

On the complex formation of CdCl₂ 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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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 CdCl₂, and with the chemical yields of the complexes obtained.

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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 $\nu(\text{C}=\text{S})$ 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), 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 physicochemical 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 CdCl₂ [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-

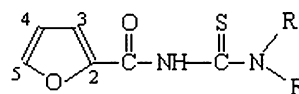
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tioned application [2]. The fact that this family of compounds has been tested, with promising results, as ionophores in ion selective electrodes [1], is the main antecedent for using 1-furoylthioureas as heavy metal complexing modifiers incorporated 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 cadmium 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 CdCl₂

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 CdCl₂ complexes of both Series were labeled as CdCl₂-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



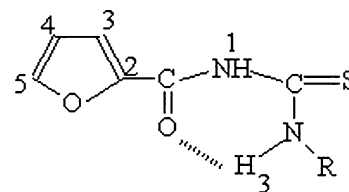
No.	R	R'
1a	-CH ₂ CH ₂ CH ₂ CH ₂ CH ₂ -	(piperidyl)
1b	-CH ₂ CH ₃	-CH ₂ CH ₃
1c	-C ₆ H ₅	-C ₆ H ₅
1d	-C ₆ H ₅	-CH ₂ C ₆ H ₅
1e	-C ₆ H ₅	-CH ₂ CH ₃
1f	-C ₆ H ₅	-CH ₃

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

of the products were collected by filtration, then washed with ethanol and finally dried in air.

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 ₆ H ₁₁
2d	-CH ₂ C ₆ H ₅
2f	-C ₆ H ₅
2g	-(o)C ₆ H ₅ CH ₃
2h	-(o)C ₆ H ₅ NO ₂
2j	-2-C ₅ H ₅ N

Fig. 2. Series 2 ligands. The C=O and C=S groups adopt an “S”-shaped conformation due to the intra-molecular N₃-H···O=C- hydrogen bond bridge.

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