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NEW CHEMICALLY MODIFIED ELECTRODES BASED ON CROWN ETHER-AZULENES FOR HEAVY METAL ANALYSIS

Veronica ANASTASOAIE [1], Elena DIACU[2], Eleonora-Mihaela UNGUREANU*[3], Magdalena Rodica BUJDUVEANU[4], Liviu BIRZAN[5], Mihaela CRISTEA[6]

*New sensors for heavy metals analysis were designed by using chemically modified electrodes with 6-crown-2-ether-il-vinyl azulene for analytical applications in environment monitoring. The new synthesized compound 4'-(Z-azulen-1-il-vinyl)-6-crown-2-ether (**L**) has been investigated to study its electrochemical behavior by voltammetric techniques, such as cyclic voltammetry (CV), differential pulse voltammetry (DPV) and rotating disk electrode voltammetry (RDEV). Poly**L** heavy metal complexing modified electrodes were obtained by electropolymerization. The detection of Hg(II), Pb(II), Cu(II) and Cd(II) ions has been performed using the prepared modified electrodes. Selective results have been obtained for Pb(II) ions determination.*

Keywords: 4'-(Z-azulen-1-il-vinyl)-6-crown-2-ether, voltammetric techniques, modified electrodes, heavy metals detection

1. Introduction

Heavy metal ions tend to bioaccumulate in the body leading to serious diseases in human body, so it is important to detect them at the trace level to prevent their ingestion. Exposure to lead, cadmium, mercury, arsenic, or copper are the main threats to human health when it comes to heavy metal poisoning.

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[1] PhD student, Department of Inorganic Chemistry, Physical Chemistry and Electrochemistry, University POLITEHNICA of Bucharest, Romania, e-mail: veronica.anastasoaie@onmicrosoft.upb.ro

[2] Prof., Department of Analytical Chemistry and Environmental Engineering, University POLITEHNICA of Bucharest, Romania, e-mail: elena_diacu@yahoo.co.uk

[3]* Prof., Department of Inorganic Chemistry, Physical Chemistry and Electrochemistry, University POLITEHNICA of Bucharest, Romania, e-mail: em_ungureanu2000@yahoo.com, corresponding author

[4] Eng., Department of Inorganic Chemistry, Physical Chemistry and Electrochemistry, University POLITEHNICA of Bucharest, Romania, e-mail: m_bujduveanu@yahoo.com

[5] Scientific Researcher, Institute of Organic Chemistry "C.D. Nenitzescu" of Romanian Academy, Bucharest, Romania

[6] Scientific Researcher, Institute of Organic Chemistry "C.D. Nenitzescu" of Romanian Academy, Bucharest, Romania, e-mail: mihcris2012@yahoo.ro

Exposure to these metals is done by smoking cigarettes, eating fish and seafood but also by breathing in the surrounding air [1]. So, determination of heavy metals ions from water samples is a very important action especially for application in food chemistry and environmental monitoring.

The determination of heavy metals in natural samples can be done by several techniques like atomic absorption spectrometry, inductively coupled plasma optical emission spectrometry, X-ray fluorescence, inductively coupled plasma mass spectrometry, and stripping voltammetric techniques such as anodic stripping voltammetry [2]. Due to the ability of crown ethers to complex silver [3] and mercury [4-5] or cations such as NH_4^+, lanthanides, heavy metal ions have been study verry often, and recent work highlights the detection of heavy metals by different methods using these classes of compounds [2, 6-10]. Other recent studies have focused primarily on crown ether-modified electrodes for Pb detection, and have demonstrated the strong affinity of these types of compounds for complexing Pb ions [11-12].

To detect heavy metal ions from water samples our approach is based on adsorptive stripping voltammetry using chemically modified electrodes prepared from crown ether azulene monomer. This monomer has been electropolymerized giving the crown ether-azulene modified electrode.

The novelty of the paper consists in investigating the electrochemical and complexing properties of a new synthesized crown-azulene ether ligand. It belongs to this class for which the synthesis has been described [13-14], but their applications not. 4’-(Z-azulen-1-il-vinyl)-6-crown-2-ether (**L**) has been synthetized [15] and characterized by electrochemical techniques. Its first application to prepare modified electrodes for analysis has been studied. The target species were heavy metals ions which were detected from synthetic water samples containing heavy metals. This detection based on modified electrodes has been tested as an application of this new structure.

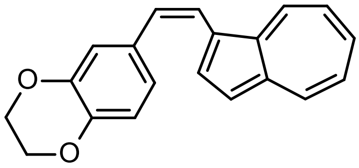

Fig. 1. **L** structure

2. Experimental part

The acetonitrile (CH_3CN) containing 0.1M tetrabutylammonium perchlorate (TBAP), both from Fluka, was used as solvent and supporting electrolyte for the electrochemical characterization of the ligand **L** and for the preparation of modified electrodes. The heavy metal ions solutions have been freshly prepared as 10^{-2}M stock solutions before each experiment using the following salts: Cd(II) nitrate tetra hydrate, Pb(II) nitrate, Hg(II) acetate, (all from Sigma Aldrich) and Cu(II) acetate monohydrate (from Fluka). From 0.2 M acetic acid solution and 0.2 M sodium acetate solution 0.1 M buffer acetate (pH = 5.5) solution was prepared.

The voltammetric measurements were performed using PGSTAT 12 AUTOLAB potentiostat connected to a three-electrode cell. The voltammetric cell was formed by working electrodes which was either a glassy carbon disk (with 3 mm diameter) (Metrohm), or poly**L** glassy carbon disk modified electrodes, platinum wire auxiliary electrode, and the reference electrode was either Ag/10 mM $AgNO_3$ in 0.1 M TBAP/CH_3CN (in electrochemical experiments performed in acetonitrile solutions), or Ag/AgCl, 3 M KCl (in electrochemical experiments performed in aqueous solutions). The working electrode was polished with diamond (2 µm) paste before each experiment and cleaned with the solvent.

The voltammetric methods used for electrochemical characterizations were: Cyclic voltammetry (CV), rotating disk electrode voltammetry (RDEV) and differential pulse voltammetry (DPV). CV curves have usually been recorded at the scan rate of 0.1 V/s. DPV curves have been recorded at 0.01 V/s, with a pulse height of 0.025 V and step time of 0.2 s, while RDEV curves were recorded at 0.01 V/s. All experiments have been recorded under argon atmosphere, at 25 ºC. For the experiments performed in acetonitrile solutions, the potentials were finally referred to the potential of the ferrocene/ferricenium redox couple (Fc/Fc^+) equal to +0.07 V in our experimental conditions.

The differential pulse stripping voltammetry for heavy metal ions detection have been performed in 0.1 M buffer acetate (pH = 5.5) solution as supporting electrolyte, at 25 ºC under argon atmosphere. Heavy metal ion solutions of different concentration ($2*10^{-5}$ M – 10^{-5} M) were prepared by successive dilutions from their stock solutions (10^{-2} M) in water.

3. Results and Discussion

3.1. Electrochemical characterization of L

For the electrochemical characterization of the crown ether derivative **L**, the CV and DPV oxidation and reduction curves have been recorded at different concentrations of **L** (1 - 2.5 mM) in 0.1 M TBAP/CH_3CN, starting from the equilibrium potential (Fig. 2). In Fig. 2A, the DPV curves show four oxidation peaks (a1 – a4) and five reduction peaks (c1 - c5). In Fig. 2B, the CV curves show 4 anodic peaks (a1 – a4) and 3 cathodic peaks (c1 - c3), respecting the notation from DPV curves.

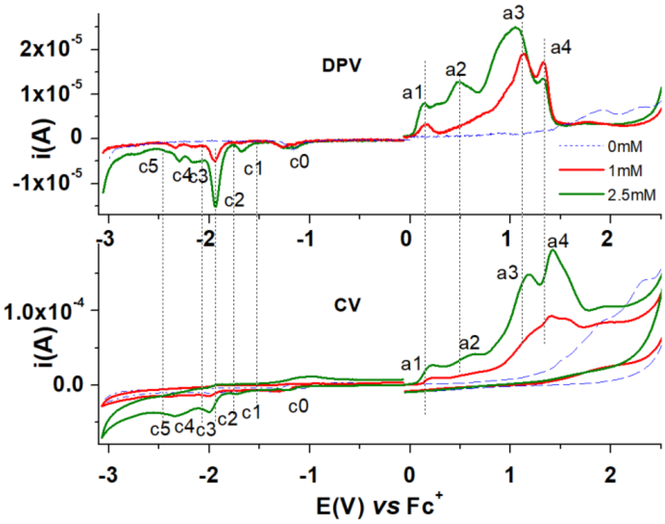

Fig. 2. DPV and CV curves on glassy carbon for **L** at different concentrations in 0.1 M TBAP, CH_3CN

Fig. 3A presents the CV curves obtained at different scan rates (0.1 – 1 V/s) within potential domains of the anodic peak a1 and cathodic peak c1 for 1 mM solution of **L,** showing that a1 peak is not reversible in the range of the investigated scan rates. Also, all current values increase with the scan rate. Linear dependences for the peak current on the square root of the scan rate are obtained for a1 (Fig. 3B) showing a diffusion-controlled process.

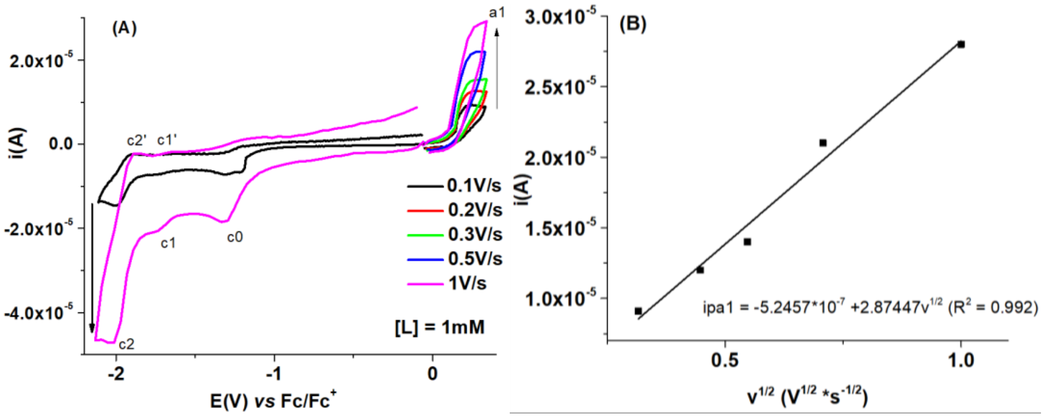

Fig. 3. CV curves at different scan rates of glassy carbon electrode in solution of 1 mM **L** in 0.1 M TBAP/CH_3CN (A) and linear dependences of a1 currents on the square root of the scan rate (B)

Fig. 4 shows the CV curves (0.1 V/s) obtained on different scan potential domains for 1 mM solution of **L**, while Table 1 presents the characteristics of processes and potential values for each peak, all estimated from CV and DPV curves measured for 1 mM solution of **L**. In the anodic domain the peaks a1, a3 and a4 are quasireversible and peak a2 is irreversible, while in the cathodic domain, the peaks c1 and c2 is quasireversible, and the peaks c3 and c4 are irreversible. In the beginning of cathodic scans, the parasite peak of oxygen reduction from the residual water is present (c0), even if the solution was bubbled with argon.

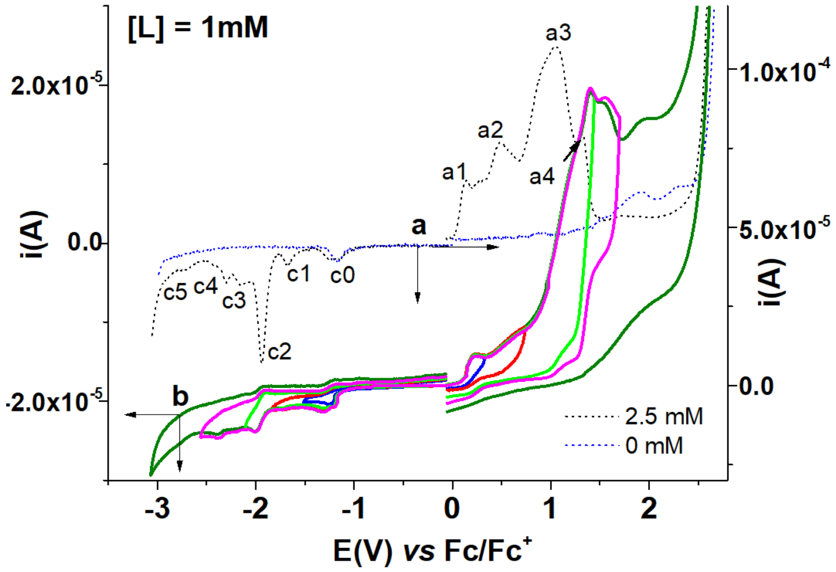

Fig. 4. DPV curves for 2.5 mM of **L** (**a**) and CV curves at different potential scan domains for 1 mM of **L** (**b**) on glassy carbon electrode in 0.1M TBAP/CH_3CN

Table 1

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

Peak	CV		DPV		Process characteristics
	E(V)	i x 10^{-5}(A)	E(V)	i x 10^{-5}(A)	
a1	0.25	0.97	0.13	0.79	quasireversible
a2	0.61	1.56	0.48	1.26	irreversible
a3	1.4	9.41	1.05	2.45	quasireversible
a4	1.56	9.1	1.32	1.34	quasireversible
c0	-1.3	-	-1.18	-	-
c1	-1.73	-0.84	-1.67	-0.27	quasireversible
c2	-1.99	-1.43	-1.94	-1.53	qvasireversible
c3	-2.23	-1.45	-2.12	-0.53	irreversible
c4	-2.4	-1.63	-2.3	-0.49	irreversible
c5	-	-	-2.72	-0.34	-

Fig. 5 presents RDEV curves on glassy carbon electrode obtained at different rotation rates (500 – 1500 rpm). The RDEV method is used to estimate the characteristics of oxidation and reduction processes in the specific domains put in evidence by DPV curve. The RDEV curves for 2.5 mM of **L** (Fig. 5B) show no influence of the rotation rate on the anodic processes, but quite regular influence on the cathodic processes (increase of the limiting currents with the rotation rate).

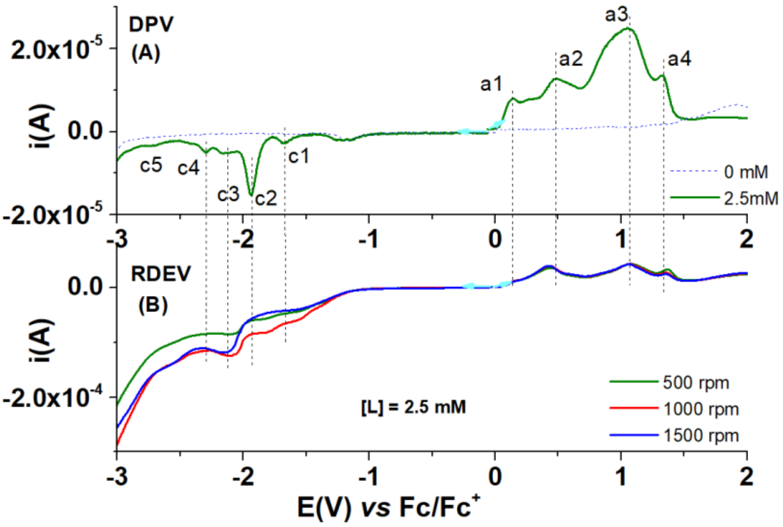

Fig. 5. DPV (A) and RDEV (B) curves (0.01 V/s) at different rotation rates (500 – 1500 rpm) for 2.5 mM of **L** in 0.1 M TBAP/CH_3CN

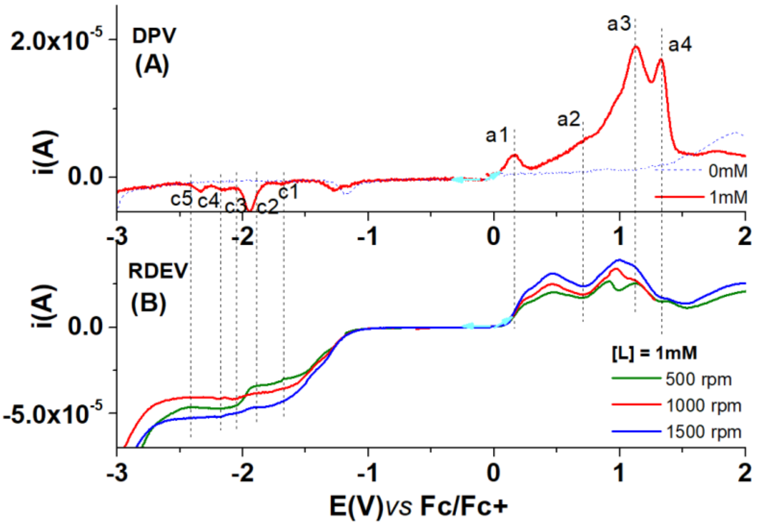

Fig. 6. (A) RDEV curves (0.01 V/s) at different rotation rates (500 – 1500 rpm) and (B) DPV curves for 1 mM of **L** in 0.1 M TBAP/CH_3CN

The RDEV curves for 1 mM of **L** from Fig. 6B are quite different in respect to those in Fig. 5B in the anodic domain: the increase of the rotation rate leads to regular increase of the currents in a1 process, behaviour kept for a2 and partially for a3 processes. Assuming that polymerization occurs at the potentials in the domain of a2, these changes are in agreement with the differences of electropolimerization process occurring at quite different concentrations of the monomer (at higher concentration of 2.5 mM the polymerization is faster than at 1 mM, and the decrease of the current following this process is more evident).

3.2. Modified electrodes based on polyL

Poly**L** modified electrodes have been prepared from 1 mM **L** in 0.1 M TBAP/CH_3CN by either successive potential scans, or by controlled potential electrolysis (CPE). The prepared modified electrodes were transferred into a ferrocene solution (1 mM) in 0.1M TBAP/CH_3CN. The ferrocene signal in CV curves on bare electrode has been compared with the ferrocene signal on modified electrodes (Fig. 7C). The formation of the film on the electrode is normally followed by the diminution of the peak currents of ferrocene and potential shifts of the anodic and cathodic peaks, due to the restricted access of the redox ferrocene couple to the electrode surface, due to the presence of the film. The thicker the film, the greater these changes.

Fig. 7A shows that by cycling the potential (at 1mM of **L**) in the domain of a2 process, the formation of a conductive film can be noticed, which has a reversible couple with Epa = 0.229 V and Epc = 0.066 V. If the cycling goes to limits at more positive potentials in the domain of a3 process (+1.2 V), it is no longer seen the conductive film (the reversible couple for the polyazulene reduction and oxidation does not appear anymore) and the currents decrease continuously in successive cycles, which shows that the film formed in this case is insulating (Fig. 7B).

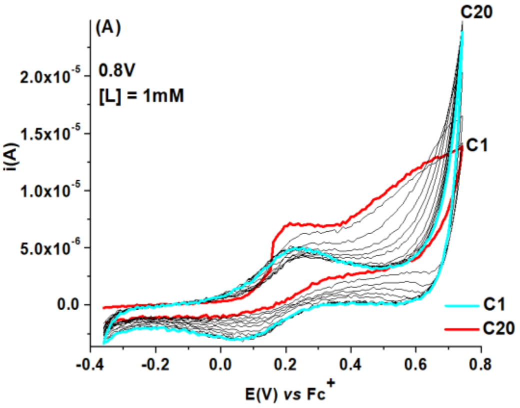

Fig. 7A. CV curves (0.1 V/s) during the formation of poly**L** modified electrodes by successive potential scanning with anodic limit in the potential domain of a2 peak (A)

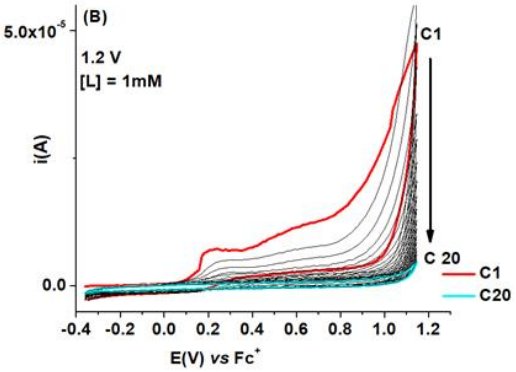

Fig. 7B. CV curves (0.1 V/s) during the formation of poly**L** modified electrodes by successive potential scanning with anodic limit in the potential domain of a3 peak (B)

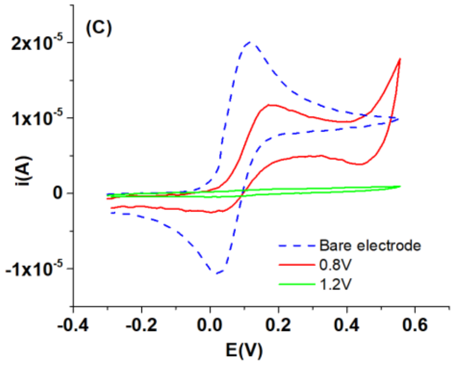

Fig. 7C. The corresponding CV curves of the resulting modified electrodes (0.5 V/s) in 1mM ferrocene solution (C)

This insulating film formation was confirmed after the transfer of the modified electrodes in ferrocene solution (Fig. 7C). Consequently, the signal for ferrocene on the electrode obtained by scanning up to 0.8 V retains the characteristics of the reversible signal of the ferrocene on the uncovered electrode, while the signal on the electrode obtained by scanning up to 1.2 V shows the complete loss of the ferrocene signal due to the electrode coating with non-conductive film.

3.3. Heavy metals recognition

The modified electrodes obtained by successive potential scans showed us that two kind of films could be deposited on the electrode at specific potentials. For the heavy metals' recognition, the modified electrodes were obtained by CPE because the film deposited on electrodes is more easily to be controlled (being specific for the selected potential) by the charge and potential used in electropolymerization, and the time for preparation is shorter. Poly**L** modified electrodes were obtained by CPE from the solution of **L** (1 mM) in 0.1M TBAP/CH_3CN. The modified electrodes were cleaned with acetonitrile and immersed in the transfer solution containing 0.1 M acetate buffer at pH 5.5. The conditioning of the modified electrode was made according to a procedure already tested for similar azulene ligands [16] through 15 cycles of equilibration (by CV with a scan rate of 0.1 V/s between -0.9 V and +0.6 V) and overoxidation (by CV with a scan rate of 0.1 V/s between -0.2 V and +1.5V. After that, the modified electrodes were taken out from the cell, washed with water, and put in the accumulation solution (water solutions containing heavy metals ions of different concentrations), under magnetic stirring for 15 minutes.

For similar ligands we noticed experimentally that this procedure increases the electrode response to all metal ions (from figure 8A it is observed that the electrode prepared at 1.5 V has a higher signal than the electrode obtained at 1.2 V for the peak of Pb from -0.48 V which would confirm the fact that reaching higher positive potentials - during overoxidation - favors the increase of the number of active complexing groups on the electrode surface).

After the accumulation step, the modified electrodes were polarized at -1.2 V, where all cations were reduced, and their DPV stripping currents were recorded between -1.2 V and +0.5 V (Fig. 8A). The tested heavy metal ions solutions have been prepared from mixtures of the following cations: Cd(II), Pb(II), Hg(II) and Cu(II) in equal concentrations. The result of the scan reveals the presence of only one ion, Pb(II), from the investigated ones. Il appears as one or two peaks situated at -0.53 V or -0.57 V and -0.48 V, respectively. A possible explanation of the fact that the signal for Pb is doubled (-0.57 V and -0.48 V) considers the formation of Pb-Hg amalgam and Pb during the striping procedure (electroreduction step at -1.2 V). The dissolution of Pb and Pb-Hg during the stripping occurs as two distinct peaks at close potentials leading both to Pb(II) cations. Another explanation for the double peak obtained for Pb(II) could result from the comparison of DPV curves obtained at 0.8 V (curves (a) and (b) in Fig. 8A) with those at 1.2 V (c) and 1.5 V (d). From the electrochemical study presented in 3.1. it has been shown that the films obtained at 0.8 V is conductive, while that obtained at 1.2 V is insulating, the complexing units from these films could be also different leading to distinct complexation forces.

The dependences of the DPV stripping currents on Pb ions concentration can be estimated from Fig. 8A. The peak current for curve (b) is higher than for (a) showing that the current increases with the concentration of the target (Pb(II) ions) in the accumulation solution. An estimation of method sensitivity using these curves gives a slope of 16 mA/M. The real performance of this potential sensor are expected to be much better because this comparison for concentration influence has been done for modified electrodes prepared at potential of 0.8 V.

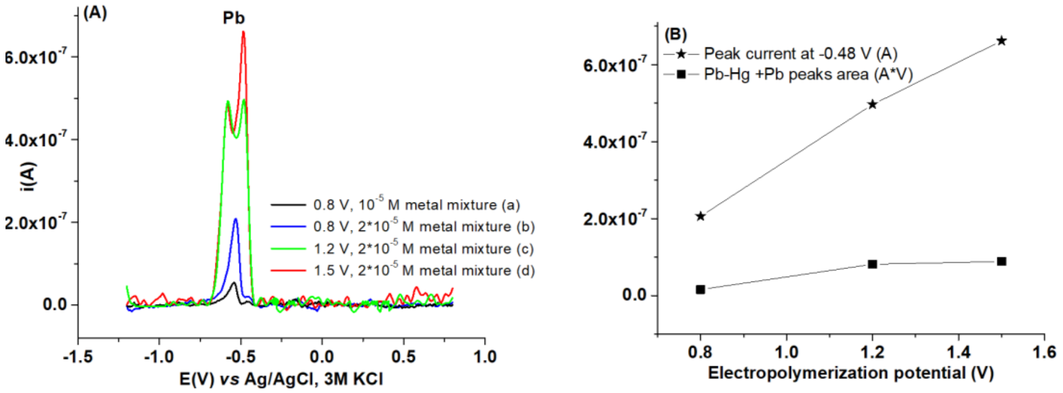

Fig. 8. A - DPV stripping currents for the modified electrodes (1mC) obtained by CPE at different potentials in 1 mM solution of **L** in 0.1M TBAP/CH_3CN, after being soaked in water containing different concentrations of heavy metals; B – dependence on electropolymerization potential of Pb stripping peak current (at -0.48 V in the DPV curve) and of area (of the peaks between -0.7 and -0.4 V)

From the comparison of curves from Fig. 8A, it can be seen also that the response for Pb(II) in (c) and (d) is much higher than for (b), because the response of the modified electrode is influenced by the potential at which the electrode was prepared by electropolymerization. Consequently, the slope at 1.2 V and 1.5 V will be higher than 16 mA/M value obtained for the modified electrodes prepared at 0.8 V.

In Fig. 8B it is shown the dependence on electro polymerization potential of Pb stripping peak current (at -0.48 V in the DPV curve) and of area (of the peaks between -0.7 and -0.4 V). The sum of the areas of the two peaks for Pb increases if the modified electrode is prepared at 1.2 V compared to the one prepared at 0.8 V. However, at higher potentials (1.5 V) the increase is much smaller. At detailed study is compulsory for the implementation of poly**L** modified electrodes for Pb(II) detection to establish if the peak current or peaks area should be taken for the calibration curve of the future sensor.

The experimental results obtained indicate a clearly preferential complexation for Pb(II). The obtained results are preliminary, because a detailed study is necessary for the choice of the support electrolyte (nature and pH).

The curves in Fig. 8A are processed because under the tested conditions a satisfactory baseline was not obtained. In the different experiments there was also a signal for Cu(II) at -0.19 V and for Hg(II) at the potentials of +0.009 V and 0.25 V. However, their intensity was much lower than that for Pb, and the accuracy of their area’s evaluation was reduced because the baseline had a high noise level. Subsequent studies to obtain a Pb (II) sensor based on this ligand also consider elucidating these unknowns.

4. Conclusions

4’-(Z-azulen-1-il-vinyl)-6-crown-2-ether has been systematically studied by electrochemical methods. The potentials for the main oxidation and reduction processes have been established by voltammetric methods. The modified electrodes with poly**L** were characterized by cyclic voltammetry in ferrocene solutions. The modified electrodes were used for heavy metals recognition through preconcentration and anodic stripping. The best response has been obtained for Pb (estimated detection limit of 10^{-5} M) which indicates that this crown ether is more selective *versus* Pb than for the other ions (Cd, Cu, Hg). The response of the modified electrode is influenced by the potential at which the electrode was prepared by electropolymerization.

Acknowledgments

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