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Complexing Polymer Films in The Preparation of Modified Electrodes for Detection of Metal Ions

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Summary: The complexing properties of poly (3-(pyrrol-1-yl)propylmalonic acid) (poly1) and poly(N,N′-ethylenebis[N-[(3-(pyrrole-1-yl)propyl) carbamoyl) methyl]-glycine (poly2) coated electrodes (C|poly1 and C|poly2) towards Cu(II), Pb(II), Hg(II) and Cd(II) cations using the open circuit chemical preconcentration-anodic stripping technique were studied. Sorption process of metal cations onto complexing surfaces was readily investigated through the combination of a chemical pre-concentration-anodic stripping technique with a Langmuir isotherm model. The modified electrodes were used for the voltammetric determination of Cu(II), Pb(II), Hg(II) and Cd(II) ions, giving low detection limits for Cu(II) (5×10^{-9} mol L^{-1}) and Pb(II) (5×10^{-10} mol L^{-1}). The ability of the modified electrodes to analyze Cu(II) ions in natural sample has been demonstrated by the analysis of a tap water sample. The results of the preconcentration process under competitive conditions clearly shows that the selectivity of complexing molecular electrode materials can be subtly tuned upon playing on the accumulation time, polymer thickness and/or memory effect of the binding polymers, opening up new avenues towards evolutive and efficient smart sensing materials.

Keywords: electrochemical sensing; functionalized polypyrrole; imprinted polymers; metal ions analysis

Introduction

Humans have used heavy metals for thousands of years. Although several adverse health effects have been known for a long time, exposure to heavy metals continues, and is even increasing in some parts of the world, in particular in less developed countries, though emissions have declined in most developed countries over the last 100 years. The main risk to human health from heavy metals is associated with exposure to lead, cadmium, mercury and arsenic. Cadmium for example, produce kidney damage, bone effects and fractures, meanwhile mercury have low risk of neurological damage in adults but high risk to the fetus in pregnant women. Additionally lead has neurotoxic effects even at lower levels of exposure.[1–3]

Once emitted, metals can remain in the environment for hundreds of years. Heavy metals have been found in the ice cores in Greenland and seawater in the Antarctic. Moreover, the lead contents of ice layers in Greenland exceeds hundred times the natural background level.[4] Because of the above, World Health Organization (WHO) has reduced the maximum permitted level of several metal species in water. It results in an ever increasing demand for the determination of metal contaminants in environmental matrices (principally aqueous) at low concentration.[5]

Electrochemical stripping analysis has long been recognized as one of the most sensitive methods for the determination of trace metals and is very suitable for the task

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of real time and *in situ* analysis.[6–9] The method is based on preconcentration by electrodeposition followed by anodic stripping of an analyte in the sample solution. For many years, mercury was the electrode material of choice due to its good properties including reproducibility and purity of the surface, and high hydrogen overpotential.[7] However, because of the toxicity of mercury, difficulties in the determination of metals whose dissolution potentials are more positive than that of mercury, and also problems with metals insoluble in mercury, new alternative solid electrode materials are highly desired.

Stripping analysis also found applications related to the characterization of the interactions of metal ions with simple and macromolecular-ligands and for the determination of metal complex apparent stability constants. Moreover, improved metal cation sensing efficiency and selectivity can also be achieved through the combination of stripping voltammetry with a complexing polymer based preconcentration method.

It is now well established that the analytical scope of solid electrodes, including trace metals voltammetric analyses, can be greatly enhanced through a deliberate modification of their surface.

Complexing electrode materials appear particularly attractive for trace metals analysis, because the metal complex formation is used in the preconcentration step at open circuit.

The use of an electrode modified with a ligand, with high affinity for a given metal cation will ensure highly sensitive and selective measurements, and can reduce interferences compared to conventional voltammetric techniques.

Various ligands and surface manipulation strategies have been explored for the accumulation-voltammetry of metal cations, including adsorbed and self-assembled monomolecular layers of ligand on gold electrodes,[10] composite electrode materials prepared by mixing ligands with carbon paste,[11] nanoparticles modified electrodes [12–15] or complexing polymer film modified electrodes.[16,17] Electrode modification with complexing polymer films is an attractive approach as it yields large amounts of ligand at the electrode surface and hence allows large amounts of metal ions to be accumulated. Among the different processes that can be carried out for electrode surface modification, electropolymerization of heteroaromatic monomers, such as pyrrole, aniline or thiophene compounds, provides a straightforward and efficient route to coat polymer films onto electrode surfaces. Therefore, conducting polymer films have received considerable attention for generating modified electrodes with analytical utility, especially for trace metals detection.[18] The functionalization of polypyrrole [19–22] and polyaniline [23] films electrodes can be achieved by electrostatic incorporation of anionic complexing ligands during the electropolymerization step. In order to increase the selectivity of the polymer film for one or another metal ions, the imprinted polymer strategies could be follow by conducting the electropolymerization in presence of the metal ion of interest. After that, it could be removed by soaking the electrode in a properly solution.

We report herein the complexing properties of poly (3-(pyrrol-1-yl)propylmalonic acid) (poly1) and poly(N,N′-ethylenebis[N-[(3-(pyrrole-1-yl)propyl) carbamoyl) methyl]-glycine]) (poly2) coated electrodes (C|poly1 and C|poly2) towards Cu(II), Pb(II), Hg(II) and Cd(II) cations using the open circuit chemical preconcentration-anodic stripping technique.

We focused our view not only in the analytical application of the modified electrodes, but also in the preconcentration process. It is, in the complex formation between the acid polymer ligands of the film surface with metal ions. In this sense we studied also the thermodynamic and the kinetics of the process.

Experimental Part

Reagents and Materials

3-(pyrrol-1-yl)propylmalonic acid (monomer 1) and N,N′-ethylenebis[N-[(3-(pyrrole-1-yl)propyl) carbamoyl) methyl]-glycine] (monomer 2) were synthesized according to a known procedure.[24–27] Acetonitrile (Rathburn, HPLC grade S) was used as received. Tetra-n-butylammonium perchlorate (TBAP, Fluka puriss) was dried under vacuum at 80 °C for 3 days. Suprapur grade sodium acetate and acetic acid were from Merck. The disodium salt of ethylenediamine tetraacetic acid was purshased from Roth. Cu(II) sulphate and Pb(II) acetate were from Prolabo. Hg(II) trifluoromethane sulfonate was from Strem. Cd(II) nitrate was obtained from Merck. All reagents were used without further purification. Distilled water was obtained from an Elgastat water purification system (5 MΩ cm). Glassware and polyethylene bottles were soaked in $KMnO_4$-H_2SO_4, and then carefully cleaned with distilled water before use to avoid contamination.

Preparation of Modified Electrodes

Electrochemical Equipment

Electropolymerization of monomer 1 and 2 in organic electrolyte were carried out using an EGG PAR model 173 potentiostat equipped with a model 179 digital coulometer and a model 175 programmer. All electroanalytical experiments were performed in aqueous acetate buffer (0.1 mol L^{-1}, pH 4.4) with a CHI 660B electrochemical analyzer (CH Instruments), using a conventional three-electrode system. The working electrode was a 3 mm diameter modified carbon disk; the counter electrode was a platinum wire and a SCE electrode served as reference. Solutions were degassed with N_2 for 20 min before each measurement and kept under a N_2 atmosphere during the entire experimental period. All experiments were run at 25 °C.

Preparation of C|poly1[25]

Poly1 films were grown on vitreous carbon disk electrodes (see Figure 1), (3mm diameter, from CH Instruments) in solutions of 1 (3×10^{-3} mol L^{-1}) in CH_3CN containing 0.1 mol L^{-1} TBAP, by oxidative electropolymerization at 0.85 V vs. Agi|Ag^+ 10^{-2} mol L^{-1} in $CH_3CN + 0.1$ mol L^{-1} TBAP. The modified electrodes exhibit upon transfer into pure $CH_3CN + 0.1$ mol L^{-1} TBAP electrolyte the regular electroactivity of N-substituted polypyrroles. Apparent surface coverage of complexing sites Γ_L (mol cm^{-2}) was determined from the charge recorded under the polypyrrole oxidation wave by cyclic voltammetry at the scan rate of 2 mV cm^{-1}, taking into account that one malonic group is attached to each pyrrole ring and assuming that one in three pyrrole units is oxidized. Typically films of Γ_L between 3×10^{-8} and 6×10^{-8} mol cm^{-2} were obtained using polymerization charges of 0.5 and 1 mC, respectively. Modified electrodes were stored in aqueous buffer solution (pH 4.4) or in air.

Preparation of C|poly2 and Imprinted C|poly2[27]

Poly 2 films were grown on vitreous carbon disk electrodes (Figure 2), (3mm diameter, from CH Instruments) in solutions of 2 (3×10^{-3} mol L^{-1}) in CH_3CN containing 0.1 mol L^{-1} TBAP + two equivalents oh $HClO_4$, by oxidative electropolymerization at 0.9 V vs. Ag| Ag^+ 10^{-2} mol L^{-1} in $CH_3CN + 0.1$ mol L^{-1} TBAP. The modified

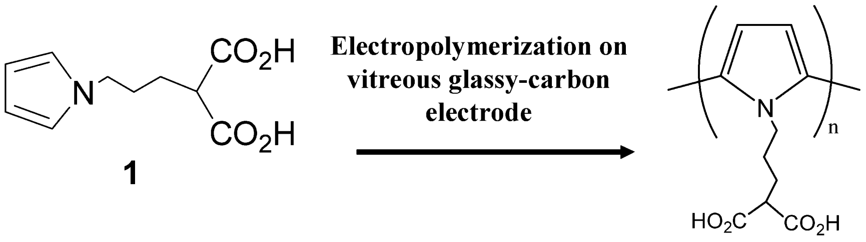

Figure 1.
Preparation of C|poly1.

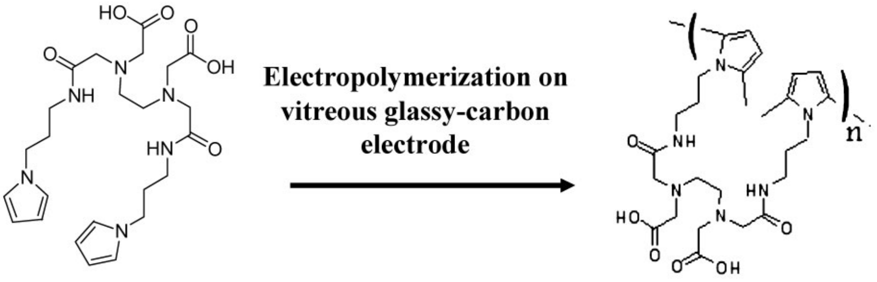

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Figure 2.
Preparation of C|poly2.

electrodes exhibit upon transfer into pure $CH_3CN + 0.1\,mol\,L^{-1}$ TBAP electrolyte the regular electroactivity of N-substituted polypyrroles. Apparent surface coverage of complexing sites Γ_L ($mol\,cm^{-2}$) was determined from the charge recorded under the polypyrrole oxidation wave by cyclic voltammetry at the scan rate of $2\,mV\,cm^{-1}$, taking into account that one malonic group is attached to each pyrrole ring and assuming that one in three pyrrole units is oxidized. Typically films of Γ_L between 1×10^{-8} and 5×10^{-8} mol cm^{-2} were obtained using polymerization charges of 0.25 and 1 mC, respectively. Modified electrodes were stored in aqueous buffer solution (pH 4.4) or in air.

Imprinted C|poly2 was grown on vitreous carbon disk electrodes in the same conditions that above, but in the presence of four-molar equivalents of Cd(II) cations. Under these experimental conditions clean electropolymerization takes place because the amine groups of 2 are complexed with cadmium cations.

Analytical Procedure

Accumulation of metal ions into the poly1 and poly 2 film was carried out at open circuit by dipping the C|poly1 and C|poly2 modified electrode for a given time (the accumulation time, typically 10 min) into 25 mL of stirred buffered solutions (pH 4.4) of metal salts maintained at 25.0 ± 0.5 °C. The electrode was removed from the accumulation cell and washed thoroughly with purified water. It was transferred to the electrochemical cell containing acetate buffer solution (pH 4.4). Square wave voltammetry experiments were then conducted under quiescent conditions. The accumulated metal ions were reduced for 40 s at 0.9 V (Cu(II), Pb(II), Hg(II)) or 1.1 V (Cd(II)), and the potential was scanned from the reduction potential to 0.4 V. Square wave voltammetry was applied with a 50 mV modulation amplitude, a 60 Hz frequency and a 5 mV step potential. After each metal determination, regeneration of the metal-free electrode involved the elimination of metal ions by soaking the electrode for 3 min in 10^{-3} mol L^{-1} EDTA. Alternatively, the effective regeneration of free films could also be obtained by dipping the complexed electrodes in $10^{-2}\,mol\,L^{-1}$ sodium diethyldithiocarbamate for 3 min. The electrode was then washed thoroughly with purified water, and scanned in the differential pulse mode into a blank solution of acetate buffer until the background current was reproducible. Usually two to four scans were necessary to obtain a stable background. The freshly electropolymerized electrodes were also conditioned in the same way.

Thermodynamic Studies of Complexing Process for C|poly1

Accumulation of metal ions at the C|poly1 modified electrode was carried out at open circuit by dipping the electrode for 48 h into 25 mL of a stirred buffered solutions (pH 4.4) of metal salts kept at a constant temperature. To that, four different temperatures (20, 25, 30, and 35 °C) were studied. Each isotherm curve was done with ten modified electrodes at ten different concentrations. The electrodes were removed from the accumulation cell and washed thoroughly with purified water. It was then transferred to the electrochemical cell containing acetate buffer solution (pH 4.4). Cyclic voltammetry experiments were conducted immediately under quiescent conditions. The accumulated metal ions were reduced at $-0.9\,V$ for 40 sec and the potential was scanned from the reduction potential to 0.4 V. Cyclic voltammetry was applied at the scan rate of 25 mV/sec.

After each metal determination, regeneration of metal-free electrode involved the elimination of metal ions by soaking the electrode for 20 min in 0.1 M EDTA. The electrode was washed thoroughly with purified water, and then scanned by cyclic voltammetry into a blank solution of acetate buffer until the background current was reproducible.

Kinetics Studies of Preconcentration Process for C|poly2 in Competitive Conditions

Competitive complexation of Pb(II) and Cu(II) into C|poly2 modified electrodes were carried out at $pH = 5.0$ upon varying the pre-concentration time (1 to 20 min.) and the films thickness ($\Gamma_L = 9.7 \times 10^{-9}$, 3.1×10^{-8} and $5.1 \times 10^{-8}\,mol\,cm^{-2}$). All the conditions for the preconcentration step and determination of accumulated metal are the same that described in analytical procedure.

Results and Discussion

Complexing Properties of 1 and 2 toward Cu(II), Pb(II) and Cd cations in Homogeneous Media

The formation of complexes between monomer 1 and 2, and the tested metal ions have been further confirmed from electrospray (ES) mass spectrometry (MS). ES–MS data were obtained from equimolar aqueous solutions of metal ions and monomer 1 or 2 ($1\,mg\,L^{-1}$ in 1:1 CH_3CN:H_2O solutions, flow rate of $5\,mL\,min^{-1}$).

For monomer 1, the soft ionization of the metallated species gave only two signals with isotopic peaks separated by 1.0 m/z unit in accordance with a +1 charge state of the corresponding ions. Both signals were compared with calculated spectra and could be unambiguously attributed. The signals at m/z = 627.02 (100%) and m/z = 838.0 (7, 20%) were indeed assigned to Pb(II) complexes characterized by 1:2 and 1:3 (M^{2+}:1) stoichiometries, wherein one metal ion is coordinated by two and three malonic fragments, respectively. The formation of insoluble species unfortunately precluded the study by ES-MS of Cu(II) complexation with 1. However, the formation of 1:2 and 1:3 Pb(II) complexes contrasts with the results obtained for malonate–Cu(II) complexes for which stable 1:1 and 1:2 stoichiometries have been evidenced. This difference could be explained by the smaller ionic radius of Cu(II) (73 pm) compared to Pb(II) (119 pm).

For monomer 2 and Pb(II), the ES–MS spectra of a solution displayed characteristic signals of 1:1 and 1:2 (2:M) complexes. As a matter of fact, a signal was observed at m/z = 709.1 (negative mode) for the $[(2–3H^+)Pb]^-$ anion, along with signals at 711.0 and 916.9 (positive mode) for the $[(2–H^+)Pb]^+$ and $[(2–3H^+)Pb_2]^+$ cations. The formation of a 1:1 complex between 2 and Cd(II) was evidenced by the presence of a characteristic signal at m/z = 615.0 (negative mode) for the $[(2–3H^+)Cd]^-$ species (see Figure 3). All isotopic peaks are separated by 1.0 m/z unit. In the same way that monomer 1, formation of insoluble species in the course of the experiments with Cu(II) precluded the analysis of copper-monomer 2 complexes by this technique.

Complexation of C|poly1, C|poly2 and Imprinted C|poly2 Films with Copper, Lead, Mercury and Cadmium Ions

Oxidative electropolymerization of monomer 1 and characterization of poly1 films has already been described in details.[24] It is known that the dianion of malonic acid

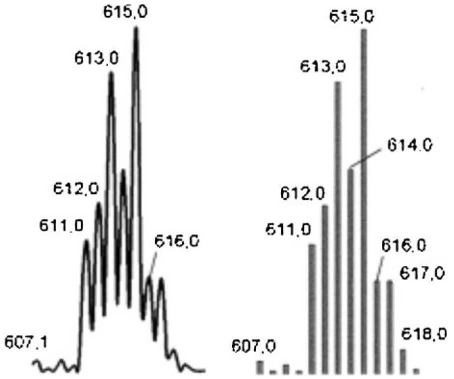

Figure 3.
Experimental and calculated ES-MS spectra for [{2-3H}Cd]$^-$ complex.

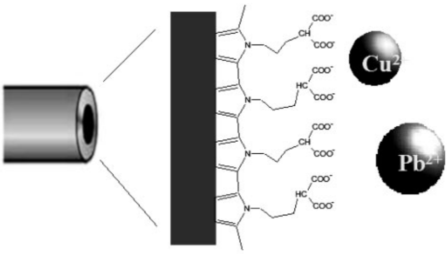

Figure 4.
Representative zoom view of the C| poly1 surface showing the malonic ligand groups.

forms various complexes with metal ions, since malonate group can adopts bidentate chelating and different carboxylate-bridging coordination modes. Complexation of Cu(II) in poly1 films has been evidenced by electrochemical and FT-IR experiments.[24] In particular the infrared spectrum of poly1 films was deeply changed after immersing for a few minutes in 10^{-2} M $CuSO_4$ at pH 3. The C=O stretching vibrations bands for carboxylic acid groups at 1718 and 1733 cm^{-1} markedly decreased, while a very broad band attributed to OCO stretching vibrations in copper-malonate complexes appeared at 1580 cm^{-1}. These observations are in agreement with the effective formation of copper-malonate complexes in poly1.

To evaluate the properties of poly(pyrrole-malonic acid) film electrodes in the determination of metal ions, using the chemical preconcentration anodic stripping method, the modified electrode was immersed into a buffered solution containing a given metal ion leads to the chemical accumulation of the cations in the film through complexation between the metal ions and the malonic acid groups attached to the polymer (see Figure 4).

The accumulation of metal ions was carried out without applying a reduction potential, in order to avoid interferences with other reducible species. After the preconcentration step the modified electrode is transferred to a blank solution of sodium acetate/acetic acid buffer where the complexed metal ions are reduced for 40 s before recording the stripping currents. After accumulation in buffer solutions containing a given metal ion at a concentration of 10^{-6} mol L^{-1}, square-wave voltammetry (SWV) curves exhibited anodic peaks at 0.84 V, 0.62 V, 0.10 V, and 0.25 V vs. SCE, corresponding to the oxidation of reduced Cu(0), Pb(0), Hg(0), and Cd(0) to their M(II) ions, respectively.

The C|poly1 modified electrode has been applied to the determination of Cu(II), Pb(II), Hg(II) and Cd(II) ions. The variation in peak current with the concentration of metal ion in the accumulation solution is shown in Figure 5 for Cu(II), Pb(II), Hg(II) and Cd(II) cations. Linear calibration plots were obtained in the concentration range

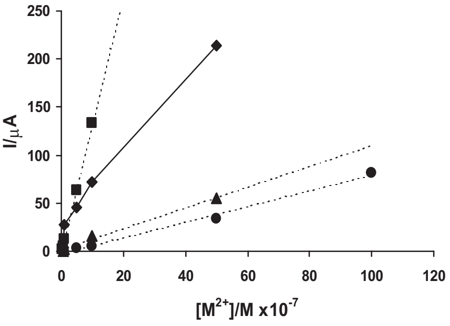

Figure 5.
SWV peaks current in function of metal ion concentration; -(◆)- Cu(II), -(■)- Pb(II), -(▲)-Hg(II), and -(●)- Cd(II), for C| poly1 modified electrode of $\Gamma_L \approx 3 \times 10^{-8}$ mol cm^{-2}.

from 2.5×10^{-8} to 2.5×10^{-7} for Cu(II), 10^{-8} to 10^{-6} mol L^{-1} for Pb(II), 5×10^{-8} to 5×10^{-6} mol L^{-1} for Hg(II), and 10^{-7} to 10^{-5} mol L^{-1} for Cd(II), with correlation coefficients of 0.990, 0.999, 0.991 and 0.993 for Cu(II), Pb(II), Hg(II) and Cd(II), respectively. At 10-min preconcentration time the detection limits (based on a signal-to-noise ratio of 3 were determined to be 5×10^{-9} for Cu(II), 5×10^{-10} mol L^{-1} for Pb(II), 10^{-7} mol L^{-1} for Hg(II), and 5×10^{-7} for Cd(II), with electrodes modified with films of $\Gamma_L \approx 3 \times 10^{-8}$ mol cm^{-2}.

Considering the slope of the calibration curves (Figure 5), it appears that the poly1 film modified electrodes give better results for the determination of copper and lead than for cadmium and mercury in terms of sensitivity. In fact, in terms of limit of detection (LOD), we can establish that for both thickness of the Poly 1 film, the sensitivity follow the order; LOD Cu(II)< LOD Pb(II)< LOD Hg(II))< LOD Cd(II). Moreover, we found that the LOD for Cu(II), Pb(II), Hg(II) and Cd(II) is lower for the thicker film ($\Gamma_L = 6 \times 10^{-8}$ mol cm^{-2}) that for de thinner film ($\Gamma_L = 3 \times 10^{-8}$ mol cm^{-2}). These observations show that the sensing behavior clearly depends on the complexing properties of the malonic acid moieties.

As an example, C| poly1 was used for the determination Cd(II) ions in a reference sample (787 ppb of cadmium) obtained by appropriate dilution of a standard reference solution. The concentration of cadmium in the standard reference sample was measured as 750 ± 19 ppb using the electrode modified with the thinner poly1 film, and 816 ± 21 ppb with that modified with the thicker polymer film (average values for 3 measurements with each electrode).

Also simultaneous determination of studied cations in real water samples was conducted.

A local tap water sample (containing 22.9 ppb copper and 15.9 ppb lead, from ICPMS analysis) was analyzed for copper. After adjustment of the pH of the sample to 4.4 with acetate buffer, copper was determined by the single standard addition method. Pb(II) and Cu(II) ions were detected. Owing to the competitive complexation of copper cations in this metal ions concentration range, Pb(II) ions cannot be accurately determined since the lead stripping current is strongly disturbed by the presence of Cu(II) ions. In contrast, it should be emphasized that copper analysis gave a result (21.8 ppb) in good agreement with the result obtained by ICPMS (22.9 ppb), confirming the effectiveness of the poly1 modified electrode for copper analysis in real samples.

The complexation ability of C|poly2 materials was investigated using the chemical preconcentration-anodic stripping method. Dipping the modified electrode into metal containing aqueous 0.1 M acetate buffered solutions led to the complexation of metal ions within the polymeric binding structure (i.e. chemical accumulation at open circuit). After this preconcentration step, the modified electrode was transferred into a metal-free aqueous 0.1 M acetate buffered solution in which all the previously extracted complexed metal ions were reduced. The stripping currents were then recorded using square wave voltammetry (SWV). Typical SWV curves, obtained after 10 min of pre-concentration in 10-5 M Pb(II) or Cu(II) solutions, exhibit stripping peaks at −0.6 V and 0 V vs. SCE corresponding to the re-oxidation of previously precipitated Pb(0) and Cu(0) respectively

No clear and accurate SWV responses could be obtained in the same conditions with C|poly2 electrodes submitted to Cd(II) solutions. Moreover, no cadmium stripping peak was observed when the metal ions collection was carried out in a mixture of Cd(II), Cu(II) and Pb(II) cations.

With the idea to elaborate Cd(II) sensitive modified electrodes, we turned our attention towards an imprinted polymer strategy. The electropolymerization of 2 was performed in the presence of four-molar equivalents of cadmium cations, without added perchloric acid. Under these experimental conditions electropolymerization takes place because the amine groups of 2 are complexed with the metal ions. The Cd(II) cations were then removed from the metallopolymer film upon soaking the polyL-Cd(II) film modified electrode in an EDTA solution. As in the case of poly2 films synthesized in acidic electrolyte, the apparent surface concentration of complexing sites (Γ_L) in metal-free films was assessed from the charge under the polypyrrole oxidation wave.

In contrast to what was observed with polymer films grown in acid media, the SWV curve recorded at an imprinted C|poly2 electrode after metal ion preconcentration in a solution containing equimolar concentrations of Cu(II), Pb(II) and Cd(II), (10^{-5} M), exhibited three peaks corresponding to the stripping of Cu(0), Pb(0) and Cd(0), the stripping peak of cadmium being observed at –0.67V. Moreover, the analysis of solutions containing only Cd(II) cations could be readily performed by the chemical preconcentration-anodic stripping technique using "cadmium-imprinted" electrodes. Calibration curves recorded at an imprinted C|poly2 film electrode ($\Gamma_L = 2 \times 10^{-8}$ mol cm^{-2}) adopt the usual shape of chemisorption process, with a saturation occurring at 0.9 ppm and a detection limit of 0.1 ppm (9-min preconcentration).

Reproducibility and Stability of the Modified Electrode

The reproducibility for the preparation of C|poly1 and C|poly2 electrodes was examined in the following manner. Five carbon electrodes were modified by electropolymerization (charge passed 1 mC) in a 3×10^{-3} mol L^{-1} solution of respective monomer, then used in the determination of lead with 10-min preconcentration in 10^{-6} mol L^{-1} Pb(II) solution. Stripping currents mesured shows the good reproducibility (higher than 95%) of the elaboration process for both electrodes.

Moreover, 10 consecutive determinations of 5×10^{-8} and 10^{-6} mol L^{-1} Pb(II) were performed using the same modified electrodes, giving relative standard deviations less than 10% for both electrodes. This result emphasized that by regenerating the metal free polymer film, the modified electrodes can be used for multiple measurements.

In addition, electrodes can be stored in buffer solution or in air without significant loss of sensitivity. For example, the same current response was obtained for two determinations of lead (preconcentration in 10^{-6} mol L^{-1} Pb(II)) at a 3-week interval and using the same electrode stored in air.

Thermodynamic Studies of Complexing Process for C|poly1

For each temperature investigated, plotting the surface coverage rate (s) as a function of the equilibrium concentration led to isothermal sorption curves which proved to be in perfect agreement with a type I isotherm. A typical isothermal sorption curve is depicted in for Pb(II) at 298 K in poly1 film electrode. This adequacy specially confirms that the accumulation of Cu(II) or Pb(II) into poly1 modified electrodes is a true chemisorption process. Cu(II) and Pb(II) binding constant values calculated at different temperature are given in Table 2. It clearly shows that the affinity of Pb(II) cations for the ligating materials deposited onto the electrode surface is higher than that of Cu(II). In addition, the affinity of both Cu(II) and Pb(II) turned out to significantly decrease upon increasing the temperature.

For films with C values in the 2.2×10^{-8}–5.6×10^{-8} mol cm^{-2} range, τ_{max} was found to be much higher for Cu(II) (0.571) than for Pb(II) (0.140). In a first approximation, it could be concluded that the chemisorption of one copper cation mobilizes an average of 1.8 malonate units, whereas the complexation of one Pb(II) mobilizes approximately seven malonate units. This assumption is in good agreement with the higher stoichiometry (1:2 and 1:3) found in homogeneous solution for the malonate–Pb(II) complexes as compared to the corresponding Cu(II) complexes showing 1:1 and 1:2 stoichiometries.[25]

As judged from the calculated K values, the difference between the affinities of

Cu(II) and Pb(II) for C|poly1 surface comes from the entropic terms solely, with Δ_rS° equal to −98.4 and −82.8 J mol^{-1} K^{-1} respectively. The negative sign of Δ_rS° is obviously related to the notion of increased order consecutive to the formation of a polymeric complex onto the electrode surface. The Δ_rS°value thus clearly suggests a more important ordered re-organization of the poly1 system upon complexation with Cu(II) leading consequently to an improved ability to extract metal ions highlighted by the higher measured surface coverage rate τ_{max}: 0.571 for Cu(II) and 0.140 for Pb(II).

Kinetics Studies of Preconcentration Process for C|poly2 in Competitive Conditions

Competitive complexation of Pb(II) and Cu(II) into C|poly2 modified electrodes was carried out at pH 5.0, using increasing preconcentration time (from 1 to 20 min) and different films thickness (Γ_L =3.1 × 10^{-8} and 5.1 × 10^{-8} mol cm^{-2}). The intensity of the stripping peak for the dissolution of Pb (I_{Pb}) and Cu (I_{Cu}), as a function of the preconcentration time in an equimolar solution (10^{-5} M) of Pb(II) and Cu(II) is showed in Figure 6a. The results clearly put forwards that the extraction selectivity depends on both film thickness and accumulation time. I_{Pb} increases with the accumulation time to reach a maximum that depends on the film thickness, then decreases and fully disappears for longer accumulation times as could be seen in Figure 6b.

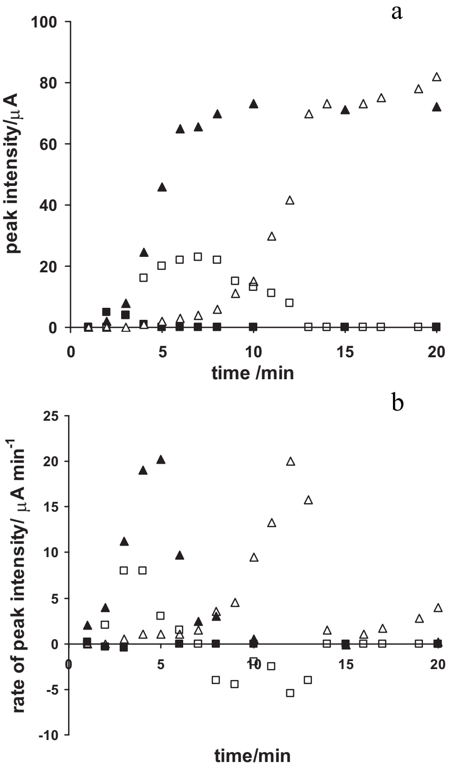

Figure 6.
(a) Stripping peak currents and (b) rate of stripping peak currents obtained with C|poly2 electrodes (Γ_L = 3.1 × 10^{-8} mol cm^{-2}), -(▲)- Cu(II), -(■)- Pb(II) and (Γ_L = 5.1 × 10^{-8} mol cm^{-2}), -(△)- Cu(II), -(□)- Pb(II) as a function of the accumulation time in an equimolar aqueous solution (10^{-5} M) of Pb(II) and Cu(II) in acetate buffer, pH 5.

As for the non-prestructured poly2, the selectivity of cadmium-free imprinted C|poly2 turned out to be strongly dependant on the accumulation time. For all studied mixtures (Cd(II) + Cu(II), Cd(II) + Pb(II), or Cd(II) + Cu(II) + Pb(II)), the amount of collected Cd(II) reached a maximum for short accumulation times (around 7 min under our experimental conditions). For longer accumulation times, cadmium cations were progressively replaced by Cu(II) or Pb(II) ions. The cadmium-based imprinting procedure thus clearly influences the binding and sensing abilities of the electrosynthesized films, as proved by the effective extraction of cadmium from metal mixtures. However, like the non pre-structured polymer, the imprinted poly2 films displayed a greater affinity towards towards Cu(II) and Pb(II) ions. In addition, the imprinted C|poly2 films extract more efficiently Pb(II) than Cu(II) cations. Since EDTA displays similar binding ability towards Cu(II) and Pb(II) cations, this result could be explained by the fact that the cadmium (ionic radius= 95 pm) based imprinting process ensures an improved access for Pb(II) ions (ionic radius = 119 pm) to the binding sites than does the non pre-structured film, which appeared more adapted to smaller Cu(II) ions (ionic radius = 73 pm).

Conclusion

The modified electrodes have been exploited for the voltammetric determination of Cu(II), Pb(II), Cd(II) and Hg(II) ions, giving low detection limits for copper (5×10^{-9} mol L^{-1}) and lead (5×10^{-10} mol L^{-1}). The study of the interference between Cu(II), Pb(II) and Cd(II) ions has shown that the polymalonic acid films show a greater affinity to copper. The ability of the modified electrodes to analyze Cu(II) ions in natural sample has been demonstrated by the analysis of a tap water sample. The concentration of copper in this natural sample agreed well with results of ICPMS.

Sorption process of metal cations onto complexing surfaces can thus be readily investigated through the combination of a chemical pre-concentration-anodic stripping technique with a Langmuir isotherm model. The incorporation of both Pb(II) and Cu(II) into the C|poly1 material has been clearly shown to be a chemisorption process (coordination process)

Pb(II) turned out to present a higher affinity for the C|poly1 surface than Cu(II), as judged from the respective binding constant values. However, a lower amount of Pb(II) could be immobilized onto the electrode surface, as proved by the estimated maximal surface coverage rates (ionic radii). Both parameters, binding constant and maximal surface coverage rate, are thus required for the full characterization of the sorption process. As a consequence, the difference in affinities between Pb(II) and Cu(II) for the C|poly1 surface could be explained on the basis of the respective entropy variations of the sorption equilibrium.

Non pre-structured C|poly2 electrode materials show greater affinity towards Cu(II) ions and are almost insensitive to Cd(II) cations. On the contrary, imprinted polymer film electrodes synthesized by electropolymerization of 2 in the presence of Cd(II) cations allowed the effective binding and sensing of Cd(II) in competitive mixtures of metal cations. The results of the preconcentration process under competitive conditions clearly shows that the selectivity of complexing molecular electrode materials can be subtly tuned upon playing on the accumulation time, polymer thickness and/or memory effect of the binding polymers, opening up new avenues towards evolutive and efficient smart sensing materials.

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