



Article Electrochemical and Spectral Studies on Benzylidenerhodanine for Sensor Development for Heavy Metals in Waters

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Featured Application: Developing new sensing materials.

Abstract: Electrochemical and spectral studies of benzylidenerhodanine (**BR**) were performed in order to develop new sensors for heavy metals (HMs) based on chemically modified electrodes (CMEs). CMEs were obtained by cycling and by controlled potential electrolysis at different potentials and charges. Film formation was demonstrated by recording the CV curves of CMEs in transfer solutions containing ferrocene in 0.1 M TBAP/CH₃CN. **BR**-CMEs were used for the analysis of HMs. Samples of Cd(II), Pb(II), Cu(II), and Hg(II), each possessing concentrations between 10^{-7} and 10^{-5} M, were analyzed by using CMEs prepared in different conditions. The most intense signal was obtained for the Pb(II) ion. These **BR**-CMEs can be used for the analysis of Pb(II) in monitored waters. An electrochemical study was performed at different concentrations of **BR** in 0.1 M TBAP/CH₃CN on a glassy carbon electrode by differential pulse voltammetry, cyclic voltammetry, and rotating disk electrode voltammetry. The complexation ratio in the homogeneous solution has been established by the Mollard method in acetonitrile solutions.

Keywords: benzylidenerhodanine; voltametric methods; chemically modified electrodes; complexation stoichiometric ratio; heavy metal ions; UV-Vis

1. Introduction

Given the heavy metals' (HMs) tendency to accumulate in ecosystems, careful monitoring of their content in waters is required to avoid associated health problems. Monitoring conducted by methods with high sensitivity and accuracy is desirable, in addition to online and on-site monitoring. Electrochemical sensors are an alternative that can meet all these requirements. They can be included in portable devices that allow continuous on-site tracking of HMs. Compared to classical spectroscopic and optical techniques, electrochemical sensors based on chemically modified electrodes (CMEs) have fast responses and high sensitivities [1]. The design of new structures based on complexing ligands for HMs is a current challenge for the development of new CMEs for new analytical methods.

The goal of this study is to characterize and investigate the electrochemical behavior of 5-benzylidene-2-sulfanylidene-1,3-thiazolidin-4-one (benzylidenerhodanine, **BR**) for the preparation of new CMEs, which are useful for the analysis of HMs.

BR (Figure 1) is a derivative of rhodanine (**R**), a five-membered heterocyclic organic compound possessing a thiazolidine ring (Figure 1). The rhodanines are derivatives of rhodanine with aryl and alkyl substituents in positions 3 and 5. They have complexing



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Copyright: © 2022 by the authors. Licensee MDPI, Basel, Switzerland. This article is an open access article distributed under the terms and conditions of the Creative Commons Attribution (CC BY) license (https:// creativecommons.org/licenses/by/ 4.0/). properties with respect to HMs due to the heteroatoms involved in their electronic structure. These compounds are important for the production of drugs for the treatment of diabetes and cancer [2,3]. Some rhodanine derivatives have antimicrobial properties [4–6]. Rhodanine derivatives can be used as pan-assay interference compounds for biological samples [7–9], for water treatment in efficient removal of HMs cations [10], and as fluorescence sensors for organic compounds [11] or HMs (Fe [12], Hg [13–15], and Cu [13]; Ag [15,16], Zn [17], and Cd [17] targets). There are no reported electrochemical sensors based on CMEs by using rhodanine derivatives for the detection of HMs.



Figure 1. Structures of rhodanine R and BR.

Rhodanine derivatives act as efficient organic corrosion inhibitors because they possess high electron density heteroatoms such as sulfur, nitrogen, or multiple bonds acting as adsorption centers [18]. They form polymeric protective films against corrosion and are involved both in physical or chemical adsorption, reducing the corrosive attack in the case of mild steel [19,20] or copper [21–23], and they can be used in the construction of photovoltaic cells [24–26].

As mentioned above, the polymerization of rhodanine and its derivatives intended for various industrial applications has already been reported [18–23]. Polyrhodanine films have been obtained by electrochemical oxidation of rhodanine solutions in water [27,28] or organic media [29]. Newly synthesized homogeneous polyrhodanine films proved to have good properties such as high thermal stability and suitable solubility in common organic solvents, indicating their potential utilization as polymeric films to be applied on metal surfaces [27]. In this work, it is shown that such films had the potential to be used for complexing electrochemical sensors based on CMEs. Taking into account the confirmed complexing properties of rhodanine moiety [29,30], the ligands based on benzylidenerhodanine are good candidates to serve as HM sensors for the analysis of HM content in waters.

2. Materials and Methods

Benzylidenerhodanine (BR) from ALFA AESER (98%) and acetonitrile (CH₃CN) and tetrabutylammonium perchlorate (TBAP) from FLUKA were used as received. Mercury (II) acetate (Fluka, Munich, Germany, \geq 98%), copper (II) acetate monohydrate (Fluka, Munich, Germany, \geq 98%), lead (II) nitrate (Fluka, Munich, Germany, \geq 98%), and cadmium nitrate tetrahydrate (Fluka, Munich, Germany, \geq 98%) were used as received to prepare the synthetic stock solutions (10⁻³ M) of heavy metal (HM) ions. HM solutions with different concentrations were prepared by successive dilution.

Electrochemical experiments were carried out on PGSTAT302N AUTOLAB potentiostat coupled to a three-compartment cell. The working electrode was a glassy carbon (GC) disk (3 mm in diameter, from Metrohm, Herisau, Switzerland). Before each experiment, its surface was polished with diamond paste (0.25 μ m) and cleaned with CH₃CN. The reference electrode was Ag/10 mM AgNO₃ in 0.1 M TBAP, CH₃CN. At the end of the experiments, the potentials were referred to the ferrocene/ferricinium redox couple (Fc/Fc+) potential. The auxiliary electrode was a platinum wire. The experiments were performed at 25 °C under an argon atmosphere.

The cyclic voltammetry (CV) curves were recorded at 0.05-0.5 V/s scan rates. The differential pulse voltammetry (DPV) curves were recorded at 0.01 V/s with a pulse height of 0.025 V and a step time of 0.2 s. The rotating disk electrode voltammetry (RDE) experiments were performed at 0.01 V/s with rotation rates between 500 and 1500 rpm.

Chemically modified electrodes (CMEs) were prepared from millimolar solutions of BR in 0.1 M TBAP/CH₃CN by scanning or controlled potential electrolysis (CPE). Then, each modified electrode (BR-CME) was washed with acetonitrile and introduced in a 0.1 M acetate buffer solution (pH = 4.5) where it was equilibrated and overoxidized as previously described [31,32]. The resultant electrodes were immersed for 10–15 min under stirring in synthetic solutions of HMs ions. After that, the electrodes were taken out and cleaned with deionized water; then, they were immersed in a cell containing 0.1 M acetate buffer solution (pH = 4.5). Here, they were polarized for 3 min at -1.0 V, and then their DPV curves were recorded between -1.0 and +0.6 V.

The study by UV–Vis spectrometry was performed on JASCO V-670 in 1 cm pathlength quartz cuvettes in freshly dried acetonitrile. Aliquots of heavy metal solutions were added to the R solution, and UV–Vis spectra were recorded between 800 and 200 nm one minute after each addition.

3. Results

3.1. Electrochemical Study

The electrochemical behavior of **BR** was examined in solutions of 0.1 M TBAP, CH_3CN , with millimolar concentrations by using electrochemistry methods. Oxidation and reduction curves were recorded starting from the equilibrium potential. The curves recorded in the supporting electrolyte ([**BR**] = 0 mM) were plotted with a dashed line. Anodic and cathodic peaks are denoted in the order in which they appear in the voltammograms. To compare the current's values for anodic and cathodic processes, cathodic CV currents are shown in absolute values.

3.1.1. CV and DPV

The characterization of **BR** was performed by CV at different concentrations of **BR** (Figure 2), different scan rates (Figure 3), and different scan domains (Figure 4). CV curves are shown in parallel with those obtained by DPV to compare their peak potentials (Table 1).



Figure 2. DPV (0.01 V/s) and CV (0.1 V/s) curves (with currents in absolute values) on glassy carbon for **BR** in 0.1 M TBAP/CH₃CN at different concentrations (mM): 0 (dotted blue line), 0.5 (magenta line), 1 (wine line), 2 (olive line), and 5 (red line) M; insets: dependences of peak currents vs. **BR** concentration (c).



Figure 3. Anodic and cathodic voltammograms at different scan rates for [BR] = 1 mM(A); linear dependences of the currents from (a1) and (c1) processes at 1.15 V and -1.65 V, respectively, on the square root of the scan rate (**B**).



Figure 4. Anodic and cathodic CV (0.1 V/s) curves for **BR** (1 mM) in 0.1M TBAP/CH₃CN on different scan domains.

Table 1. Potentials (V vs. Fc/Fc+) of the peaks for anodic (a) and cathodic (c) processes from CV and DPV curves and the half-wave potential ($E_{1/2}$) values from RDE for **BR** (2 mM), and the characteristics of the peaks.

Peak		Process			
	CV	DPV	RDE (E _{1/2})	Characteristics	
a1	0.715	0.681	-	irreversible	
a2	0.897-	0.811	-	irreversible	
a3	1.43	1.384	-	quasireversible	
a4	1.95	1.64	-	irreversible	
	-1.176	-1.132			
c1	-1.534	-1.522	−1.522 (1500 rpm)	irreversible	
c2	-1.802	-1.843	-	irreversible	
c3	-2.267	-2.102	-	reversible	
c4	-2.457	-2.294	_	irreversible	
c5	-2.904	-2.83	-2.652 (1500 rpm)	quasireversible	

3.1.2. RDE

Figure 5 illustrates the RDE curves obtained at different **BR** concentrations at a 1500 rpm rotation rate and the RDE curves that resulted for the concentration of 2 mM at various rotation rates of the electrode.



Figure 5. DPV (**A**), RDE curves at 1500 rpm (**B**) at different concentrations (mM) in 0.1 M TBAP/CH₃CN, and RDE curves (**C**) on glassy carbon at different rotation rates (rpm) for [BR] = 2 mM in 0.1M TBAP/CH₃CN; the cathodic currents are in absolute values.

3.2. Evidence for BR Films

The electrochemical immobilization of **BR** on the GC electrode has been achieved in millimolar solutions of **BR** in 0.1 M TBAP/CH₃CN either by scanning or by CPE at potentials in the region of **BR** anodic processes (as shown in previous papers [31,32]). After preparation, the modified electrodes were cleaned with acetonitrile and transferred into ferrocene solutions in 0.1 M TBAP/CH₃CN to check the film's formation by an ferrocene redox test probe. For recognition experiments using poly **BR** films, CMEs were prepared by using the CPE method as it ensures the control of potential and charge during electropolymerization and leads to reproducible CMEs, which are compulsory for HMs analysis.

3.2.1. BR Films by Scanning

Figure 6 presents the evolution of CV curves during successive scans in the domain of a2 and a3 processes, respectively. The comparative recorded CV curves in Fc solution on the obtained modified electrodes and on a bare electrode (Figure 6) suggested the formation of thin films.

3.2.2. Film Formation by CPE

Electrochemical immobilization of **BR** on the GC electrode has also been carried out by CPE in **BR** solutions at different concentrations (in 0.1 M TBAP/CH₃CN), potentials, and charges (Figure 7). The corresponding chronoamperograms are provided in Figure 7. The modified electrodes obtained by CPE, transferred in the ferrocene solution, possess the CV curves shown in Figure 8.



Figure 6. Ten successive CV cycles (0.1 V/s) in 2 mM solution of **BR** in 0.1 M TBAP/CH₃CN performed with different anodic limit scan potentials (V) that were increasing in the following order: (**A**) < (**B**) < (**C**) < (**D**) < (**E**). The curves in ferrocene solution (1 mM in 0.1 M TBAP/CH₃CN) of the corresponding CMEs with respect to those on the bare electrode (dashed lines).



Figure 7. Chronoamperograms during the preparation of **BR**-CMEs in 1 mM solution of **BR** in 0.1 M TBAP, CH₃CN, by CPE at different potentials and charges.



Figure 8. CV curves (0.1 V/s) after the transfer of **BR**-CMEs in ferrocene solution (1 mM) in 0.1 M TBAP/CH₃CN vs. bare electrode.

3.3. HMs Recognition Experiments Using PolyBR Films

For HM ions recognition, **BR**-CMEs were obtained by CPE in 2 mM solution of **BR** in 0.1 M TBAP/CH₃CN in various conditions (Figures 9–12). The CMEs were conditioned similarly to other experiments [31,32], and then the influence of several parameters (HMs accumulation time, potential, and charge in CPE) on DPV response was examined. After preparation and cleaning with acetonitrile, the modified electrodes were immersed in an

acetate buffer (0.1 M) at pH 4.5 and cycled for equilibration and overoxidation. Next, they were introduced in synthetic aqueous solutions containing a mix of HMs ions under magnetic stirring for 10 min; after that, they were introduced in an acetate buffer (pH 4.5) and polarized at -1.0 V (3 min) and, finally, linearly swept in anodic scans using DPV. Figure 9 shows the DPV curves obtained on CMEs prepared at different potentials. DPV stripping peak currents were recorded for each investigated ion vs. the HM ion concentration (c) in accumulation solutions (Figure 9 inset). Figure 10 shows the DPV curves recorded on CMEs obtained at different charges at the same potential. The DPV stripping peak currents, corresponding to Figure 10, recorded for Cd and Pb vs. HM ion concentration (c) in accumulation solutions are shown in the inset of Figure 10.



Figure 9. DPV curves (0.01 V s^{-1}) recorded on poly**BR**-modified electrodes prepared by CPE at 1.5 mC and different potentials, 1.1 V (blue), 1.4 V (red), and 1.6 V (olive), corresponding to 10^{-6} M concentration of each mixed metal; inset: DPV peak currents dependence on potential.



Figure 10. DPV curves (0.01 V s^{-1}) recorded on poly**BR**-modified electrodes, prepared by CPE at 1.4 V and different charges, 0.5 mC (blue), 1 mC (red), and 1.5 mC (olive), for 10^{-6} M concentration of mixed metals; inset: DPV peak currents dependence on charge.



Figure 11. DPV curves (0.01 V s^{-1}) recorded on poly**BR**-modified electrodes, prepared by CPE at 1.4 V, 1.5 mC, and 10^{-6} M concentrations of mixed metals with different accumulation times; inset: DPV peak currents dependence on accumulation time.



Figure 12. DPV curves (0.01 V s^{-1}) recorded on **BR**-modified electrodes (obtained by CPE at 1.4 V and 1.5 mC) for different concentrations of mixed metals at 10 min accumulation times; insets: dependence of the ions' stripping peaks currents (**I1**) or areas (**I2**) from DPV on the metallic ion's concentrations (c).

3.3.1. Influence of HMs Accumulation Time on DPV Response

Larger accumulation times correpond to larger responses, as anticipated. Figure 11 shows a significant increase (over 10 times) in the signal for Pb when the accumulation time increased from 10 to 15 min.

3.3.2. Influence of HMs Ions Concentrations on DPV Response

BR-CMEs have been obtained and studied in various accumulation solutions containing HMs with concentrations ranging from 5×10^{-7} M to 10^{-4} M (Figure 12). The I1 inset of Figure 12 is the DPV plot of Cd(II), Pb(II), Cu(II), and Hg(II) stripping currents on the concentration of HMs in accumulation solutions (c) on **BR**-CMEs, expressed through the calculated Δi peak (between the peak current and the background current). The I2 inset of Figure 12 is the DPV plot of the same ions stripping currents areas on **BR**-CMEs calculated as the area (A) of the DPV peaks (versus the background current).

3.4. Study by UV-Vis

Figure 13A shows the UV-Vis curves of **BR** in CH_3CN solutions, and Figure 13B shows the linear variations of absorbance at 374 nm wavelength as a function of **BR** concentration.



Figure 13. (A)—UV-Vis spectra obtained for different concentrations of **BR** and (**B**)—dependence of absorbances on **BR** concentration ([**BR**]).

Influence of Pb Concentration on UV-Vis Spectra

Figure 14 illustrates the UV-Vis spectra during the addition of Pb(II) aliquots to a solution (5.7 μ M) of **BR** in acetonitrile. S1 and S2 insets of Figure 14 show the evolution of the peak's absorbance at 374 nm vs. [Pb]/[**BR**] and vs. [Pb]/([Pb]+ [**BR**]), respectively.



Figure 14. UV-Vis spectra at t = 1 min for different [Pb]/[**BR**] ratios; insets: variation of the absorbance for the peak at 374 nm vs. [Pb]/[**BR**] (**S1** inset) and vs. [Pb]/([Pb]+ [**BR**]) (**S2** inset).

4. Discussion

CV and DPV oxidation and reduction curves recorded at different concentrations of **BR** show DPV and CV currents for anodic and cathodic peaks that increase with the concentration of **BR** (at low concentrations the dependences are linear, as shown in their insets). The oxidation and reduction processes that occur during potential scans were denoted according to DPV peaks. The results show that peaks a1–a4 and c1–c5 are related to electron transfers to **BR**. The characteristic peak of oxygen reduction at the anion radical (O_2/O_2^-) appears in the cathodic CV scans, at about -1.2 V, due to the traces of water in the solvent. However, this peak was reduced as intensity because the experiments took place under argon overpressure.

CV curves at different scan rates (Figure 3) and domains (Figure 4) allowed the estimation of the reversibility degree of the processes highlighted during anodic or cathodic scans (Table 2). Additional information was obtained from RDE curves at different concentrations and electrode rotation rates (Figure 5). Figure 4 shows that c1, c2, and c4 peaks are irreversible (no response peaks in the return sweeps). Cathodic peak c5 is quasireversible. Almost all processes in the anodic domain are irreversible. Only a3 had a small response in the return sweep, and it was mentioned as quasireversible in Table 2. Due to the complexity of functional groups and heteroatoms from the **BR** cycle, it was difficult to attribute the reactions for each of the peaks.

Table 2. Potentials of Fc/Fc⁺ anodic (E_{pa}) and cathodic (E_{pc}) peaks in 1 mM Fc solution in 0.1 M TBAP/CH₃CN for the bare electrode and modified electrodes prepared by 10 successive cycles on different anodic potential domains in solution with [**BR**] = 2 mM.

CV Scan Potentials (V)	E _{pa} vs. Fc/Fc ⁺ (V)	E _{pc} vs. Fc/Fc ⁺ (V)	$\Delta Ep = E_{pa} - E_{pc}$ vs. Fc/Fc ⁺ (mV)	$Ef = (E_{pa} + E_{pc})/2$ vs. Fc/Fc ⁺ (mV)
Bare electrode	0.051	-0.049	100	1
0-0.8	0.041	-0.050	91	-5
0-1.1	0.051	-0.04	91	6
0-1.4	0.041	-0.048	89	-3
0-1.6	0.052	-0.04	91	6
0–2.0	0.051	-0.05	101	1

It can be observed that the occurrence of the linear relationship of the peak currents versus the square root of the scan rate when analyzing the CV curves resulted in scan rates between 0.05 and 0.5 V/s (Figure 3B) on the potential domains of a1 and c1. These variations on the scan rate show absolute slopes of 7.868×10^{-5} and 5.871×10^{-5} A \cdot V^{-1/2} \cdot s^{1/2} for a1 and c1 peaks, respectively. From the obtained slopes, a ratio of 3:2 between the number of electrons participating in the first oxidation/reduction mechanism can be estimated.

The RDE curves obtained at different **BR** concentrations and the RDE curves that resulted in various rotation rates of the electrode (Figure 5) illustrate the high degree of asymmetry between oxidation and reduction processes. Reduction processes reveal a rise in RDE currents with the concentration and rotation rate of the electrode. Cathodic RDE curves have normal behavior, while anodic ones have small currents only for processes a1–a2; for processes developed at more positive potentials the currents are close to those for the supporting electrolyte. The shape of anodic curves is in agreement with the formation of films by electrooxidation at potentials higher than 1.2 V.

4.1. Evidence for BR Films Formation

The electrochemical immobilization of **BR** on the GC electrode has been accomplished either by scanning or by CPE as gray films on the surface. After preparation, the modified electrodes were transferred into ferrocene solutions to check the films' formation.

The formation of **BR** by scanning showed that the ferrocene signals on modified electrodes prepared by successive cycling are slightly shifted as anodic and cathodic peak potentials, but the peak currents remain practically constant. The study of the Fc/Fc+ system (Table 3) reveals a constant formal potential (Ef ~ 0 mV) and a peak-to-peak separation similar to the bare electrode (Δ Ep = E_{pa} - E_{pc}), indicating the formation of thin films. When the film formation of **BR** was carried out by CPE, reproducible CMEs based on **BR** (denoted **BR**-CMEs) were obtained. Their transfer in ferrocene solutions revealed CV curves with small changes in comparison with that recorded on the bare electrode. This fact indicates also the formation of thin films, as in the case of preparation by scanning.

E _{EPC} (V); q (mC)	Epa vs. Fc/Fc ⁺ (V)	Epc vs. Fc/Fc ⁺ (V)	$\Delta Ep = E_{pa} - E_{pc}$ vs. Fc/Fc ⁺ (mV)	$Ef = (E_{pa} + E_{pc})/2$ vs. Fc/Fc ⁺ (mV)	
Bare electrode	0.046	-0.045	91	1	
0.8; 0.2	0.045	-0.046	91	-1	
1.1; 0.5	0.056	-0.035	91	10	
1.4; 0.5	0.046	-0.043	89	1	
1.6; 0.5	0.056	-0.035	91	10	
2.0; 0.5	0.047	-0.043	90	2	

Table 3. Potentials of Fc/Fc+ anodic (E_{pa}) and cathodic (E_{pc}) peaks in 1 mM Fc solution in 0.1 M TBAP/CH₃CN for bare electrode and modified electrodes prepared by CPE at different anodic potentials (E_{EPC}) and charges (q) in solution with [**BR**] = 2 mM.

4.2. HMs Analysis Experiments Using BR Films

BR-CMEs obtained by CPE have been used for HM ions analyses. The DPV curves (Figures 9–12) show stripping peaks for all studied ions, suggesting that these ions have been complexed in the electrogenerated films (which ensure the immobilization of **BR** complexing units). Peaks for Cd, Pb, Cu, and Hg dissolution were observed at the potentials of -0.796, -0.548, -0.098, and 0.269 V, respectively, for CMEs obtained at 1.4 V and 1.5 mC. These values are slightly different from those obtained in similar conditions of preparation for rhodanine-modified electrodes, **R**-CMEs, which are as follows: -0.766, -0.547, -0.118, and +0.269 V, respectively [13]. The difference between the potentials on **BR**-CMEs and **R**-CMEs shows that the change of the ligand by the introduction of a phenyl group selectively influences the complexation ability of CMEs (the signals potentials for the investigated ions). This influence is strong enough for Cd and Cu. No influence occurs in the case of Pb and Hg.

From the tested potentials for CPE (1.1 V; 1.4 V; and 1.6 V) corresponding to the processes highlighted by the DPV and CV curves a1 and a2–a3 (Figure 9), the potential value of 1.4 V corresponds to an optimal response for Pb(II). This potential was further maintained for the synthesis of **BR**-CMEs during the process to optimize the preparation conditions of these CMEs. The increase in polymerization charge from 0.5 to 1 mC resulted in a two-times increase in Pb(II) response (Figure 10). A further increase to 1.5 mC did not add another significant increase. The peaks for all ions are influenced by the electropolymerization charge, which is connected to the film's thickness. Figure 10 inset curves show a selective complexation for Pb (which has the highest signal) and a specific influence in the electropolymerization charge in case of Pb analysis (the DPV peaks increase with charge) and Cd (the DPV peaks decrease with charge).

Other parameters connected to the conditioning of the modified electrodes have influence on HM analyses. Larger accumulation times result in larger responses, as anticipated. Figure 11 shows a significant increase (over 10 times) in the signal for Pb when the accumulation time increased from 10 to 15 min for **BR**-CMEs prepared by using a charge of 1.5 mC. This is accompanied by an increase in selectivity in the analysis of Pb(II) compared to Cd(II) and Hg(II).

To obtain the calibration curves on **BR**-CMEs plots of Cd(II), Pb(II), Cu(II), and Hg(II), stripping currents on [**BR**] have been performed for various accumulation solutions containing HMs (with concentrations ranging from 5×10^{-7} M to 10^{-4} M). Their stripping peaks are shown in Figure 12 insets, as the difference between the peak current and the background current (Δ i peak) in I1 inset of Figure 12 and the calculated area (*A*) of the DPV peak (versus the background current) in I2 inset, respectively. All plots indicate the greatest sensitivity of **BR**-CMEs for Pb(II) among the other complexed ions such as Cd(II), Cu(II), and Hg(II)).

The complexation of Pb(II) ions with **BR** was also studied in solution, taking into account that the signal obtained for Pb(II)'s detection by using **BR**-CMEs is much higher than that for the other investigated HMs ions, following the changes of the UV-Vis spectrum of **BR** (Figure 13). Complexation was a fast process (the spectra recorded during a 15 min

interval were not changed), and the time of 1 min after addition was respected. The UV-Vis spectra during the addition of Pb(II) aliquots to a solution (5.7 μ M) of **BR** in acetonitrile show two isosbestic points (at 387 nm and 348 nm) and a continuous decrease in UV peaks (marked with red arrows in Figure 14).

4.3. Calculation of Pb:BR Stoichiometric Ratio for the Complex in Solution

Two methods were employed to deduce the stoichiometry of the complex formed between **BR** and Pb(II) in solution by taking into consideration the absorbance–concentration data of Pb(II) as follows: (i) the variation of the maximum peak absorbance with the molar ratio [Pb]/[**BR**] (Figure 14 inset S1) and (ii) the variation of the maximum peak absorbance as a function of the molar fraction of Pb(II) (Figure 14 inset S2). Both models have resulted in consistent results (Table 4). A molar ratio (r) of 2 between [**BR**]/[Pb(II)] was obtained, suggesting that the complex's stoichiometry is Pb **BR**₂.

Table 4. Ratios r/m for $(Pb)_m(BR)_r$ according to the Mollard method for absorbance (A).

Crt. Nr.	Excess of Pb		Excess of Ligand			r/m	m	R	Complex	
	[Pb]/[R]	[R], μM	Α	[Pb]/[R]	[Pb], µM	Α	- 1/111		ĸ	Formula
1.	3/1	5.692	0.341	0.5/1	2.887	0.346	2.001	1	2.001	PbBR ₂
2.	2.5/1	5.708	0.337	0.5/1	2.887	0.346	2.03	1	2.03	PbBR ₂
3.	2/1	5.724	0.336	0.5/1	2.887	0.346	2.041	1	2.041	PbBR ₂
4.	1.8/1	5.731	0.333	0.5/1	2.887	0.346	2.063	1	2.063	PbBR ₂
5.	1.5/1	5.741	0.327	0.5/1	2.887	0.346	2.1	1	2.1	PbBR ₂

5. Conclusions

The characterization of benzylidenerhodanine by electrochemical (cyclic voltammetry, differential pulse voltammetry, and rotating disk electrode voltammetry) and UV-Vis methods showed taht this compound has potentiality to build electrochemical sensors for the analysis of HMs by using CMEs based on this ligand. Our study relates the main parameters that can be optimized (potential and charge for films formation, accumulation time) for subsequent applications, such as developing new sensing materials based on CMEs for HMs analysis in water.

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