

Electrochemical Behavior of Copper(II) salen in Aqueous Phosphate Buffer at the Mercury Electrode

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The electrochemical behavior of copper(II) complexed with the Schiff base N,N'-ethylenebis(salicylideneimine) in aqueous phosphate (pH 7.0) was studied by polarographic and voltammetric techniques (DC, DPP, DPV, CV, and SWV) at a mercury electrode. The resulting polarograms and voltammograms consist of a single quasi-reversible one-electron transfer attributable to the coupling of Cu(II)salen/Cu(I) salen via an EC mechanism. In differential pulse adsorptive stripping voltammetry (DPV) the response of the Cu(II) salen complex is linear over the concentration range 0 to 3.2×10^{-7} mol.L⁻¹. For an accumulation time of 30 seconds, the detection limit was found to be 1.0×10^{-8} mol L⁻¹. Square-wave (SWV) and cyclic voltammetric (CV) measurements indicated that the Cu(II)-salen complex and its reduction product adsorb at the electrode surface.

Keywords: Schiff base, copper, salen, polarography and voltammetry

1. INTRODUCTION

Salen is a Schiff base derived from the condensation of salicylaldehyde and ethylenediamine. It is a symmetrical molecule and exhibits chiral properties. Schiff bases are frequently studied due to their biological activity [1-3], as well as their optical [4,5], catalytic [6,7] chromophoric [8], thermochromic [9] and photochromic [10] properties. The structure of its metal complexes is represented in Figure 1.

Analytical determinations of metallic ions have been performed by using Schiff bases. Salen impregnated with ion-exchange resins were used for the determination of Cu(II), Co(II) and Ni(II) [11]. Also, Ga(III) and Fe(III) were quantitatively determined after the solvent extraction of their salen complexes [12]. In addition, several other works involving the use of metallic ions –Schiff base complexes have been described [13-23].

Electrochemical techniques using Schiff bases ligands also have been widely used for the determination of low concentrations of organic and inorganic compounds in a number of different matrices. Several authors have studied the electrochemical behavior of salen-type complexes of transition metals and some of their applications mainly in different organic media [24-28]. Transition metal complexes with tetradentate Schiff bases ligands have been extensively used as catalysts for organic reactions [29] and to mimetic enzymatic reactions [30]. Pasini et al. [31] studied the oxidation of copper complexes of quadridentate Schiff bases derived from salicylaldehyde. Losada et al. [32] studied the electrochemical and spectroelectrochemical properties of the Cu(II) salen complex in acetonitrile. Zolezzi et al. [33] studied the electrochemical reduction of Cu(II) complexes with salen Schiff base ligands by cyclic voltammetry using dimethyl sulfoxide as a solvent and vitreous carbon electrode. Bedioui [34] and Audebert [35,36] independently studied the electrooxidative polymerization of some metal-salen complexes. Peters et al. [37,38] found that Ni(II) salen may anodically form polymeric films at the surface of electrodes other than mercury; and investigated the electrochemical reduction of Cu(II) salen at carbon cathodes in dimethylformamide. Ding et al. [39] reported the electrochemical study of Schiff bases, mainly of the salen type and some metal complexes, by the formation of self-assembled monolayers.

The complexes of copper with salen-type ligands appear to be promising ones, especially in view of the role played by copper in some aqueous biochemical processes [40,41,42]. Salen complexes have proved to be efficient in the cleavage of DNA, antimicrobial activity and interaction bovine serum albumin [43-50].

The present study describes some characteristics and quantitative utility of the redox reaction of the Cu(II) salen complex in an aqueous phosphate buffer using DC, DPP, DPV, CV, and SWV at the mercury electrode. Preliminary results indicated that Cu(II) salen and the product of its reduction adsorb at the electrode surface with a one-electron reduction reaction through an EC mechanism.

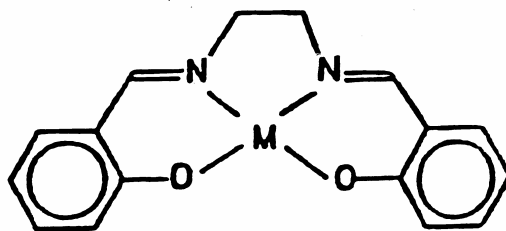


Figure 1. Molecular structure of metal-salen complexes.

2. EXPERIMENTAL PART

2.1. Apparatus

DC and DP polarograms, as well as differential pulse stripping voltammograms were obtained with an EG&G Princeton Applied Research Corp. (PAR) Model 264A analyzer. The working

electrodes were a EG&G PAR Model 303A dropping mercury electrode (DME) for the DC polarography experiments and a hanging mercury drop electrode (HMDE) with medium size (0.016 cm^2) for the differential pulse stripping and linear voltammetric techniques. Stair-case cyclic and square-wave stripping voltammetric measurements were performed with a BAS CV-50W voltammetric analyzer with a Controlled Growing Mercury Electrode (CGME) in the static mode. A computer system was used for the collection of experimental data. For all experiments, the sample cells were fitted with a Ag/AgCl (3M KCl) reference electrode and a platinum wire auxiliary electrode. A magnetic stirrer and stirring bar provided the convective transport during the preconcentration step for the stripping techniques.

2.2. Chemicals and Solutions

Milli-Q (Millipore) was used in all dilutions and sample preparations. All chemicals were of analytical reagent grade. A 0.4 mol.L^{-1} stock solution of copper(II) (Merck) was prepared in water and a $4.0 \times 10^{-2} \text{ mol.L}^{-1}$ solution of salen (Sigma) was prepared in dimethylformamide (Merck). The complex was prepared by mixing equimolar solutions of salen and copper acetate in ethyl alcohol. The precipitated complex was removed by filtration, washed with alcohol and placed in a desiccator containing P_2O_5 . Elemental analysis gave 58.36% C, 4.26% H, 8.52% N and 9.71% O. The copper was determined by atomic absorption spectroscopy and gave an equivalent quantity of 9.15% Cu. Ion-spray spectrometry and IR spectra confirmed these results. The stock solution of Cu(II) salen was prepared by dissolving the complex in dimethylformamide (Merck) to a concentration of 0.01 mol.L^{-1} . The stock solution of a 0.2 mol.L^{-1} phosphate buffer was prepared by dissolving a suitable quantity of reagent KH_2PO_4 (Sigma) in water, followed by the addition of 0.2 mol.L^{-1} NaOH solution to achieve pH 7.0.

2.3. Procedure

A known volume (10 mL) of the supporting electrolyte solution (0.2 mol.L^{-1} phosphate buffer (pH 7.0)) containing Cu(II) salen was added to the voltammetric cell and deaerated with nitrogen for 8 minutes (and again for 30 seconds before each cycle). The initial potential (usually -0.2 V to differential pulse and $+0.1 \text{ V}$ to square-wave stripping) was applied to the electrode during a selected time (usually 30 seconds), while the solution was slowly stirred. The stirring was then stopped, and after 30 seconds under rest the voltammogram was recorded by applying a negative-going potential scan. The scan was terminated at -1.3 V (square-wave), and the stripping cycle was repeated with a new mercury drop. The entire procedure was automated, as controlled by Stripping Analyzer. Throughout this operation, nitrogen was passed over the solution surface. The cyclic voltammograms were scanned (50 mV.s^{-1}) in the potential range of -0.0 V to -1.4 V . For DC polarographic measurements the scan rate used was 10 mV.s^{-1} and for DPP the pulse amplitude was -25 mV . All data were obtained at ambient temperature.

3. RESULTS AND DISCUSSION

The electrochemical reduction of $\text{UO}_2(\text{II})$ salen in buffered aqueous solution of HEPES or phosphate at hanging mercury drop electrode (HMDE) was studied in our laboratory[51,57]. In connection with such studies, the present work reports an electrochemical behavior of copper(II) complexed with the Schiff base N,N' -ethylenebis(salicylideneimine), $\text{Cu}(\text{II})$ salen, in aqueous phosphate medium. The free Schiff base salen hydrolyzes in aqueous media but stabilizes after complexation with copper(II). The characterization and electrochemical studies of $\text{Cu}(\text{II})$ -salen in the present work were performed in a 0.02 mol.L^{-1} phosphate buffer at pH 7.0. The characterization was performed by mass spectrometry [51] and the electrochemical studies were realized using different polarographic and voltammetric techniques (DC, DPP, DPV, CV, and SWV). The resulting polarograms and voltammograms obtained consist of a single quasi-reversible one-electron transfer attributable to the coupling of $\text{Cu}(\text{II})$ salen/ $\text{Cu}(\text{I})$ salen via an EC mechanism.

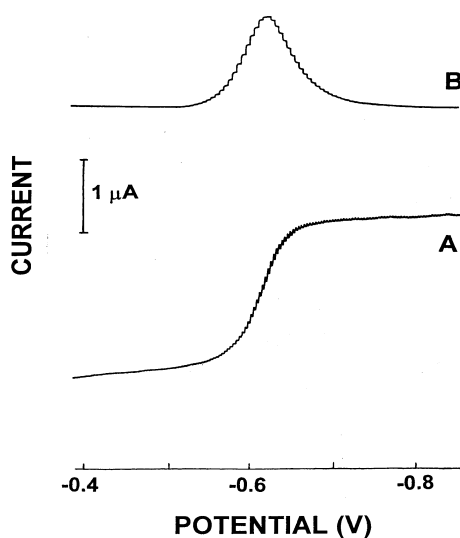


Figure 2. DC (A) and DP (B) polarograms for $1.00 \times 10^{-5} \text{ mol L}^{-1}$ $\text{Cu}(\text{II})$ salen complex. Supporting electrolyte, 0.2 mol.L^{-1} phosphate buffer (pH 7.0). $E_{\text{initial}} = -0.20 \text{ V}$ and $E_{\text{final}} = -1.00 \text{ V}$. Scan rate, 10 (A) and 5 mV s^{-1} (B). Pulse height, 25 mV (B).

3.1. Polarography (DC and DPP)

The DC polarographic wave of $\text{Cu}(\text{II})$ salen complex is illustrated in Figure 2A. The log-plot (E versus $\log [i/(i_d-i)]$) obtained from this wave was a straight line with a slope of 70 mV, which approximately corresponds to a one-electron quasi-reversible reduction. The calculated $E_{1/2}$ is -0.62 V . The logarithmic analysis of reversible redox reaction is a straight line with a slope of $59/n \text{ mV}$. The logarithmic analysis of totally irreversible redox reaction is a straight line with a slope of $59/\alpha n \text{ mV}$. Logarithmic analysis of quasi-reversible reduction is a curve with two asymptotic slopes: $59/n$ at higher potentials and $59/\alpha n \text{ mV}$ at lower potentials. The straight line with the slope of 70 mV indicates

either quasi reversible reduction with $n=1$, or totally irreversible redox reaction with $n = 2$ and $\alpha = 0.5$. As the latter is less probable, it is possible to conclude that the number of electrons in the redox reaction is $n=1$. Note that if $n=1$ and $\alpha = 0.5$, the slope would be 140 mV for totally irreversible redox reaction. The results obtained with differential pulse polarography (Figure 2B) gave a value of 85 mV for the half-peak width ($W_{1/2}$) measured at the half-wave potential of -0.62 V. The theoretical value for a one-electron reduction is 90.4 mV [52]. The application of the Birke [53] criterion to the results obtained with differential pulse polarography indicated a quasi-reversible redox mechanism ($\alpha \geq 0.5$) with a coupled chemical reaction. An EC mechanism was proposed and consisted of an electron transfer reaction (E) followed by a chemical reaction (C).

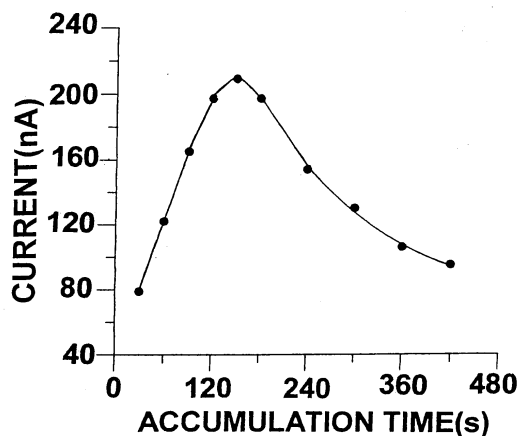
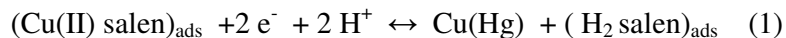


Figure 3. Dependence of the differential pulse adsorptive stripping peak current on the accumulation time for $6.4 \times 10^{-8} \text{ mol L}^{-1}$ Cu(II) salen complex. Supporting electrolyte, 0.02 mol.L^{-1} phosphate buffer (pH 7.0). Accumulation potential at -0.10 V with stirring solution. Equilibrium time, 30s. Scan rate, 10 mV s^{-1} . Pulse height, 25 mV. Medium drop size

3.2. Differential Pulse Voltammetry (DPV)

A linear dependence of the differential pulse adsorptive stripping peak potential of the Cu(II) salen complex with pH was observed over a range of 6.0 to 8.0. A slope of 64 mV was observed. This value is very close to 59 mV which is the theoretical value for a two-electron redox reaction with $\alpha = 0.5$. However, this slope also indicates that equal number of electrons and protons participate in the reversible redox reaction. Thus, it could be preliminarily postulating the following mechanism:



Important parameters such as the accumulation time and quantitative utility (analytical chemistry) also were studied. The height of the reduction peak current (equation 2) depends on the period during which the solution is stirred while a deposition potential is applied to the hanging mercury drop electrode. Figure 3 shows the dependence of adsorptive stripping peak current (for the

Cu(II) salen complex) with the accumulation time. There was a linear increase on peak current up to 150 seconds. After this time, an abrupt decrease in the stripping peak was noted, probably due to the saturation of the electrode surface and consequent diffusion of the reduced species to the bulk solution.

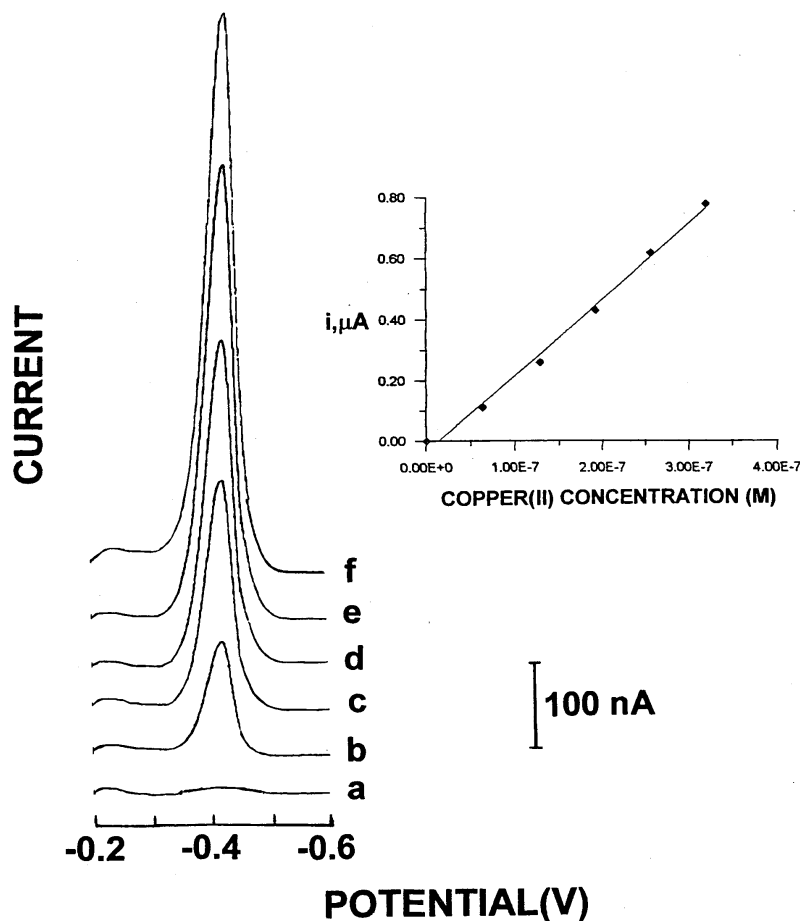


Figure 4. Differential pulse adsorptive stripping voltammograms obtained for increasing Cu(II) salen complex concentrations in $6.0 \times 10^{-8} \text{ mol L}^{-1}$ steps (b-f). Supporting electrolyte, 0.02 mol.L^{-1} phosphate buffer (pH 7.0). Accumulation time, 30 s at -0.20V with stirring solution. The curve “a” represents the blank. Other conditions as in Figure 3. Also shown is the resulting calibration plot.

Figure 4 shows voltammograms for increasing Cu(II) salen complex concentration (0 to $3.2 \times 10^{-7} \text{ mol.L}^{-1}$) after 30 seconds of accumulation time. Well-defined stripping peaks were observed over this concentration range. The resulting calibration curve is also shown in Figure 4. The effective pre-concentration associated with the adsorption process results in significant lowering of the detection limit compared to the corresponding blank solutions measurements. A detection limit near $1.0 \times 10^{-8} \text{ mol L}^{-1}$ Cu(II) salen was estimated. The present adsorptive stripping method developed allows quantitation of trace levels of Cu(II) salen complex, using relatively short accumulation times and inexpensive instrumentation. The method was preliminary applied to a sample of waste samples (with

the presence of iron, nickel and zinc) from a copper electro deposition Brazilian industry. The resulting voltammograms by the method of standard additions for a typical determination were realized. The standard addition plot was linear (correlation coefficient of 0.995). The average of two determinations yielded a copper concentration of 37.9 mg L^{-1} in the original sample. (Note that for the determination, the solution used was diluted to obtain a concentration in the linear range of the method.) This value falls within the ranges previously reported for samples of the same Brazilian industry as determined by atomic absorption spectrometry (AAS). Also, this methodology may be applied to trace measurements of other metal-salen, which are difficult to quantify with conventional stripping methods.

3.3. Cyclic Voltammetry (CV)

Cyclic voltammetry is widely used for the initial characterization of electrochemically active systems. In addition, CV can also be used for mechanistic studies of systems in which the electron transfer reactions are coupled to chemical reactions [54].

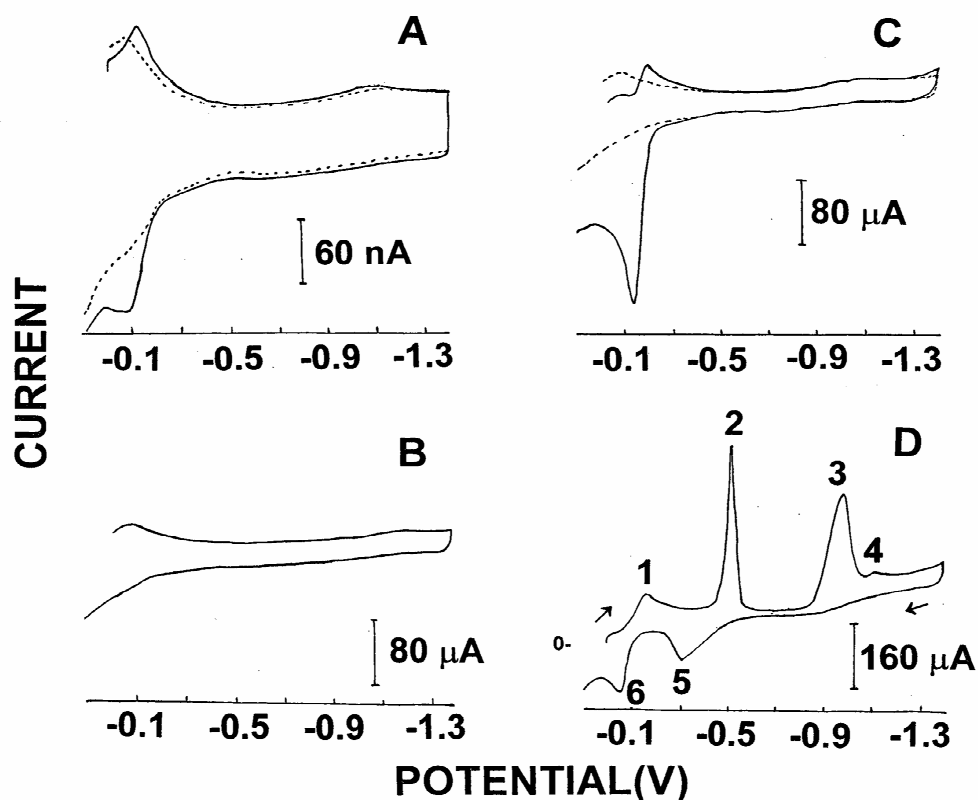


Figure 5. Cyclic voltammogram for the reduction of copper ($4.0 \times 10^{-6} \text{ mol L}^{-1}$) (curve A), of ethylenediamine ($1.8 \times 10^{-2} \text{ mol L}^{-1}$) (curve B), of ethylenediamine with copper (curve C), and of the Cu(II) salen complex ($4.0 \times 10^{-6} \text{ mol L}^{-1}$) (curve D) in unstirred 0.02 mol L^{-1} phosphate buffer (pH 7.0). Scan rate, 50 mV s^{-1} . Initial potential, -0.0 V . Switching potential, -1.4 V . Equilibrium time, 30s (Other details of the figure are explained on the text.) Apparatus, an BAS analyzer.

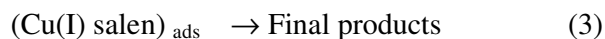
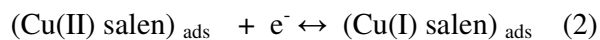
The cyclic voltammograms for the reduction of Cu(II) salen in phosphate buffer (pH 7.0) is shown in Figure 5D. As the potential is swept from 0 to -1.4, the reduction of Cu(II) salen proceeds through three distinct processes (signal 2 at -0.53 V, 3 at -1.0 V and 4 at -1.1 V). An electrochemically quasi-reversible Cu(II) salen/Cu(I) salen is responsible for signal 2; results confirmed by DC, DPP and DPV. The reduction of Cu(I) salen to Cu(0) is associated with signal 3 and the reduction of free dianionic ligand [38] or the disproportionation of Cu(I) salen (an irreversible chemical reaction)[33] with signal 4. Signal 1 (at -0.16V) refers to the reduction of copper I or II (from different equilibrium) or the presence of $[\text{Cu}(\text{en})_2]^{2+}$. In the reverse scan, two peaks appear at -0.31 V (signal 5) and at -0.05 V (signal 6). Signal 5 seems to be correlated with signal 2 and signal 6 with 1. A cyclic voltammogram for the reduction of Cu(II) in phosphate buffer (at pH 7.0) is also shown in Figure 5 A. One little peak in the forward scan appears at - 0.12 V and one in the reverse scan at -0.07V. Figure 5B shows the presence of electroinactive ethylenediamine. Figure 5C shows a little peak at - 0.2 V in the forward scan due to the reduction of the copper-ethylenediamine complex, and one higher peak on the reverse scan at -0.14 V.

The heights of the cathodic and anodic Cu(II) salen complex peaks are not the same, which is a characteristic of a non-reversible reduction process. These data are correlated with those obtained using DC polarography. From Table 1, it can be seen that as the scan rate increases, signal 2 shifts to more negative potentials. Further, the peak separation $E_{pc} - E_{pa}$ becomes larger indicating that the system becomes more irreversible as the scan rate increases. The plot of E_{pc} versus the logarithm of the scan rate (70 - 1000 mV s^{-1}) was linear with a slope of 50 seconds. The ratio i_{pa} / i_{pc} remains almost constant in the range of 20 - 200 mV.s^{-1} . A plot of peak current versus scan rate for the surface-adsorbed Cu(II) salen complex, over the range of scan rates studied (20 - 1000 mV.s^{-1}), was linear which is characteristic of a surface wave[57]. Further evidence of the adsorption of the Cu(II) salen complex at the electrode surface is the negative shift of the peak potential with increasing scan rate. These results suggest a mixed diffusion-adsorption reduction process. Moreover, the slope of plot $\log i_c$ versus $\log v$ was 0.8 $\text{nA mV}^{-1} \text{s}$ (between 0.5 and 1.0), also suggesting an adsorption-controlled reduction process. The results in Table 1 also show that the reduction of Cu(II) salen is kinetically controlled.

Table 1. Effects of scan rate on the staircase cyclic voltammograms adsorptive current and potential peak for $2.0 \times 10^{-4} \text{ mol.L}^{-1}$ Cu(II) salen complex. Supporting electrolyte, 0.02 mol L^{-1} phosphate buffer (pH 7.0). Initial potential: 0.0 V. Switching potential, -1.2 V. Equilibrium time, 30s.

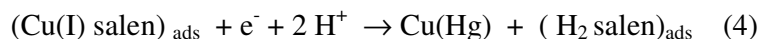
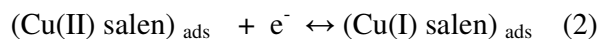
scan rate , mV.s^{-1}	Peak potential, mV	$E_{pc} - E_{pa}$	i_{pa} / i_{pc}
20	-556	-74	0.252
50	-589	-226	0.288
70	-594	-231	0.275
100	-602	-246	0.295
200	-631	-280	0.249
300	-648	-302	0.111
500	-674	-333	0.086
700	-692	-354	0.078
1000	-710	-386	0.087

The CV results suggest a mixed diffusion-adsorption reduction process at the mercury electrode surface. In addition, two oxygen atoms in salen molecule are most probably protonated at pH 7. If reaction (1) is correct, one would expect two reduction peaks in cyclic voltammetry: the first one corresponding to the reduction of Cu(II) salen; and the second one for the reduction of Cu(I) salen. Another more probable alternative is that these results indicate that Cu(II) salen and the product of its reduction adsorb at the electrode surface with a one-electron reduction through an EC mechanism. Thus the following redox reaction could be suggested:



Equation (3) does not produce any electrochemical signals in DPV but it does appear in faster techniques such as the CV and SW voltammetry (signal 3 or 4 showed in Figures 5 and 6). These final products could be the reduction of Cu (I) to copper metal (signal 3) and the reduction of the salen-dianion (signal 4) [38] or the disproportionation of Cu(I) salen (an irreversible chemical reaction)[33].

An EE mechanism with the stabilization of intermediate ((Cu(I) salen)_{ads}) also could be considered:



Note that the equation (2) is quasireversible as show the peaks 2 and 5 in Figure 5D and the equation (4) is totally irreversible (Faradaic) reaction (and not a chemical reaction as the equation (3)). The participation of 2 H⁺ in equation (4) was proved by the variation of pH in DPV. Maybe one proton participates in both equations (2) and (4). Evidences of adsorption of the reactants of the first and the second charge transfers also were considered. The second charge transfer is not recorded in Figure 2 (DC (A) and DP (B) polarogramms) because the final potential is not low enough; or there is no time for the stabilization (absence of the stabilization) of intermediate and a single wave appears according to equation (1). The surface reaction from the possible diffusion controlled electrode reaction not it was distinguished.

A separate and similar experiment was performed by linear cyclic voltammetry with repetitive scan. These voltammograms were developed using an unstirred solution of the phosphate buffer (pH 7.0) as supporting electrolyte containing 4.0 x 10⁻⁶ mol.L⁻¹ Cu(II) salen complex (other conditions: Scan rate, 50 mV s⁻¹; equilibrium time, 30s; EG&G apparatus). The shape of the cyclic voltammogram shows an interesting characteristic of the redox reaction. The cathodic (signal 1) and anodic (signal 6) current (like Figure 5D) gradually increase upon repetitive scans. The peak current, with the adsorbed compound at saturation, is several times greater than that of the solution species alone (estimated from the first scan). These increases could be related to the formation of a film at the electrode surface. These processes are probably the formation and reduction, respectively, of a poly[copper (I) salen] film on the electrode or the reduction of the Cu(II) or (I) (from equilibrium). In cases where metal

salens form polymers on electrodes, the process also involves oxidative polymerization to form poly[metal(III) salen] [36]. Thereafter, for the second and succeeding scans, signal 3 (like Figure 5D) becomes smaller due to the rapid desorption of the salen (from equilibrium).

3.4. Square-Wave Voltammetry (SWV)

The square-wave voltammetry (SWV) is particularly appropriate for studying various types of electrode mechanisms coupled with adsorption phenomena. The mechanism of a redox reaction can be clarified by the relationships between the square-wave response and the parameters of the charge transfer. The relationships between the potential and current peak, with the square-wave frequency and pulse amplitude, give the characteristics of the redox mechanism [55,56]. Figure 6 shows a characteristic SW-voltammogram of Cu(II) salen in aqueous phosphate at pH 7.0. Like CV voltammetry, signal 1 refers to the reduction of ions copper or the presence of $[\text{Cu}(\text{en})_2]^{2+}$. An electrochemically Cu(II) salen/Cu(I) salen is responsible for signal 2. The reduction of Cu(I) salen to Cu(0) is associated with signal 3 and the reduction of free dianionic ligand [38] or the disproportionation of Cu(I) salen (an irreversible chemical reaction)[33] with signal 4.

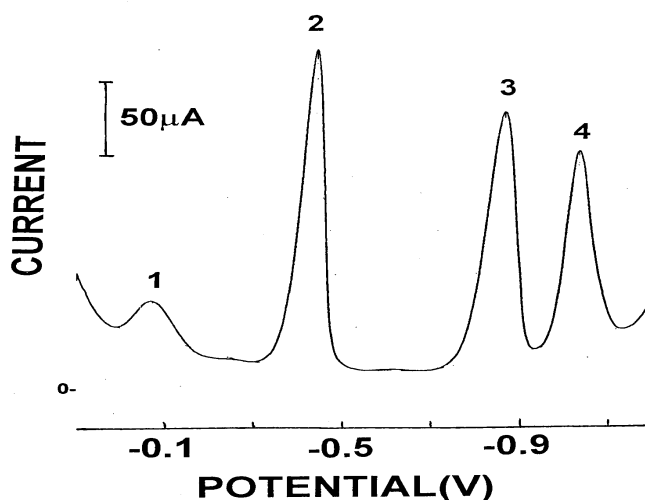


Figure 6. Square wave voltammogram for $7.5 \times 10^{-8} \text{ mol L}^{-1}$ of Cu(II) salen complex. Supporting electrolyte, 0.02 mol L^{-1} phosphate buffer (pH 7.0). Initial potential, 0.1 V. Final potential, -1.3V. E step, 2 mV. SW amplitude, 25 mV. SW frequency, 15 mV. Accumulation time, 30 s. Equilibrium time, 10 s.

The different potential peak observed in DC (Figure 2; at -0.62 V), CV (figure 5D; at -0.53V (peak 2)), and in SWV (Figure 6; at -0.4 V (peak 2)) could be explained by stabilization of intermediate ((Cu(I) salen)_{ads}) of electrode reactions (2) and (4). In CV, DPV, and SWV on static drop mercury, the adsorption of Cu(II) salen induces this stabilization and the first one-electron transfer

occurs at higher potential, while the second one-electron transfer occurs at lower potential than the two-electron transfer in the absence of the stabilization.

The reduction current for the Cu(II) salen complex increases linearly with square wave amplitude up to 60 mV for square wave frequencies of 10, 20, 60 and 120 Hz. The plot of $\log i_{pc}$ versus $\log SWf$ for the same complex showed a linear relationship with slope = 1.0. Figure 7 shows the dependence of peak potential on the logarithm of the square-wave frequency. The peak potential shifts in a negative direction with an increase in frequency. A slope of 70 was observed and is a characteristic of a quasi-reversible redox reaction of the adsorption with EC mechanism. Chronocoulometry and multistep chronoamperometry methods are also particularly appropriate for studies with adsorption phenomena.

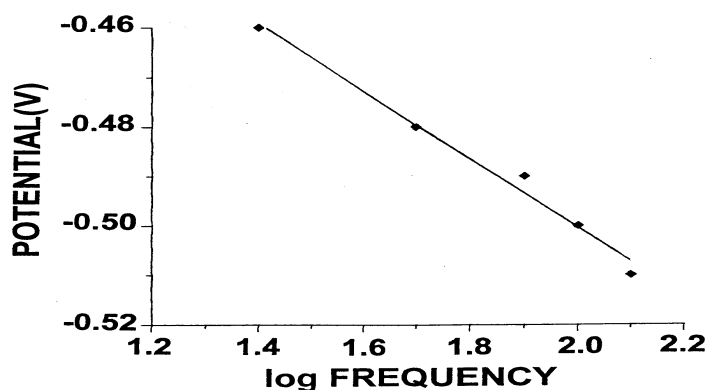


Figure 7. Dependence of the square wave adsorptive stripping peak potential on the log frequency for $7.5 \times 10^{-8} \text{ mol L}^{-1}$ Cu(II) salen complex. Supporting electrolyte, 0.02 mol L^{-1} phosphate buffer (pH 7.0). Accumulation time, 30 s at -0.1V with stirring solution. Scan rate, 200 mV s^{-1} . Scan increment, 2 mV. Pulse height, 75 mV. Equilibrium time, 30 s.

4. CONCLUSIONS

The results obtained by DC, DPP, DPV, CV, and SWV indicate that Cu(II) salen and the product of its reduction, in aqueous phosphate electrolyte, adsorb at the mercury electrode surface with a one-electron reduction reaction through an EC mechanism. Similar results were obtained by Samide and Peters [38] and Zolezzi et al.[33] using CV, organic supporting electrolyte, and glassy carbon as the working electrode. The present study describes an effective assay for the determination of trace levels of copper (II) in presence of salen. The detection limit of $1.0 \times 10^{-8} \text{ mol L}^{-1}$ is comparable to that seen for other adsorptive stripping methods [57]. Repetitive cyclic voltammograms also indicate the possible formation of a polymer film at the mercury electrode surface. Properties of Cu(II) salen complex as potential intercalate of DNA are being tested at present in our laboratory.

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