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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Abstract

Two series of 1-furoylthiourea 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 $\nu$(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-