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Sensors and Actuators B 120 (2007) 766–772

SENSORS AND ACTUATORS B CHEMICAL

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On the complex formation of $CdCl_2$ with 1-furoylthioureas: Preconcentration and voltammetric behavior of Cd(II) at carbon paste electrodes modified with 3-monosubstituted and 3,3-disubstituted derivatives

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Received 2 December 2005; received in revised form 27 March 2006; accepted 27 March 2006
Available online 15 May 2006

Abstract

Two series of 1-furoylthioureas were used as modifiers of carbon paste electrodes (CPE). The preconcentration of Cd(II) at CPE modified with these 3-monosubstituted and 3,3-disubstituted 1-furoylthioureas and its subsequent voltammetric determination was studied with Cd(II) test solution. The preconcentration of cadmium at the surface of the modified CPE varied with the steric and electronic nature of the present CS neighboring groups. This is in accord with the changes observed in the Raman spectra of the ligands after complexation with $CdCl_2$, and with the chemical yields of the complexes obtained.

Keywords: Raman; Furoylthioureas; Cd(II) complexes; Carbon paste electrode; Surface complex

1. Introduction

The thiourea derivatives studied (3-monosubstituted and 3,3-disubstituted 1-furoylthioureas) have been successfully used as ionophores in ion selective electrodes (ISEs) for Cd(II), Hg(II) and Pb(II) [1]. This application required a sharp modulation of the coordination strength. Formation of very stable complexes is usually related to a short electrode lifetime due to the poisoning of the ISE membrane. The best performance in that application has corresponded to 3-monosubstituted 1-furoylthioureas, with a relatively high Raman frequency values of their ν(C=S) vibration [2]. It is dependant on an appropriate nucleophilic character of its sulphur atom. Thiourea and its derivatives are a versatile family of ligands appropriate for forming complexes with ions of transition (e.g. Ni(II), Cu(II/I), Co(III), Zn(II), Ag(I), Cd(II), Pt(II), Pd(II), Au(III), Rh(III), Re(III), Tc(III)) and post-transition (e.g. Pb(II), Sb(III), Bi(III)) metals [3–6]. It is well known that the coordination chemistry of such derivatives is much more varied than that of simple thiourea. Thus, the physiochemical properties of their metal complexes are more pronounced, resulting in a number of interesting potential technical and analytical applications [5]. Coordination compounds formed by the organic ligand thiourea and metal(II) ion with d^{10} electronic configuration (Zn(II), Cd(II), Hg(II)) have recently received renewed attention for two main reasons: their non-linear optical properties [7,8] and the convenient preparation of semiconducting materials based on CdS through the thermal decomposition of those complexes [9,10]. With d^{10} metal ions (Zn(II), Cd(II), Hg(II), Ag(I), Cu(I)), thiourea and its derivatives show certain regularity concerning the metal coordination through only the S atom [4]. We have previously studied the Raman spectra of two series of 1-furoylthiourea derivatives [2] and their complexes with $CdCl_2$ [11] in order to identify those vibrations involving contributions from motions within the thioureido (NCSN) core, because they are the mainly affected after coordination. This has proved an appropriate technique for shedding light on the suitability of the thiourea derivatives studied in the men-

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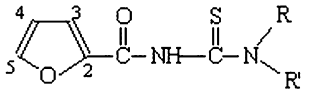
doi:10.1016/j.snb.2006.03.042

tioned application [2]. The fact that this family of compounds has been tested, with promising results, as ionophores in ion selective electrodes [1], is the main antecedent for using 1-furoylthioureas as heavy metal complexing modifiers incorporated in carbon paste electrodes (CPE). We have now carried out preliminary studies of the preconcentration of cadmium at carbon paste electrodes modified with these compounds and its subsequent voltammetric determination with test solutions. Chemically modified electrodes consisting of carbon paste and modifying reagent have been widely used, since they can be prepared easily and have a stable electrode response [12,13]. Therefore they have been used to accumulate analytes selectively and to protect them from interference by other ions. Similar studies have been reported using thiourea derivatives for Ag(I) [14] and Pd(II) [15]. Electrodes modified with selective ligands enable the immobilization of metal ions by the formation of surface complexes at the electrode [16–18]. Different modifiers for carbon paste have been reported in the last years for the electrochemical stripping analysis of Cd(II): bismuth-powered [19], carbamoylphosphonic acid [20], organofunctionalized amorphous silica [21], diacetyldioxime [22], polycyclodextrin [23] and *N-p*-chorophenylcinnamohydroxamic acid [24]. The detection limits for these carbon paste modified electrodes are in the range from 0.0011 to 0.22 mg L^{-1}, with relative standard deviations from 2.6 to 6.5%; these results agree with those reported in this paper. We present here the first results concerning the preconcentration and voltammetric determination of cadmiun at 1-furoylthioureas modified electrodes. We have correlated the electroanalytical results (dependence of the binding capabilities of the CPE modified with different 1-furoylthioureas on the Cd(II) uptake) with those changes seen in the 1-furoylthiourea derivatives Raman spectra after complexation with cadmium chloride in neutral media (ethanol), and the chemical yield of the complexes obtained. A preliminary electrochemical analysis of Cd(II) with a 3-monosubstituted 1-furoylthiourea modified carbon paste electrode is also described.

2. Experimental

2.1. Synthesis of ligands and their complexes with $CdCl_2$

The 1-furoylthioureas were synthesized as previously reported by Otazo-Sánchez et al. [1,25]. According to their substituents, these ligands were labeled as Series **1** and **2** (Figs. 1 and 2). Series **1** (compounds **1a**, **1b**, **1c**, **1d**, **1e** and **1f**) involves 3,3-disubstituted 1-furoylthioureas while Series **2** (compounds **2b**, **2d**, **2f**, **2g**, **2h** and **2j**) concerns to 3-monosubstituted. In order to provide certain continuity with previous studies on these families of thiourea derivatives [1,2,11,25], the same numerals used there are preserved. The respective $CdCl_2$ complexes of both Series were labeled as $CdCl_2$-ligand. Complexation occurred when isoconcentrated ethanolic solutions of thiourea derivatives and cadmium chloride were mixed at room temperature in 1:1 molar ratio. The reactive mixture was left to evaporate until complexes precipitated. The cadmium chloride mixtures with **1c**, **1d** and **1e** ligands did not form precipitate, although the solution turned turbid. The rest of the products were collected by filtration, then washed with ethanol and finally dried in air.

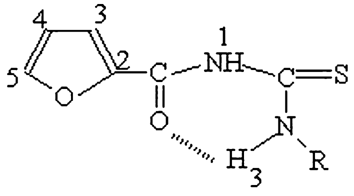


No.	R	R'
1a	$- CH_2 CH_2 CH_2 CH_2 CH_2$-	(piperidyl)
1b	$-CH_2CH_3$	$-CH_2CH_3$
1c	$-C_6H_5$	$-C_6H_5$
1d	$-C_6H_5$	$-CH_2C_6H_5$
1e	$-C_6H_5$	$-CH_2CH_3$
1f	$-C_6H_5$	$-CH_3$

Fig. 1. Series **1** ligands. The C=O and the C=S groups adopt a “U”-shaped conformation.

2.2. Raman measurements

Raman spectra were collected by a capillary sample technique on a Perkin-Elmer system 2000 NIR-FT-RAMAN and a Lexel model 98 krypton ion laser ($\lambda = 647.1$ nm). The laser power at the sample surface was restricted to 40 mW. The spectral band pass of the Raman spectrometer was 4 cm^{-1} and the 90° configuration used with an incidence angle of 60° on the metal surface when taking surface-enhanced Raman scattering (SERS) spectra.



No.	R
2b	$-C_6H_{11}$
2d	$-CH_2C_6H_5$
2f	$-C_6H_5$
2g	-(o)$C_6H_5CH_3$
2h	-(o)$C_6H_5NO_2$
2j	-2-C_5H_5N

Fig. 2. Series **2** ligands. The C=O and C=S groups adopt an “S”-shaped conformation due to the intra-molecular N_3-H···O=C– hydrogen bond bridge.

2.3. Chemicals, solutions and electrochemical setup

The working electrode was a CPE with a surface area of 7 mm^2 (from Metrohm, Herisau, Switzerland), the counter electrode was a platinum wire, and a silver/silver chloride/3 M KCl electrode was used as the reference. The modified carbon paste consists of 5 g graphite powder (spectroscopic grade RBW, from SGL Carbon, Ringsdorff, Germany); 1.0 g modifier (20% with respect to the amount of the graphite powder) and 1.8 mL paraffin oil (Merck, Darmstad, Germany) thorougly mixed with mortar and pestle. The surface of the CPE was renewed after each measurement and then polished with No. 1200 emery paper and wiped gently with weighing paper.

Voltammetric measurements were performed with an Autolab PGSTAT20 (Ecochemie, Utretcht, The Netherlands) potentiostat/galvanostat interfaced with a personal computer, using the Autolab software GPES for waveform generation and data acquisition and processing. The experiments were carried out in a single-compartment three-electrode cell, at room temperature (25 ± 1 °C), under nitrogen atmosphere where was necessary.

For the measurements, 25 μL of Cd(II) stock solutions (1000 mg L^{-1}, prepared by dissolving 0.0500 g of $CdCl_2 \cdot 2H_2O$ from Merck in 50 mL of water) were added to the cell containing 25 mL of Britton-Robinson buffer solution (pH 4) in order to have a Cd(II) concentration of 1 mg L^{-1}. Boric acid, orthophosphoric acid, acetic acid and sodium hydroxide for the Britton-Robinson buffer solution were from Merck. Nanopure water was obtained by passing twice-distilled water through a Milli-Q system (18 MΩ cm, Millipore, Bedford, MA).

2.4. Electrochemical procedure

Differential pulse anodic stripping voltammetry (DPASV) was the electrochemical technique applied for the determination of Cd(II) following a preconcentration step at −1.0 V for 5 min. After equilibration of 5 s DPASV was carried out from −1.0 to −0.5 V. Other instrumental parameters for DPASV were as follows: pulse amplitude +100 mV, pulse repetition time 0.6 s and scan rate 10 mV s^{-1}. Cadmium was preconcentrated with rotation of the CPE at 1500 rpm.

3. Results and discussion

3.1. The structure of the ligands used

From published data we [1] we can generalize that in Series **1** ligands (Fig. 1) the dihedral angles in the CO-NH-CS-NH system are nearly 0° in a *Z,Z* conformation, resulting in a “U”-shaped arrangement with respect to the CO and CS groups. For Series **2** ligands (Fig. 2) the dihedral angles in the system CO-NH-CS-NH are close to 0° in a fixed *E,Z* conformation with CO and CS groups in an “S”-shaped arrangement. An intramolecular hydrogen bond between the available proton on N_3 and the carbonyl group has been previously confirmed [1,25]. This last Series of ligands may be appropriate for complex formation through the S atom because the latter remains practically free of steric impediment from the substituents groups.

Table 1

$CdCl_2$ complexes with Series **1** and **2** ligands: chemical yield and ν(C=S) decrease after complexation

Sample	Synthesis yield (%)	Thioureido band IV (ν(C=S)) (cm^{-1})	ν(C=S) downshift after complexation (cm^{-1})
1a		699	
$CdCl_2$-**1a**	48	693	6
1b		693	
$CdCl_2$-**1b**	39	686	7
1c		710	
$CdCl_2$-**1c**	Not precipitated		
1d		713	
$CdCl_2$-**1d**	Not precipitated		
1e		701	
$CdCl_2$-**1e**	Not precipitated		
1f		709	
$CdCl_2$-**1f**	55	708	1
2b		759	
$CdCl_2$-**2b**	47	750	9
2d		750	
$CdCl_2$-**2d**	71	737	13
2f		743	
$CdCl_2$-**2f**	81	726	17
2g		744	
$CdCl_2$-**2g**	77	728	16
2h		760	
$CdCl_2$-**2h**	95	747	13
2j		796	
$CdCl_2$-**2j**	86	791	5

3.2. Stability of the complex formed

In Table 1 are collected the chemical yield obtained for the complexes and the Raman band values (thioureido band IV) used as sensor for the complex formation. The analysis of Raman spectra was carried out principally to reveal the effect of coordination on the vibrational band of the ligand in the metal complexes in the region of 685–795 cm^{-1}. This is a spectral zone practically free of other bands, where a fundamental with a majority contribution from ν(C=S) motion (band IV) has been assigned. Certainly, the most significant spectral change caused by complex formation is the decrease of the ν(CS) stretching frequency. Although this vibration is also strongly coupled with other modes, our assignment of the band with the highest ν(CS) character is based on the previously IR and Raman study of the ligands [2]. For all the complexes with 1-furoylthioureas 3-monosubstituted examined, there is a clear lowering of this band by about 12 cm^{-1} in average for the Cd(II) complexes. The lowering of wavenumber can be investigated to the reduced double bond character of the C=S bond. In the case of the complexes with the 1-furoylthioureas 3,3-disubstituted the ν(CS) stretching frequency is less affected by coordination by about 6 cm^{-1}. Some of this kind of ligand (**1c**, **1d** and **1e**) did not yield the expected $CdCl_2$ complexes. For the ligand **1f** it was possible to obtain the complex, but the change in the thioureido band IV was not significant. It seems that the complexes with 1-furoylthioureas 3,3-disubstituted are difficult to form for steric reasons (ligands **1c**, **1d**, **1e** and **1f** present at least one aromatic rings as N_3-substutuent) that affect not only the nucleophilic character of the CS group (a weaker M–S interaction) but also the crystallization process. This behavior is consistent with the chemical yield obtained for the $CdCl_2$ complexes of both ligand families. Although the chemical yield obtained during the complex synthesis can be affected for certain ligand features (e.g. steric factor, solubility) it can also be used as indication of the stability of these complexes. Thus, the higher yields were observed for the coordination compounds formed with Series **2** ligands. As already mentioned, for some ligand-$CdCl_2$ mixtures within Series **1** no solid precipitates are obtained, suggesting low stability of the corresponding complexes. From both criteria, the chemical yield and the decrease of the Raman ν(CS) stretching frequency after coordination of the ligand with cadmium chloride, the complexes of higher stability are those formed with ligands from Series **2**.

3.3. Electrochemical studies

In order to ascertain the general characteristics of the 1-furoylthioureas-modified CPE, the electrochemical response of the ligands-modified CPE was examined, after exposure to an aqueous solution of Cd(II) ions. As far as preconcentration analysis is concerned, the rate determining step is most often diffusion on the target analyte to the binding sites located inside the electrode modifier (3-monosubstituted 1-furoylthioureas and 3,3-disubstituted ones) during the accumulation step, and from these sites to the conducting portion of the electrode to undergo charge transfer (detection step), mainly for a reversible process. Hence, high sensitivity and low detection limit would be achieved using an electrode modifier containing a large amount of accessible binding sites, which could be easily reached by the analyte in a short time. Considering the different structure of both Series of ligands and the nature of the N_3-substituent groups (Figs. 1 and 2) in the nearby of the principal nucleophilic center (CS group) variations in terms of sensitivity (different Cd(II) ion uptake) were expected.

The preconcentration of Cd(II) at the modified CPE succeeds with potentiostatic pretreatment. As presented in Table 2, the oxidation of Cd(II) ions occurs at the average electrode potential of −0.77 V. This value shifts for each CPE. The results obtained also implied that different 1-furoylthioureas as CPE modifiers exerted significantly different binding capabilities, since different peak currents of the differential pulse voltammograms were recorded at the same exposure time (Figs. 3 and 4), and the following uptake order was found (PC-**2h** > PC-**2d** > PC-**2f** > PC-**2g** ≈ PC-**1e** ≈ PC-**1d** > PC-**2b** > PC-**2j** > PC-**1c** ≈ PC-**1a** ≈ PC-**1f** ≈ PC-**1b**). The peak currents variations are attributed primarily to the increased amount of Cd(II) preconcentrated at the electrode surface. The 1-furoylthioureas (presumably through the CS group) act as preconcentration sites for metal ions. From the similar shape of curves presented with different final equilibrium currents recorded at the same Cd(II) concentration, the assumption could be made that a similar interaction process was involved in all ligands studied, including the possibility that metal ions were binding only through the C=S group. However, the number (concentration) of available C=S bending sites were different for each CPE and therefore different equilibrium currents were detected. It is assumed that the preconcentration at the

Table 2
Series **1** and Series **2** modified CPEs: observed DPASV peaks for 1 mg L^{-1} of Cd(II)

PC-modified	E_p (V)	I_p (μA)
PC-**1a**	−0.77	0.3
PC-**1b**	No peak	No peak
PC-**1c**	−0.79	0.9
PC-**1d**	−0.77	9.9
PC-**1e**	−0.77	10.2
PC-**1f**	−0.77	0.1
PC-**2b**	−0.79	5.2
PC-**2d**	−0.77	23.0
PC-**2f**	−0.77	15.6
PC-**2g**	−0.76	10.2
PC-**2h**	−0.77	68.8
PC-**2j**	−0.80	3.7

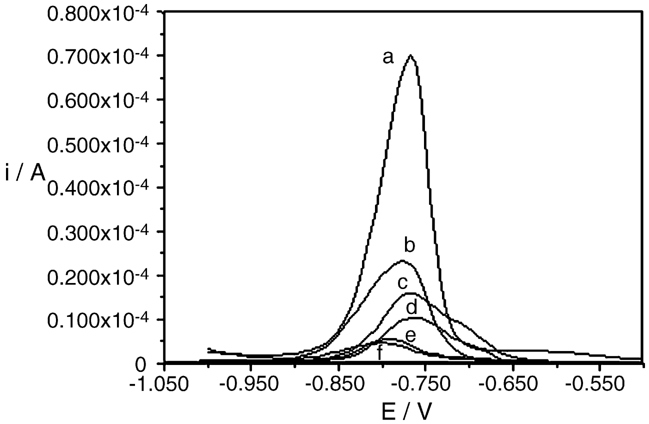


Fig. 3. DPASV of Cd(II) at the CPEs modified with 3-monosubstituted 1-furoylthioureas after 3 min of preconcentration (rotation at 1500 rpm). Supporting electrolyte Britton-Robinson, pH 4.0. Scans from −1.0 to −0.5 V, scan rate 25 mV s^{-1}, pulse amplitude +100 mV, pulse repetition time 0.2 s. (a) PC-**2h**; (b) PC-**2d**; (c) PC-**2f**; (d) PC-**2g**; (e) PC-**2b**; (f) PC-**2j**.

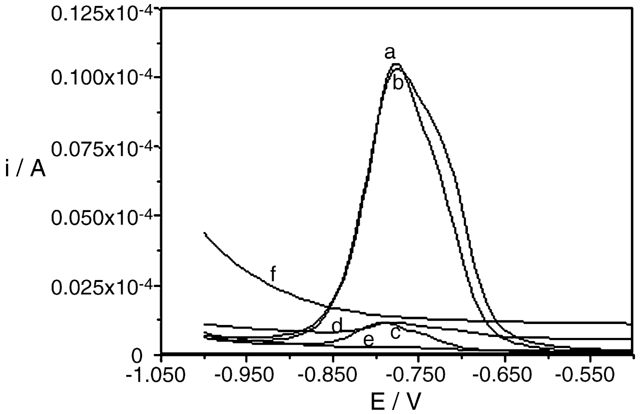


Fig. 4. DPASV of Cd(II) at the CPEs modified with 3,3-disubstituted 1-furoylthioureas after 3 min of preconcentration (rotation at 1500 rpm). Supporting electrolyte Britton-Robinson, pH 4.0. Scans from −1.0 to −0.5 V, scan rate 25 mV s^{-1}, pulse amplitude +100 mV, pulse repetition time 0.2 s. (a) PC-**1e**; (b) PC-**1d**; (c) PC-**1c**; (d) PC-**1a**; (e) PC-**1b**; (f) PC-**1f**.

modified CPE occurs by formation of cadmium complex of the respective ligand. The complex formation occurs probably via a ligand exchange reaction at the electrode surface, a reaction without charge transfer across the electrode/solution interface. Therefore, the elucidation of the reaction mechanism by electrochemical means is difficult. The analytical signal is determined in accordance with metal complex electrochemical properties.

The preconcentration is more effective at the electrodes modified with 1-furoylthioureas 3-monosubstituted (especially compounds **2f**, **2h**, **2g**, **2d**) leading to the most intense voltammetric responses. Although they display a larger double bond character of the C=S (higher frequency values of the Raman ν(CS), see Table 1) with a lower nucleophilic character of the sulphur atom than the 3,3-disubstituted compounds [26], it seems that the steric factor determines the formation and the stability of the complex. The results suggest that the formation of the surface complex (sensitivity) is not favored with the compounds of Series **1** (except compounds **1d** and **1e**) for this reason.

Thus, using the data obtained from differential pulse voltammograms, it is possible to estimate the stability of the Cd(II) ion complex compounds with the 1-furoylthiourea derivatives. This result agrees with those observed in Raman spectra, because the changes in the ν(CS) stretching frequency of the ligand after complexation are more significant (a stronger complex is probably formed) with 1-furoylthioureas 3-monosubstituted. The $\nu(\mathrm{CS})'$ decrease order founded was ($CdCl_2$-**2f** > $CdCl_2$-**2g** > $CdCl_2$-**2h** ≈ $CdCl_2$-**2d** > $CdCl_2$-**2b** > $CdCl_2$-**1b** ≈ $CdCl_2$-**1a** ≈ $CdCl_2$-**2j** > $CdCl_2$-**1f**). Again complexes formed from compounds **2f**, **2h**, **2g** and **2d** exhibit the bigger variation (average of $12\,\mathrm{cm}^{-1}$ in Raman). In Series **2** ligands, compound **2b** shows the worst combined behavior in electrochemical response, band IV diminution and complex yield (as similar as the Series **1** derivatives). It seems that the cyclohexyl group in this compound promotes a strong steric hindrance similar to that present in the 1-furoylthioureas 3,3-disubstituted.

Only the complex formed with **2j** exhibits $\nu(\mathrm{CS})'$ decrease similar to those of the Series **1**. It accords also with the higher chemical yields of the synthesis obtained for the cadmium complexes of the Series **2**′ ligands (see Table 1). Compared with the rest of the Series **2** derivatives, compound **2j** shows a low electrochemical signal and a little downshift of the Raman band IV. In fact, it has the highest frequency value of the band. It seems that the hydrogen bond bridge between N_1 proton and the pyridyl nitrogen [1] leads to a higher electronegativity of N_1 atom that limits the thioamide resonance and favors the retention of a high electron density in the C=S double bond [2].

Although compound **1b** has yield of the complex and downshift of the band IV similar to **1a**, it does not show electrochemical signal. Nevertheless, this may be due not to the complex formation with Cd(II), but only to the physical problems observed in the incorporation of this compound into the carbon paste. Its bad adhesion to the work electrode promotes the loosening of the paste during the measurement process. The aliphatic nature of the substituents in the compounds **1a**, **1b** and **2b** may explain its comparable behavior both in complex yield and the downshift of the Raman band IV. It was not possible to obtain complexes from compounds **1c**, **1d** and **1e** and that is why its electrochemical responses could be not correlated with the Raman spectra. With respect to the electrochemical results, strong and stable complexes from **1d** and **1e** could be obtained. As already mentioned in Section 2.1, the cadmium chloride mixtures with **1c**, **1d** and **1e** ligands did not form precipitate, although the solution turned turbid, suggesting a low stability in the solid state of the corresponding complexes [11]. Such behavior could be attributed to the presence of quite voluminous substituents. Probably, the Cd(II) complexes from **1d** and **1e** stay in solution, because the large N_3'-substituent groups present (ethyl-phenyl and bencyl-phenyl, respectively) hinder the formation of the crystals. Thus, in 3,3-disubstituted compounds the steric interactions in some cases reduce the stability of the complex formed (complexes $CdCl_2$-**1f**, $CdCl_2$-**1b** and $CdCl_2$-**1a**) or hinder the good crystallization of the coordination compounds ($CdCl_2$-**1d** and $CdCl_2$-**1e**). For $CdCl_2$-**1c**, both factors are observed. Such information is very important for the increase in selectivity both at the stage of surface preconcentration and the stage of voltammetric determination of Cd(II) and other heavy metal ions. Thus, the fact that 1-furoylthioureas 3,3-disubstituted apparently form a weaker complex with Cd(II) (although for these compounds chelate formation is more feasible) can be advantageously used to prevent the interference of other metal transition ions with cadmium ions.

3.4. *Electrochemical analysis*

In order to evaluate the use of 1-furoylthioureas carbon paste modified electrodes as electrochemical devices for the analysis of Cd(II), several studies were carried out with a 3-monosubstituted 1-furoylthiourea modified carbon paste electrode, specifically PC-**2d**. Although PC-**2h** gives the higher peak intensity (see Table 2), the signal obtained is asymmetric and near the background discharge; so it is difficult to obtain good peaks for lower Cd(II) concentrations.

3.4.1. *Effect of electrochemical parameters*

Accumulation potentials between −1.2 and −0.9 V were investigated. It was observed that in the interval from −1.2 to −1.0 V the same peak current was obtained for Cd(II); at more positive potentials a decrease in the anodic peak current caused by an inefficient reduction of Cd(II) at the electrode surface was observed. Thus −1.0 V was chosen as the accumulation potential in order to obtain the better peak current and to avoid the reduction of other metals.

With respect to the preconcentration time, the anodic peak current increases with increasing in the preconcentration time between 0 and 350 s; after this value peak current remains nearly constant due saturation of binding sites at electrode surface. Hence a preconcentration time of 300 s was used for subsequent studies, as compromise between sensitivity and analysis time.

The anodic peak current for Cd(II) was also evaluated as a function of scan rate between 6 and $60\,\mathrm{mV\,s}^{-1}$ and pulse amplitude from 25 to 150 mV. The peak current increased and the peak potential shifted toward more anodic values for faster scan rates. A scan rate of $10\,\text{mV}\,\text{s}^{-1}$ was chosen because it showed the better peak definition and a relatively faster analysis. Similar effect was found when pulse amplitude increased, which caused loss of peak definition and more broad peaks (less selectivity of the signals). A pulse amplitude of 100 mV was chosen as a compromise between sensitivity and selectivity. These instrumental parameters are in accordance to literature [22,24].

3.4.2. Calibration graph and influence of other metals

The sensitivity of the method was studied by recording differential pulse anodic stripping voltammograms at different Cd(II) concentrations. The anodic peak current at the carbon paste modified electrode (PC-**2d**) was proportional to the concentration of Cd(II) in the range of $0.005–0.05\,\text{mg}\,\text{L}^{-1}$, with a detection limit of $0.007\,\text{mg}\,\text{L}^{-1}$. The linear regression equation is: $I_{\text{pa}}\ (\text{A}) = 1.52 \times 10^{-8} + 6.5 \times 10^{-5}\ [\text{Cd(II)}](\text{mg}\,\text{L}^{-1})$. From $0.1\,\text{mg}\,\text{L}^{-1}$ a deviation from linearity was observed due to the saturation of the electrode surface. Relative standard deviation values below 5% were obtained for the concentrations tested.

The influence of Hg(II), Zn(II), Pb(II) and Cu(II) on Cd(II) peak current was also evaluated. Hg(II) and Zn(II) cause only negligible effect on the Cd(II) signal; however, the presence of Cu(II) or Pb(II) interfere significantly by suppressing the Cd(II) signal up to 40–50% change in peak current, because they form complexes with the modifier and prevent the complex formation and accumulation of Cd(II) at electrode surface.

4. Conclusions

Comparison of Raman-spectra and electrochemical studies (anodic stripping voltammetry) provides an appropriate procedure for estimating the coordination strength of the Cd(II) complexes with 1-furoylthiourea derivatives, although problems associated with the incorporation of the 1-furoylthiourea derivatives into the carbon paste must be considered. The 1-furoylthioureas 3-monosubstituted (Series **2**) form stronger Cd(II) complexes in ethanol media than the 3,3-disubstituted compounds (Series **1**). Structural features as steric hindering and the nature (aliphatic or aromatic) of the N_3-substituents determine the stability of the complexes.

Acknowledgements

O.E.H. thanks Faculty of Sciences (University of Cadiz, Spain), through its PhD program with Havana University. J.L.H.H. and I.N.R. acknowledge the financial support from Junta de Andalucía, FEDER (Fondo Europeo de Desarrollo Económico y Regional) and the Ministerio de Educación y Ciencia of Spain (Project CTQ2004-03708/BQU).

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