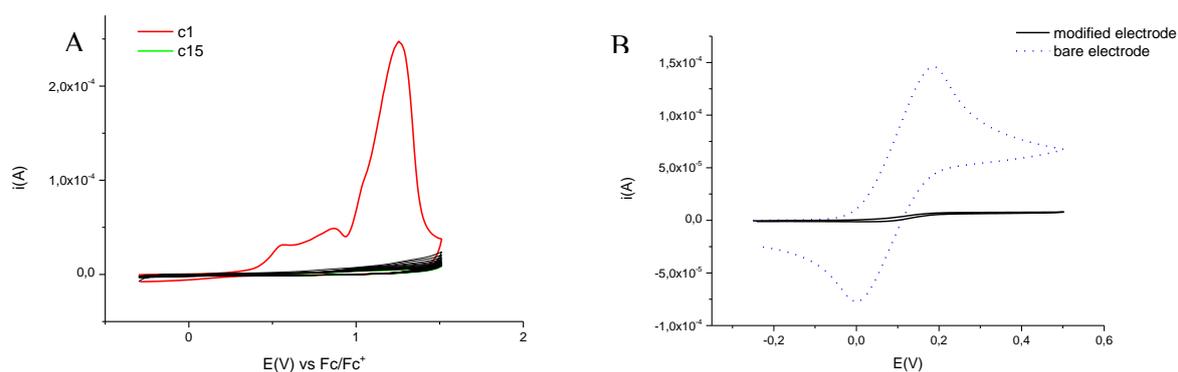


Figure 6. **A.** CV curves (0.1 V/s) for the preparation of the modified electrode by successive scans in 1,75mM solution of L in 0.1M TBAP, CH₃CN; **B.** and the corresponding CV curves (0.1V/s) obtained after the transfer of the modified electrode in 1mM ferrocene solution.

In Figure 7 are given the CV curves of ferrocene recorded on different modified electrodes obtained by CPE. The electrolyses were performed at 1.61 V vs Fc/Fc⁺ using different electropolymerization charges (0 – 1.5mC). All signals indicate coverage of the electrode with films, because the signal is modified in comparison with that on bare electrode. The modified electrode obtained by CPE at the potential of 1.61V when the charges are growing from 0.5mC to 1.5mC the signal increases (when thicker films are expected to be formed).

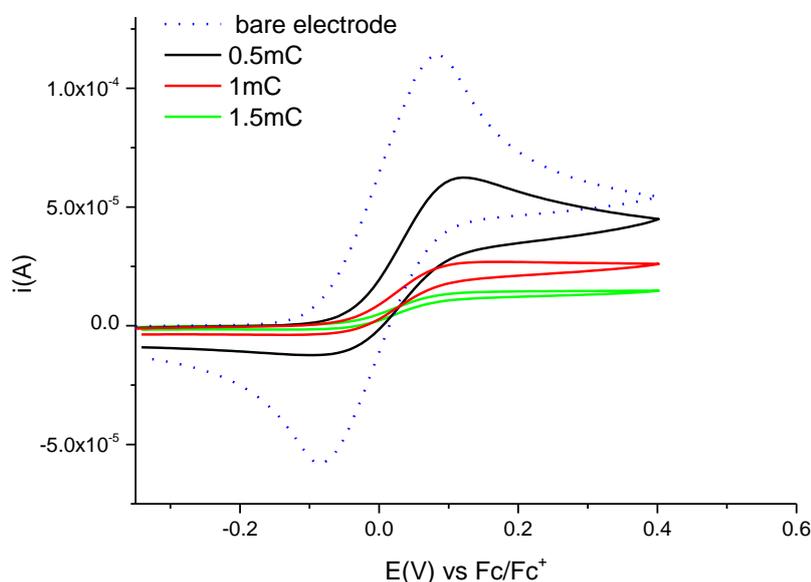


Figure 7. CV curves (0.1 V/s) of a modified electrode in 1,75mM ferrocene transfer solutions in 0.1M TBAP, CH₃CN; the modified electrodes were prepared by CPE at 1.61 V using different electropolymerization charges.

3.3. Heavy metals sensing

In order to sense the heavy metals polyL glassy carbon modified electrodes were prepared by controlled potential electrolysis at 1.61 V using 1mC from L solutions (1 mM).

Modified electrodes by CPE were introduced into the transfer cell containing 0.1M acetate buffer pH 5.5. The electrode equilibration was done during 15 CV cycles in the domain between -0.9 V and +0.6 V, and the overoxidation during 15 CV cycles between -0.2 V and +1.2 V. Then the modified electrodes were introduced in the assay solutions containing heavy metals ions, and they were maintained for 15 minutes under magnetic stirring. A potential of -1.2 V was applied during 120 s for their reduction, then the electrode was polarized in anodic sense at a scan rate of 0.01 V/s. The stripping currents for the metals dissolution were recorded. The stripping peaks at 10⁻⁶ M appeared at -0.56V, -0.164 V, and -0.8 V for Pb, Cu, and Cd respectively.

From the heavy metals tested (Cd, Pb, Cu, Hg) the recognition was suitable for lead, copper and cadmium, in the order given by the intensity of their analytical signals. In Figure 8 are shown the results obtained for the modified electrodes introduced in solutions containing heavy metal cations in different concentrations. Based on the identification of different heavy metal potential values, it can be concluded that the obtained signals can be attributed to Cu (II) and Pb (II). The other ions are not seen in the stripping. The response of the modified electrode is controlled by the concentration of these species in accumulation solutions. The detection limits for Pb (II) and Cu (II) were lower than 10⁻⁶ M. Studies about optimizing the performances of the polyL modified electrodes in view of better sensing are underway.

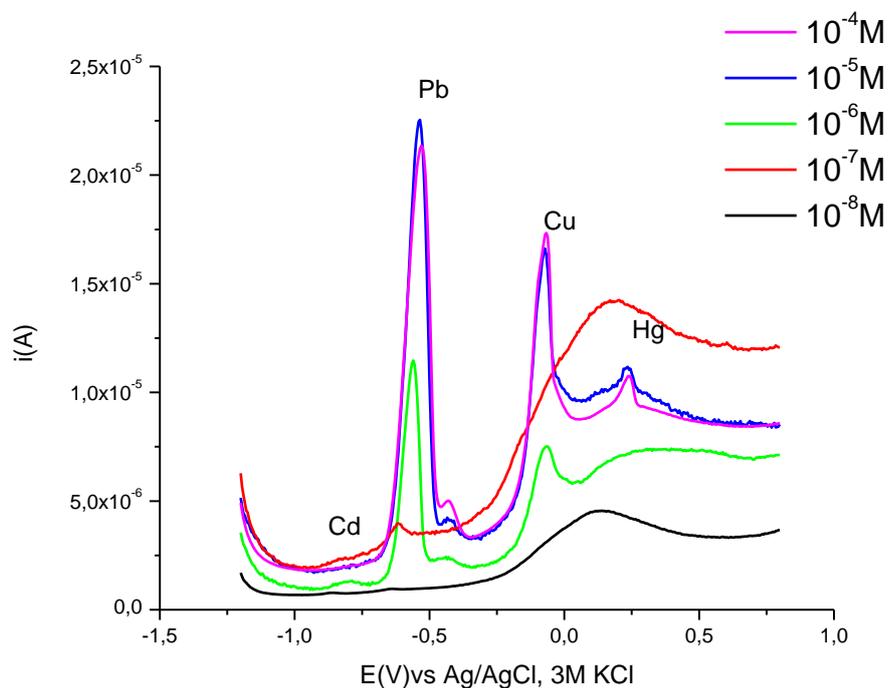


Figure 8. Anodic stripping curves recorded on polyL modified electrodes after immersion in acetate buffer at pH 5.5 (accumulation time 15 min) containing different concentrations of in Cd(II), Pb(II), Cu(II) and Hg(II) ions; the modified electrodes were obtained by CPE (1.61 V, 1mC).

Several experiments using polyL modified electrodes prepared in the same conditions were performed for Pb^{2+} detection in order to evaluate the characteristic parameters for its detection by this method.

4. Conclusions

The electrochemical characterization of 4-(azulen-1-yl)-2,6-bis((E)-2-(thiophen-3-yl)vinyl)pyridine (**L**) was performed by cyclic voltammetry, differential pulse voltammetry and rotating disk electrode methods. The anodic and cathodic processes have been established, and the conditions for obtaining electrodes modified with **L** have been identified. The films formation on the surface of the electrode was confirmed by the transfer of the modified electrode in ferrocene solutions, when the CV signal was found attenuated.

Chemically modified electrodes have been prepared by electropolymerization of **L** at positive potentials. The modified electrodes were tested for the recognition of heavy metal cations: Cd(II), Pb(II), Cu(II) and Hg(II). The best results were obtained for lead and for copper. The detection conditions have to be optimized. Using the present data, the new modified electrode can be used for analysis of lead and copper in water with a content of these heavy metals higher than 10^{-6} M.

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