The Heavy Metals Sensing Based on 2,6-Bis(-2-(Thiophen-3-yl)Vinyl)-4-(4,6,8-Trimethylazulen-1-yl)Pyrylium Modified Electrodes

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This paper focuses on electrochemical characterization of new azulene compound 2,6-bis((E)-2-(thiophen-3-yl)vinyl)-4-(4,6,8-trimethylazulen-1-yl)pyrylium (L) by cyclic voltammetry (CV), differential pulse voltammetry (DPV), rotating disk electrode voltammetry (RDE) on glassy carbon disk working electrodes. The character of redox processes was established by CV and RDE using increasing scan rates at different scan domains. PolyL modified electrodes have been prepared by scanning or controlled potential electrolysis (CPE). The complexing properties of L and polyL have been investigated towards detection of heavy metal ions by anodic stripping technique. The voltammetric curves present well defined peaks for Pb^{2+}, Cd^{2+}, Cu^{2+} and Hg^{2+}, which can be used as analytical signals for their determination. The performances of the modified electrodes obtained at different potentials and charges have been evaluated. The best results have been obtained for Pb^{2+} and Cd^{2+} with the achievement of detection limits of 10^{-7} M.

Keywords: 2,6-bis((E)-2-(thiophen-3-yl)vinyl)-4-(4,6,8-trimethylazulen-1-yl)pyrylium, voltammetric methods, modified electrodes, anodic stripping, heavy metal ions

The growing number of studies registered in recent years on azulenes synthesis and characterisation proves an increasing interest in connection with their potential applications, especially in optical and electronic fields [1-6]. These aromatic substances have a unique structure, consisting in an electrically negative pentagon and an electrically positive heptagon, which confers them interesting electroactive property. Azulenes and many of their functional compounds have also the ability to give complex combinations with different metallic cations and to form conducting polymers by electropolymerization. Azulenes became thus real candidates as advanced materials used to obtain chelating-modified electrodes for metal cations electroanalysis [3]. They could become performant with the new methods for determination of heavy metals from aqueous media which were developed by using sensors based different substrates such as bismuth on activated graphene-nafion composite, optical microfiber sensors, bismuth film electrode [3,4,7,8,11], organofunctionalized mesoporous Silica carbon paste electrode [9,10], antimony impregnated activated Carbon [9], or hanging Mercury drop electrode [12].

Although in recent times several series of azulene derivatives have been synthesized, the electrochemical characterization and applications studies on these compounds are still scarce in the literature.

This paper concerns the electrochemical behaviour of a new synthetized azulene compound (fig.1), namely 2,6-bis((E)-2-(thiophen-3-yl)vinyl)-4-(4,6,8-trimethylazulen-1-yl)pyrylium perchlorate (**L**), as chelating ligand. By oxidative polymerization of **L** in millimolar acetonitrile solutions containing TBAP (0.1 M) on glassy carbon electrode, a deposit of azulene film could be obtained, suitable for heavy metal ions analysis. The immersion of this poly**L** modified electrode into heavy metal solutions leads to the accumulation of these ions into the poly**L** film. After applying a cathodic potential, the accumulated ions are reduced, then they can be stripped from the film during an anodic scan. The occurrence of well-defined peaks on voltammetric curves for Cd, Pb, Cu and Hg cations gives the possibility to use their currents as analytical signals for their detection.

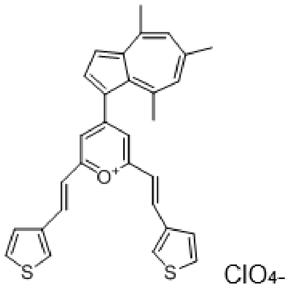

Fig.1. Structure of the investigated azulene compound (**L**)

The present study was performed by four voltammetric techniques: cyclic voltammetry (CV), differential pulse voltammetry (DPV), rotating disk electrode voltammetry (RDE), and controlled potential electrolysis (CPE).

Experimental part

Acetonitrile (CH_3CN) and tetrabutylammonium perchlorate (TBAP dissolved as 0.1M), both from Fluka were used as received as solvent and salt for obtaining the supporting electrolyte. 0.1 M acetate buffer aqueous solutions were prepared from 0.2 M acetic acid and 0.2 M sodium acetate. Metal cation aqueous solutions were purchased from Sigma Aldrich and Fluka as following:, mercury (II) acetate - Sigma Aldrich, cadmium nitrate tetrahydrate - Sigma Aldrich, copper acetate (II) monohydrate - Fluka, lead nitrate (II) - Sigma Aldrich.

A three-electrode cell connected to a PGSTAT 12 AUTOLAB was used for the electrochemical experiments. The working electrode for the ligand characterization was glassy carbon disk from Metrohm with 3 mm diameter, polished before each experiment with diamond paste (2mm) and cleaned with acetonitrile. Ag/ 10 mM $AgNO_3$ in 0.1 M TBAP/ CH_3CN was used as reference electrode, and

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a platinum wire served as auxiliary electrode. However, the potential was finally referred to the potential of ferrocene/ferricinium redox couple (Fc/ Fc^+) which in our experimental conditions was +0.07 V.

CV curves were recorded at 0.1 - 1 V/s scan rates. DPV curves were recorded at 0.01 V/s with a pulse height of 0.025 V and with a step time of 0.2 s. RDE curves were recorded at 0.1 V/s with rotation rates between 500 and 2000 rpm.

For the heavy metals detection (cadmium, copper, lead and mercury) in aqueous solutions the working electrodes were the glassy carbon electrodes modified with poly**L**, the reference electrode was Ag/ AgCl, 3 M KCl, and a platinum wire was used as auxiliary electrode. The detection was performed in 0.1 M aqueous acetate buffer (*p*H = 5.5) as supporting electrolyte, at 25°C, under argon atmosphere. Heavy metals solutions, having concentrations between 10^{-4} and 10^{-7} mol/ L were prepared by successive dilutions from 10^{-2} M stock solution containing a mixture of all ions (Cd^{2+}, Pb^{2+}, Cu^{2+} and Hg^{2+}), each of them at the same concentration.

All electrochemical experiments were performed at 25°C under argon atmosphere.

Results and discussions

Electrochemical characterization of the ligand

The electrochemical behaviour of this new azulene derivative was studied on glassy carbon electrode by electrochemical methods: cyclic voltammetry, differential pulse voltammetry, and rotating disk electrode voltammetry. Their corresponding curves were recorded starting from the stationary potential. The anodic and cathodic CV and DPV curves were registrated at different concentrations (0 – 3 mM) in 0.1 M TBAP/ CH_3CN (fig. 2).

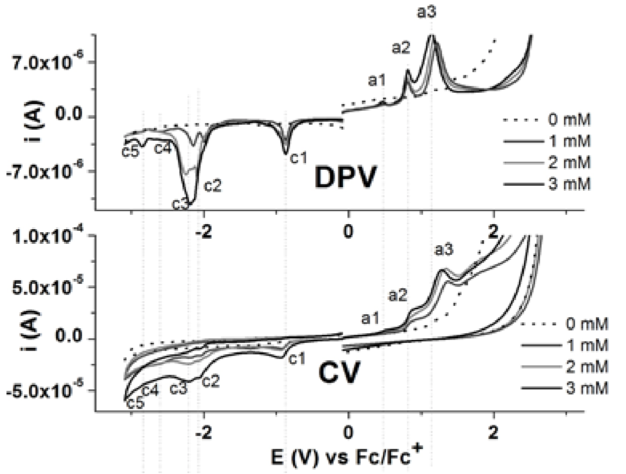


Fig.2. DPV and CV curves on glassy carbon disk (3mm diameter) for **L** at different concentrations in 0.1M TBAP/ CH_3CN

DPV curves present 3 anodic peaks (a1 – a3) and 5 cathodic peaks (c1 – c5). On CV curves could be distinguished in the anodic scans only the peaks corresponding to a2 and a3 processes, while in cathodic scans those corresponding to c1, c2, c3 processes, the peaks notation being in correspondence with that established for DPV curves. The peak currents are increasing with **L** concentration for both CV and DPV curves. Figure 3 shows the dependences of the significant peak currents on **L** concentration for CV and DPV curves, and table 1 presents the equations of the peak currents dependencies on **L** concentration as well as the correlation coefficients for CV and DPV peak current linear dependences. For the peak a4 a small value of correlation coefficient was obtained from CV curves, which indicated the coverage of the electrode with an insulating layer.

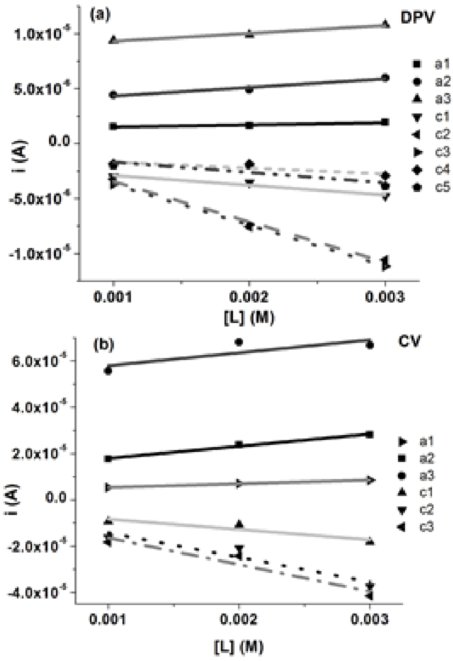


Fig.3. Dependences of the peak currents on **L** concentration in DPV (a) and CV (b) at 0.1 V/ s

The influence of the scan rate on the currents of the peaks a1, a2 and c1 and the dependency of the peak currents a2 and c1 on square root of the scan rate are presented in figure 4. The peak current increases linearly with increasing the square root of the scan rate. From these slopes the diffusion coefficient of **L** could be calculated.

The CV curves for **L** solution (1 mM) on different domains of electrode potential are presented in Figure 5. The peak potentials obtained from CV and DPV curves for **L** redox processes are given in table 2. It can be interpreted that all anodic processes are irreversible, while the cathodic ones are quasi-reversible (table 2).

Table 1
EQUATIONS OF CV AND DPV SIGNIFICANT PEAK CURRENTS*

Method	Equation	Correlation coefficient
DPV	$i_{peak\,a1} = 1.33 \cdot 10^{-6} + 0.19 \cdot 10^{-6} \cdot [L]$	0.831
	$i_{peak\,a2} = 3.55 \cdot 10^{-6} + 0.78 \cdot 10^{-6} \cdot [L]$	0.906
	$i_{peak\,a3} = 8.61 \cdot 10^{-6} + 0.71 \cdot 10^{-6} \cdot [L]$	0.943
	$i_{peak\,c1} = -2 \cdot 10^{-6} – 0.89 \cdot 10^{-6} \cdot [L]$	0.912
	$i_{peak\,c2} = 0.23 \cdot 10^{-6} – 3.67 \cdot 10^{-6} \cdot [L]$	0.979
	$i_{peak\,c3} = 0.04 \cdot 10^{-6} – 3.73 \cdot 10^{-6} \cdot [L]$	0.999
CV	$i_{peak\,a1} = 3.81 \cdot 10^{-6} + 0.00158 \cdot [L]$	0.997
	$i_{peak\,a2} = 12.64 \cdot 10^{-6} + 0.00526 \cdot [L]$	0.983
	$i_{peak\,c1} = -3.91 \cdot 10^{-6} - 0.00443 \cdot [L]$	0.730
	$i_{peak\,c2} = -3.62 \cdot 10^{-6} - 0.0106 \cdot [L]$	0.809
	$i_{peak\,c3} = -4.86 \cdot 10^{-6} – 0.0117 \cdot [L]$	0.857

*i_{peak} is expressed in A, and [L] in mol/L

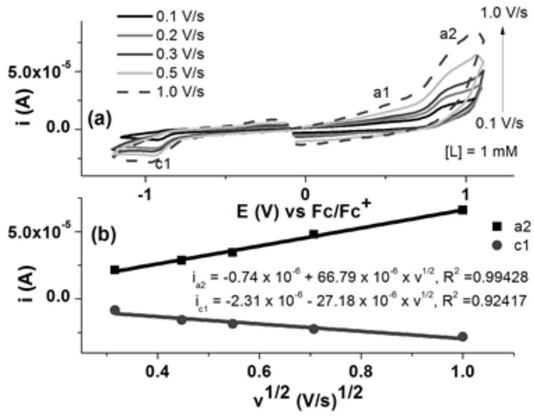


Fig.4. CV curves on glassy carbon (3 mm diameter) at different scan rates (a) and dependences of the peak currents on the square root of the scan rate (b) for **L** (1 mM) in 0.1M TBAP/ CH_3CN

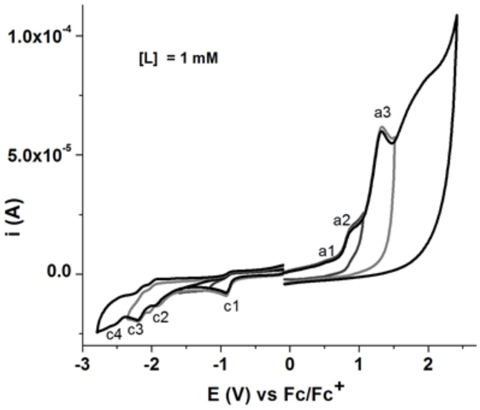


Fig.5. CV curves (0.1 V/ s) on glassy carbon (3mm diameter) at different potential domains for **L** (1 mM) in 0.1M TBAP/ CH_3CN

Table 2

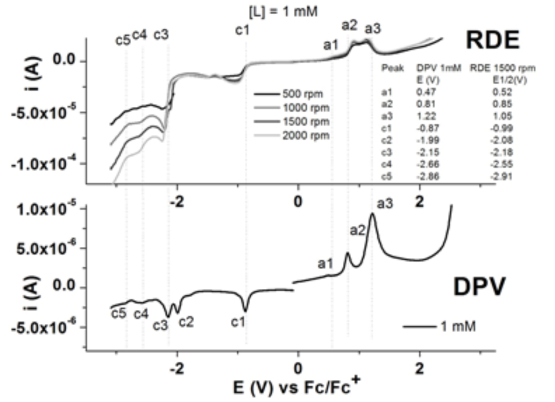
VALUES OF PEAK POTENTIALS (V) FOR **[L]** = 1mM

Peak	Method		
	DPV	CV	Process type
a1	0.48	-	-
a2	0.81	0.89	(i)*
a3	1.22	1.36	(i)*
c1	-0.87	-0.92	(q)*
c2	-1.99	-2.05	(q)*
c3	-2.15	-2.18	(q)*
c4	-2.57	-2.63	(q)*
c5	-2.84	-	

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

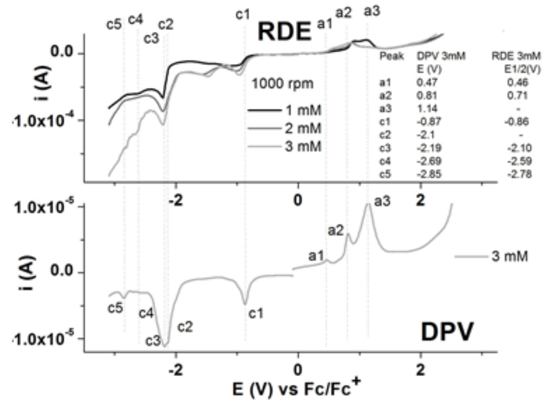
RDE voltammetric curves (fig. 6) obtained at different rotation rates in milimolar solutions of **L** in 0.1M TBAP/ CH_3CN, show 3 waves due to anodic processes and 4 waves due to cathodic processes. It can be seen that the anodic waves are less influenced by the rotation rate than the cathodic ones;, the current suddenly drops after the peak a3, and this passive current is maintained over a wide range of potential. This behaviour is characteristics for the formation of films on the electrode surface. The RDE behaviour in the cathodic domain is different; the current waves for c2 and c3 overlap in a single wave, with a height which increases with the rotation rate. The currents for c4 and c5 also increase with the rotation rate.

Figure 7 presents the RDE curves at 1000 rpm for different concentrations (1– 3 mM) of **L** in the supporting electrolyte. RDE currents increase with **L** concentration in the range of a1 process. It can be seen that the anodic peaks a2 and a3 are fused into a single process at the concentrations of 2 mM and 3 mM. This behaviour has been also found for other compounds [1], and is due to the formation of poly**L** insulating films on the electrode when scanning in the potential range of a2 process. When the concentration is higher the polymerization occurs at less positive potential and the current drops immediately after reaching this potential. RDE curves have no limiting currents, but the shapes of peaks and potentials are similar to those put in evidence by DPV (listed in the inserted table from fig. 7).



Peak	DPV 1mM E (V)	RDE 1500 rpm E1/2(V)
a1	0.47	0.52
a2	0.81	0.85
a3	1.22	1.05
c1	-0.87	-0.99
c2	-1.99	-2.08
c3	-2.15	-2.18
c4	-2.66	-2.55
c5	-2.86	-2.91

Fig.6. RDE and DPV curves on glassy carbon (3 mm diameter) at different rotation rates (rpm) for [**L**] = 1 mM in 0.1M TBAP/ CH_3CN. Inset: the Table with the values of DPV peak potentials and of RDE waves potentials



Peak	DPV 3mM E (V)	RDE 3mM E1/2(V)
a1	0.47	0.46
a2	0.81	0.71
a3	1.14	-
c1	-0.87	-0.86
c2	-2.1	-
c3	-2.19	-2.10
c4	-2.69	-2.59
c5	-2.85	-2.78

Fig.7. RDE (1000 rpm) curves at different concentrations of **L** and DPV curve for [**L**] = 3 mM in 0.1 M TBAP/ CH_3CN on glassy carbon (3 mm diameter). Inset: the Table containing values of DPV peak potentials and of RDE waves potentials

In figure 8 are given the dependences of total RDE currents on **L** concentration at 1000 rpm (fig. 8a), and on the square root of the rotation rate for [**L**] = 1 mM (fig. 8b). As figure 8a shows, RDE currents increase with **L** concentration in the range of a1 process, remain constant for a2 process and decrease for a3; for all cathodic processes RDE currents increase in absolute value with **L** concentration. Figure 8b illustrates that RDE currents for a1 – a3 processes remain almost constant with rotation rate, while they decrease with rotation rate for cathodic

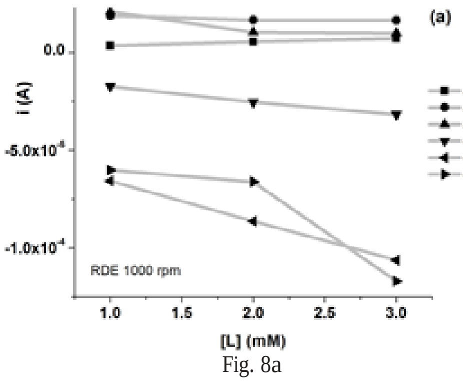


Fig. 8a

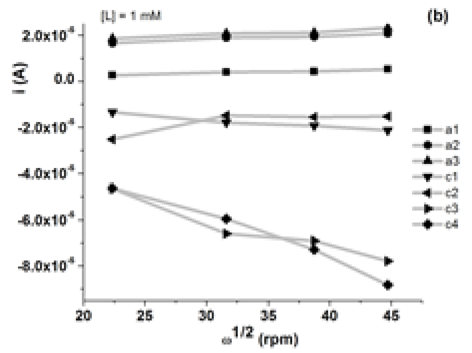


Fig.8. Dependences of total RDE currents (glassy carbon, 3 mm diameter) on **L** concentration at 1000rpm(a), and on the square root of the rotation rate (b) for [L] = 1 mM in 0.1M TBAP / CH_3CN

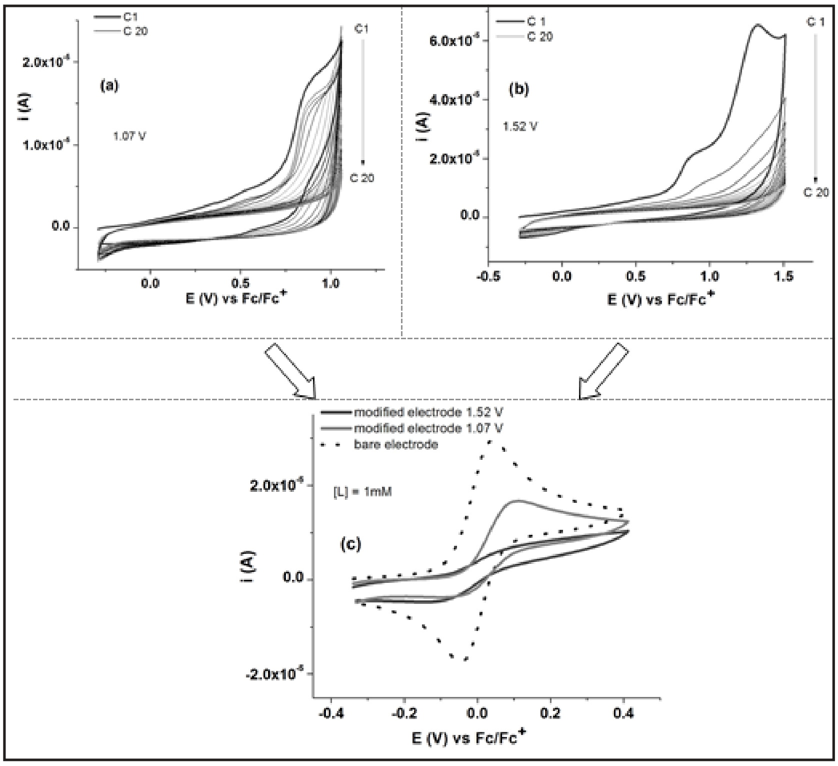


Fig.9 CV curves (0.1 V/s) during the preparation of the modified electrode by successive scanning in 1 mM solution of **L** in 0.1M TBAP/ CH_3CN; the film was obtained between -0.3 V and different anodic limits: +1.06 V (a); and +1.52 V (b). The corresponding CV curves (0.1 V/ s) obtained after the transfer of the modified electrodes in 1mM ferrocene solution are presented in figure 9c

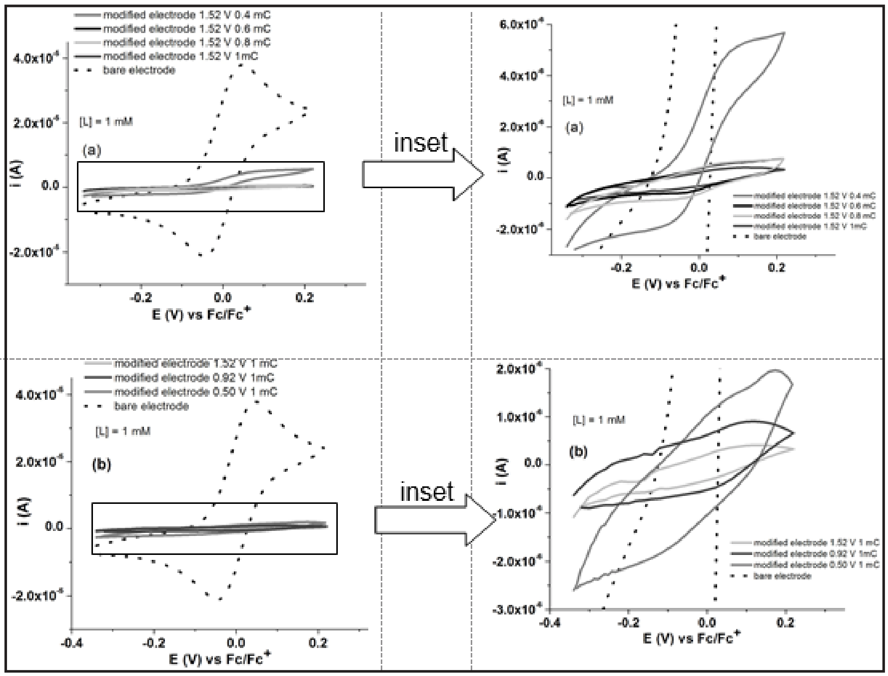


Fig.10. CV curves (0.1 V/ s) in 1 mM ferrocene dissolved in 0.1 M TBAP/ CH_3CN of the modified electrodes obtained by CPE in 1 mM solution of **L** in 0.1 M TBAP/ CH_3CN by CPE at 1.51 V using different electropolymerization charges (a), and at different electropolymerization potentials at 1 mC charges (b)

processes (except for c2 process, where the current increases up to a limit). This behaviour seems to obey the Levich equation which is valid for mass transport controlled process for a1 and c1, and not to obey it for the other processes.

PolyL modified electrodes

Poly**L** modified electrodes were obtained in **L** solution (1 mM) in 0.1 M TBAP/ CH_3CN by cycling the electrode potential (20 cycles) between -0.2 V and different anodic limits (1.07 V; 1.52 V). The modified electrodes were then transferred into a solution of ferrocene (1 mM) in 0.1M TBAP/ CH_3CN in order to test their response. In the monomer solutions the currents drop in successive scans (figs. 9a and 9b), and a hysteresis area is persistent in the potential scan range. The transfer of the modified electrode obtained by successive scanning (fig. 9) up to the anodic potential of 1.52 V leads to a ferrocene signal that is more distorted than that obtained when the scanning limit was 1.07 V. Both of them are different from the signal obtained on bare electrode (glassy carbon), indicating an electrode coverage with films during the potential scanning in **L** solutions; the films are thicker for an anodic limit of 1.52 V than for 1.07 V.

Poly**L** modified electrodes were also obtained in **L** solution (1 mM) in 0.1 M TBAP/ CH_3CN by controlled potential electrolysis (CPE) at different potentials and charges. The CV curves obtained for the transfer of the modified electrodes in ferrocene solutions are shown in Figure 10 for either different charges at constant potential limit (1.52 V), or for different values of potential at constant charge.

In case of the films produced by CPE, the signals obtained after the electrode transfers in ferrocene solution are gradually changing, following the thickening of the film (when increasing the electropolymerization charges) as seen in figure 10a. Figure 10b shows that the potential applied during CPE also influences the ferrocene signal, which is more flattened when the potential of electrolysis

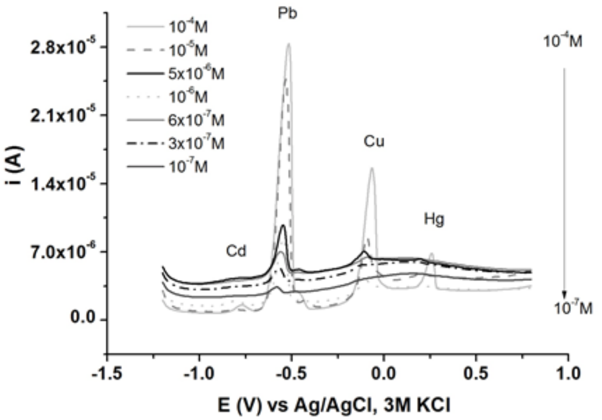


Fig.11. Stripping DPV curves recorded at poly**L** modified electrodes obtained by CPE (1.5 V, 2 mC); accumulation for 15 min in Cd^{2+}, Pb^{2+}, Cu^{2+} and Hg^{2+} ions at different concentrations in acetate buffer at *p*H 5.5

is more positive. A suitable potential to obtain poly**L** modified electrodes by CPE is recommended to be 1.52 V.

Evaluation of recognition properties

Poly**L** films prepared in solutions of **L** (1 mM) in 0.1M TBAP/ CH_3CN by CPE (1.6 V, 2 mC) were placed in a cell with three electrodes containing 0.1 M acetate buffer aqueous solution, *p*H 5.5. Each modified electrode was successively polarized between –0.9 V and +0.6 V (15 cycles) and between -0.2 V and +2.5 V (15 cycles), afterwards it was taken out and cleaned with distilled water. This conditioned modified electrode was introduced into solutions containing mixtures of heavy metal ions (Cd^{2+}, Pb^{2+}, Hg^{2+} and Cu^{2+} at different concentrations) in distilled water under magnetic stirring for 15 min. Then, the electrode was cleaned with distilled water and introduced in a three electrode cell containing 0.1 M acetate buffer *p*H 5.5. A potential of -1.2 V was applied for, 2 min, and then a potential sweep (0.01 V/ s) from -1.2 V to +0.8 V was performed. The resulted DPV curves are shown in Figure 11. The dependence of the stripping currents on cations concentration is given in figure 12. Significant stripping peaks have been obtained for all metal ions. For analytical purpose, Pb^{2+} and Cu^{2+} ions presented the best responses, as it can be seen in figure 12. This result makes the poly**L** modified electrode a promising candidate for analysis of these heavy metals from water. The range of detected concentration is suitable for a category of waste waters with a content of Pb^{2+} and Cu^{2+} between 10^{-7} and 10^{-4} M.

Conclusions

The electrochemical study of 2,6-bis(-2-(thiophen-3-yl)vinyl)-4-(4,6,8-trimethylazulen-1-yl)pyrylium perchlorate (**L**) performed by cyclic voltammetry, differential pulse voltammetry and rotating disk electrode voltammetry in acetonitrile lead to the evidence of several redox processes. One of anodic processes was the formation of poly**L** films which were evidenced by all applied methods.

The described poly**L** modified electrodes were prepared in acetonitrile by controlled potential electrolysis at different potentials and charges or by cycling at different anodic potentials. The obtained modified electrodes were tested for determination of Cu^{2+}, Cd^{2+}, Hg^{2+} and Pb^{2+} ions in aqueous media. Detection limits of 10^{-7} M have been reached for all mentioned metal ions. The best results have been obtained in the heavy metals quantification for Pb^{2+} and Cu^{2+} species. The range of detected concentrations is suitable for a category of waters with the content of these ions between 10^{-7} M and 10^{-5} M.

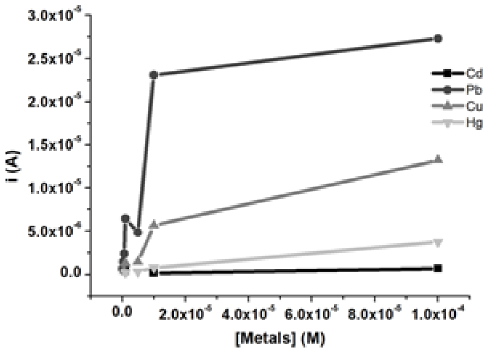


Fig.12. Dependences of the DPV stripping currents on metal ions concentration

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