

CYCLIC VOLTAMMETRY OF THE SECOND ORDER CE MECHANISM AT THE THIN MERCURY FILM COVERED STATIONARY PLANAR ELECTRODE

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ABSTRACT

A theoretical model of electrode reaction influenced by the kinetics of complex formation and dissociation is developed for cyclic voltammetry. It is assumed that the electro-reductions of free metal ions and the complex are reversible and totally irreversible, respectively, and that the ligand is not present in great excess. The results show that the stripping peak current and potential depend on the relative bulk concentration of ligand, particularly within the range $1 < c_{L,tot}^* / c_{M,tot}^* < 3$, and on the rate constant of complex formation.

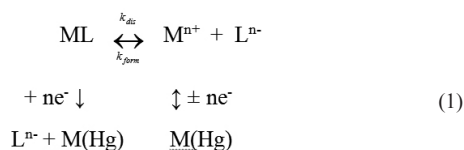
Keywords: Cyclic voltammetry, metal complexes, kinetics of chemical reaction, CE mechanism.

INTRODUCTION

A cyclic voltammogram (CV) of a certain metal-ligand complex ML depends on the stability constant and the dissociation rate constant of the complex [1 - 5]. If the first constant is big and the second one is small, the complex is characterized as being stable and inert. In the opposite case the complex is labile [6 - 8]. Generally, the formal potential of free metal ions M^{n+} is higher than the half-wave potential of the complex [3, 5, 9]. So, this electrode reaction is a CE mechanism, in which the dissociation of the complex is the preceding chemical reaction. This applies to both electro-inactive and electro-active complexes. In the later case two peaks appear in the cathodic branch of CV. In the anodic branch the current depends on the rate constant of complex formation and the concentration of free ligand L^n . In the theory of CE mechanism it is usually assumed that chemical reaction is pseudo-first order [10 - 15]. This is because in the experiment the concentration of one reactant can be adjusted to the great excess. However, the model of the second order CE mechanism was developed recently [16]. In natural waters the concentrations of free ligands that form inert complexes with heavy metal ions are low and comparable with the total metal concentrations [17 - 19]. So, in pseudopolarography of metal complexes in traces [20 - 23], a single anodic stripping voltammetric cycle is the second order CE mechanism and the potential of the stripping peak should depend on the free ligand concentration. The purpose of this work is to investigate this hypothesis theoretically.

The model

The fast and reversible reduction of an amalgam forming metal ion M^{n+} and totally irreversible reduction of its complex ML on the thin mercury film covered stationary planar electrode is considered. It is assumed that the ion and the complex are connected by the first order dissociation and the second order complex formation kinetics. The model of electrode reaction can be described by three differential equations with the following initial and boundary conditions:



$$\frac{\partial c_M}{\partial t} = D \frac{\partial^2 c_M}{\partial x^2} + k_{dis} c_{ML} - k_{form} c_M c_L \quad (2)$$

$$\frac{\partial c_{ML}}{\partial t} = D \frac{\partial^2 c_{ML}}{\partial x^2} - k_{dis} c_{ML} + k_{form} c_M c_L \quad (3)$$

$$\frac{\partial c_L}{\partial t} = D \frac{\partial^2 c_L}{\partial x^2} + k_{dis} c_{ML} - k_{form} c_M c_L \quad (4)$$

$$t = 0, x \geq 0: \quad c_M = c_M^*, \quad c_{ML} = c_{ML}^*, \quad c_L = c_L^* \quad (5)$$

$$c_{M(\text{Hg})} = 0 \quad (6)$$

$$K_{eq} = c_{ML}^* (c_M^* c_L^*)^{-1} \quad (7)$$

$$k_{form} = k_{dis} K_{eq} \quad (8)$$

$$c_{ML}^* + c_M^* = c_{M,tot}^* \quad (9)$$

$$c_{ML}^* + c_L^* = c_{L,tot}^* \quad (10)$$

$$t > 0, x \rightarrow \infty: \quad c_M \rightarrow c_M^*, \quad c_{ML} \rightarrow c_{ML}^*, \quad c_L \rightarrow c_L^* \quad (11)$$

$$x = 0: \quad D \left(\frac{\partial c_M}{\partial x} \right)_{x=0} = -\frac{I_1}{nFS} \quad (12)$$

$$D \left(\frac{\partial c_{ML}}{\partial x} \right)_{x=0} = -\frac{I_2}{nFS} \quad (13)$$

$$D \left(\frac{\partial c_L}{\partial x} \right)_{x=0} = \frac{I_2}{nFS} \quad (14)$$

$$c_{M(\text{Hg})} = -\frac{1}{L} \int_0^L \frac{I_1 + I_2}{nFS} d\tau \quad (15)$$

$$(c_M)_{x=0} = c_{M(\text{Hg})} \exp(\varphi) \quad (16)$$

$$\varphi = \frac{nF}{RT} (E - E^0) \quad (17)$$

$$\frac{I_2}{nFS} = -k_2 (c_M)_{x=0} \exp(-\alpha\varphi_2) \quad (18)$$

$$\varphi_2 = \frac{nF}{RT} (E - E_2^0) \quad (19)$$

$$E_2^0 = E^0 - \frac{RT}{nF} \ln(K_{eq}) \quad (20)$$

$$E = E_{st} + vt \quad (21)$$

The meanings of all symbols are given in Table 1. Differential equations (2) – (4) were solved by the finite difference method [24]. The simulation parameters were $D\Delta t\Delta x^{-2} = 0.4$, $\Delta E = 10^{-4}$ V and $L = \Delta x$. The diffusion was calculated within 2000 space increments and the double precision was used. The dimensionless current $\Phi = (I_1 + I_2)(nFS c_{M,tot}^*)^{-1} (DFv/RT)^{-1/2}$ was calculated as a function of the dimensionless parameters $K_{eq}^* = K_{eq} c_{M,tot}^*$, $k_{dis}\Delta t$, $c_{L,tot}^* / c_{M,tot}^*$, $\lambda = k_2 \Delta t / \Delta x$, α and n . The solutions of equations (7) – (10) are the following:

Table 1: The meanings of symbols.

α	transfer coefficient
c_M, c_L, c_{ML}	concentrations of ions M^{n+} and L^{n-} and the complex ML
c_M^*, c_L^*, c_{ML}^*	concentrations of ions and the complex in the bulk of solution
$c_{M(Hg)}$	concentration of metal atoms in the thin mercury film
D	common diffusion coefficient
E	electrode potential
E^0	standard potential of the reaction $M^{n+} + ne^- \leftrightarrow M(Hg)$
E_2^0	standard potential of the reaction $ML + ne^- \rightarrow M(Hg) + L^{n-}$
E_{st}	starting potential
ΔE	potential increment
F	Faraday constant
I_1, I_2	currents
k_{dis}	dissociation rate constant
k_{form}	complex formation rate constant
k_s^*	standard rate constant of electrode reaction
K_{eq}^*	stability constant of the complex
L	thickness of the film of mercury
n	number of electrons
R	gass constant
S	electrode surface area
T	temperature
t	time
Δt	time increment
v	scan rate (dE/dt)
x	distance perpendicular to the electrode surface
Δx	space increment

$$c_M^* = \left(-b + \sqrt{b^2 + 4K_{eq}^* c_{M,tot}^*} \right) / 2K_{eq}^* \quad (22)$$

$$b = 1 + K_{eq}^* (c_{L,tot}^* - c_{M,tot}^*) \quad (23)$$

$$c_L^* = c_{L,tot}^* (1 + K_{eq}^* c_M^*)^{-1} \quad (24)$$

$$c_{ML}^* = c_{M,tot}^* - c_M^* \quad (25)$$

The program Microsoft QuickBASIC Version 4.5 was used for the calculations.

RESULTS AND DISCUSSION

A typical cyclic voltammogram (CV) of the electrode reaction (1) is shown in Figure 1A. In the cathodic branch two peaks exist, with the minima at -0.171 V vs. E^0 and -0.510 V vs. E^0 . They are caused by the electro-reduction of free ions M^{n+} and the complex ML, respectively. The dimensionless peak currents are $\Phi_{min,1} = -0.0876$ and $\Phi_{min,2} = -0.2904$. For the equilibrium constant $K_{eq}^* = 100$ and the total ligand concentration $c_{L,tot}^*/c_{M,tot}^* = 1$, the bulk concentrations of ions and the complex are $c_M^*/c_{M,tot}^* = 0.095$, $c_L^*/c_{M,tot}^* = 0.095$ and $c_{ML}^*/c_{M,tot}^* = 0.905$. The ratio $\Phi_{min,1}/\Phi_{min,2} = 0.302$ is higher than the ratio $c_M^*/c_{ML}^* = 0.105$ because of the dissociation of the complex. Also, the difference $E_{min,2} - E_{min,1} = -0.339$ V is bigger of $E_2^0 - E^0 = -0.414$ V. These show that generally neither peak currents nor peak potentials can be used for the estimation of the equilibrium constant. In the anodic branch a stripping peak at -0.065 V appears. Its maximum current $\Phi_{max} = 1.555$ is much bigger than the reduction peak currents because of the accumulation of metal atoms in the thin mercury film. The stripping peak is preceded by the prewave, which is proven by the existence of the minimum at -0.128 V on the first derivative of CV (see Figure 1B). This minimum corresponds to the inflexion point $\Phi_{inf} = 0.702$ that connect the prewave and the stripping peak. The prewave is caused by an EC mechanism: the oxidation of metal atoms is facilitated by the complexation of metal ions. However, when the ligand ions are consumed, the remaining metal atoms are oxidized at higher potential.

The physical meanings of dimensionless parameters reported in Figure 1 can be estimated if it is assumed that the scan rate is 0.1 V/s, $D = 9 \times 10^{-6}$ cm²/s and $c_{M,tot}^* = 10^{-5}$ mol/L. Considering the simulation parameters, one obtains: $K_{eq}^* = 10^7$ L/mol, $k_{dis}^* = 1$ s⁻¹, $k_s^* = 1.5 \times 10^{-3}$ cm/s and $L = 1.5 \times 10^{-4}$ cm.

The form of CV primarily depends on the thickness of the film of mercury.

This can be seen in Figure 2, which is calculated for $c_{L,tot}^* = 0$. In the absence of complex, the dimensionless peak currents are $\Phi_{min,1} = -0.415$ and $\Phi_{max} = 2.498$, and the peak potentials are $E_{min,1} = -0.098$ V and $E_{max} = -0.060$ V vs. E^0 . If both the formation and the dissociation of the complex are infinitely fast and the ligand is in great excess, the potentials of minimum and maximum are as follows: $E_{min,1,eq} - E^0 = -0.098 - (RT/F) \ln(1 + K_{eq}^* c_{L,tot}^*)$ (V) and $E_{max,eq} - E^0 = -0.060 - (RT/F) \ln(1 + K_{eq}^* c_{L,tot}^*)$ (V). For $K_{eq}^* = 100$ and $c_{L,tot}^*/c_{M,tot}^* = 100$, the equilibrium potentials are $E_{min,1,eq} - E^0 = -0.335$ V and $E_{max,eq} - E^0 = -0.297$ V.

Figure 3 shows CV calculated under the assumption that there is neither dissociation nor the formation of the complex. This voltammogram is characterized by the following extremes: $\Phi_{min,1} = -0.040$, $\Phi_{min,2} = -0.330$ and $\Phi_{max} = 1.809$. The peak potentials are the following: $E_{min,1} = -0.099$ V, $E_{min,2} = -0.507$ V and $E_{max} = -0.061$ V vs. E^0 . No prewave to the stripping peak exists because $k_{form} = 0$. The ratio $\Phi_{min,1}/\Phi_{min,2} = 0.121$ is higher than the ratio $c_M^*/c_{ML}^* = 0.105$ because the electro-reduction of the complex ML is totally irreversible. Hence, the absolute value of the peak current $\Phi_{min,2}$ is smaller than it would be if this electrode reaction is reversible. Furthermore, the difference $E_{min,2} - E_{min,1} = -0.408$ V is not identical to the difference in standard potentials $E_2^0 - E^0$. This is because the peak potential of reversible electrode reaction depends on the mercury film thickness, while the peak potential of totally irreversible electrode reaction is independent of the film thickness, but depends on the kinetic parameter λ and the transfer coefficient α [9]. So, the stability constant of the complex can not be determined exactly from the extremes of the cyclic voltammogram.

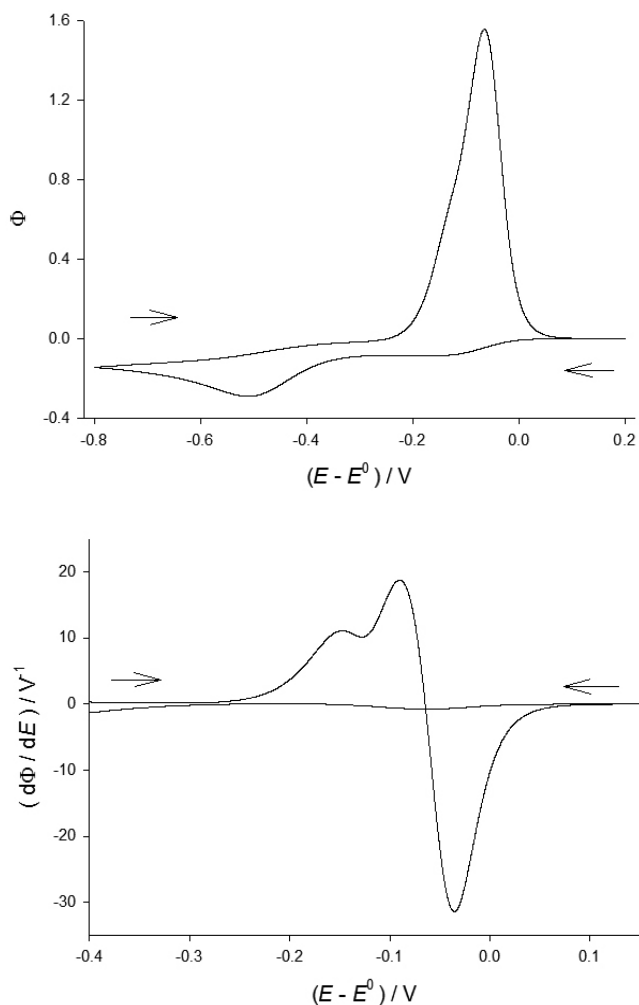


Figure 1: (A) Dimensionless cyclic voltammogram (CV) of electrode reaction (1) and (B) its first derivative. $K_{eq}^* = 100$, $k_{dis}^* \Delta t = 0.001$, $c_{L,tot}^*/c_{M,tot}^* = 1$, $E_2^0 - E^0 = -0.414$ V, $\lambda = 0.01$, $\alpha = 0.5$, $n = 1$ and $E_{st} = 0.2$ V vs. E^0 .

The equilibrium constant K_{eg} influences the concentrations of ions and the complex in the bulk of solution, the rate of complex formation and the second standard potential (see eqs. (7) – (10), (20) and (22) – (25)). If $K^* = 1000$, $E_2^0 - E^0 = -0.473$ V and all other parameters are as in Figure 3, the form of CV is similar to the one shown in Figure 3, but the reduction peak currents are $\Phi_{min,1} = -0.013$ and $\Phi_{min,2} = -0.344$. This is because of the following concentrations in the bulk of solution: $c_M^*/c_{M,tot}^* = c_L^*/c_{M,tot}^* = 0.031$ and $C^*_{ML}/c_{M,tot}^* = 0.969$. Again, the ratio $\Phi_{min,1}/\Phi_{min,2}$ is higher than the ratio C^*_M/C^*_{ML} . The first reduction peak potential and the oxidation peak potential are the same as in Figure 3, but the second reduction peak potential is -0.566 V because of the lower E_2^0 . Also, the maximum oxidation current is 1.609, which is lower than in Figure 3. This is caused by the shorter accumulation period which lasts from -0.566 V to -0.8 V and back to -0.2 V, while in Figure 3 it lasts from -0.507 V to -0.8 V and back to -0.2 V.

Figures 2 and 3 show the boundary values of peak currents and peak potentials of cyclic voltammograms of the second order CE mechanism. Neither the mercury film thickness, nor the equilibrium constant were varied in these calculations because we are primarily interested in the influence of the ligand bulk concentration and the dissociation rate constant on the stripping peak potential.

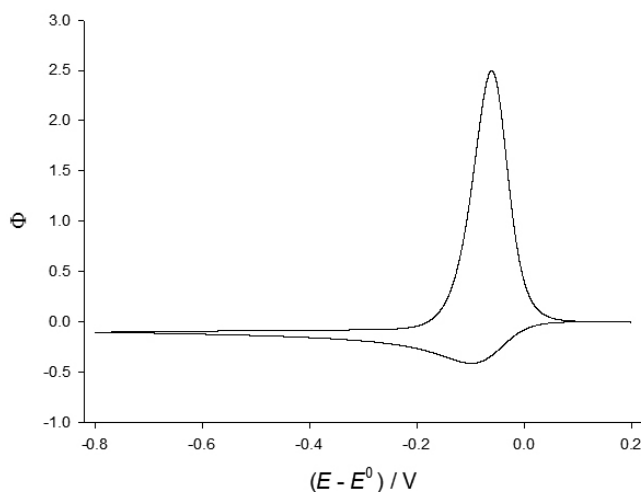


Figure 2: CV of the reaction (1) for $c_{L,tot}^* = 0$. All other parameters are as in Figure 1.

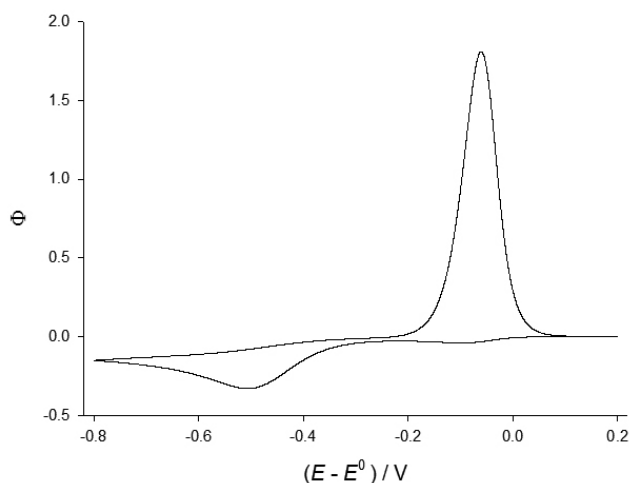


Figure 3: CV of the reaction (1) for $k_{dis} = 0$ and $k_{form} = 0$. All other parameters are as in Figure 1.

Figure 4 shows the dependence of peak currents and peak potentials on the logarithm of the dissociation rate constant for $c_{L,tot}^* = c_{M,tot}^*$. If $\log(k_{dis}\Delta t) > -3$ the peak currents of reductions depend linearly on $\log(k_{dis}\Delta t)$, with the slopes $\Delta\Phi_{min,1}/\Delta\log(k_{dis}\Delta t) = -0.054$ and $\Delta\Phi_{min,2}/\Delta\log(k_{dis}\Delta t) = 0.035$. Considering that

$\Delta c_M = -\Delta c_{ML}$, this difference in slopes is probably caused by the fact that the reduction of M^{n+} is reversible, while the reduction of ML is totally irreversible electrode reactions. The peak potential of the first reduction depends on $\log(k_{dis}\Delta t)$ sigmoidally and tends to the asymptote $E_{min,1} - E^0 = -0.023 \times \log(k_{dis}\Delta t) - 0.242$ (V) if $k_{dis}\Delta t > 2 \times 10^{-3}$. The peak potential of electro-reduction of the complex is almost independent of dissociation rate constant and changes from -0.507 V for $k_{dis} = 0$ to -0.511 V vs. E^0 for $k_{dis}\Delta t = 3 \times 10^{-3}$.

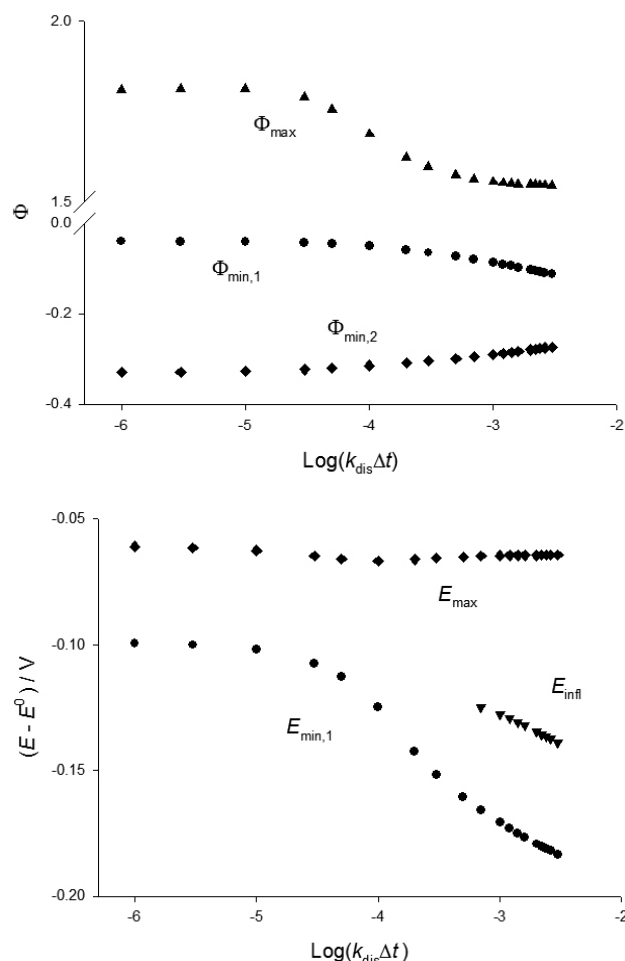


Figure 4: Dependence of dimensionless peak currents (A) and peak potentials (B) on the logarithm of dimensionless rate constant of dissociation of the complex. All other parameters are as in Figure 1.

Within the interval $-5 < \log(k_{dis}\Delta t) < -3$ the stripping peak current is diminished 14% because the half-peak width is increased from 75 mV to 92 mV. The stripping peak potential is -0.067 V vs. E^0 in the middle of this interval and -0.065 V at its limits. These changes are caused by the development of the stripping prewave. If $k_{dis}\Delta t \geq 7 \times 10^{-4}$, the inflexion point of the prewave is well defined. Figure 4B shows that the potential of inflexion is a linear function of $\log(k_{dis}\Delta t)$, with the slope $\Delta E_{infi}/\Delta\log(k_{dis}\Delta t) = -0.023$ V.

The influence of the relative bulk concentration of ligand on the maximum stripping current and peak potential is shown in Figure 5 for $\log(k_{dis}\Delta t) = -3$. The peak current is the smallest for $c_{L,tot}^*/c_{M,tot}^* = 1.9$ and increases for higher ligand concentrations. This is caused by the change of half-peak width from 75 mV, for $c_{L,tot}^*/c_{M,tot}^* = 0$, to 115 mV, for $c_{L,tot}^*/c_{M,tot}^* = 1.9$, and 81 mV for $c_{L,tot}^*/c_{M,tot}^* = 4$. In the concentration range $0.9 \leq c_{L,tot}^*/c_{M,tot}^* \leq 1.7$ the prewave precedes the stripping peak. The inflexion potential changes in that range from -0.133 V to -0.101 V vs. E^0 . Between $c_{L,tot}^*/c_{M,tot}^* = 1.3$ and $c_{L,tot}^*/c_{M,tot}^* = 2.3$ the stripping peak potential decreases from -0.068 V to -0.104 V vs. E^0 . The origin of this transformation is shown in Figure 6. As the relative ligand concentration is increased, the prewave develops into a new peak with the maximum at lower potential. This means that below $c_{L,tot}^*/c_{M,tot}^* = 2$ a simple oxidation $M(Hg) \leftrightarrow M^{n+} + ne^-$ dominates the stripping response, while above this limit the complex

is the main product of the electrode reaction ($M(Hg) + L^n \rightarrow ML + ne^-$). The rate of complex formation depends on the ligand concentration within the interval $1 \leq c_{L,tot}^* / c_{M,tot}^* \leq 3$.

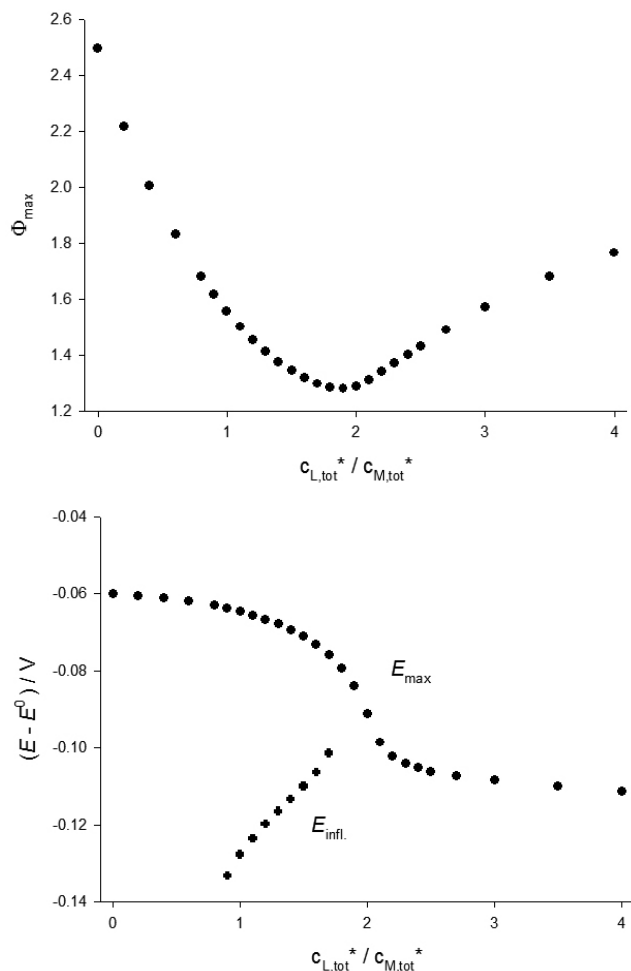


Figure 5: Dependence of stripping peak current (A) and potential (B) on the ligand to metal ratio. All other parameters are as in Figure 1.

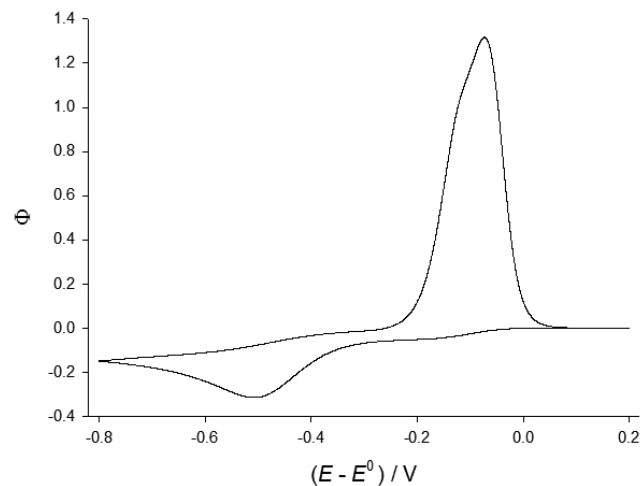


Figure 6 A

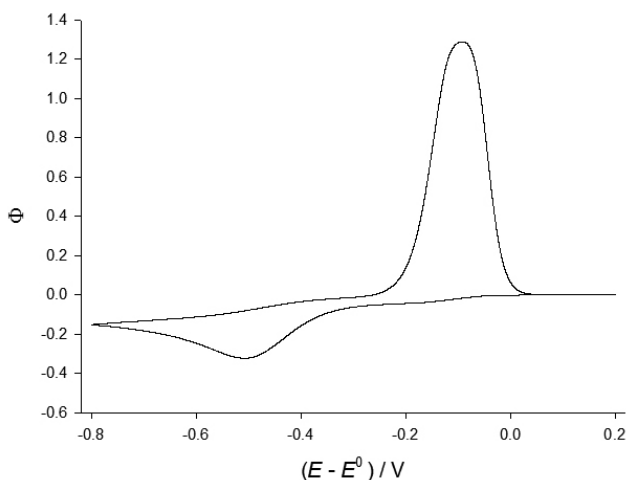


Figure 6 B

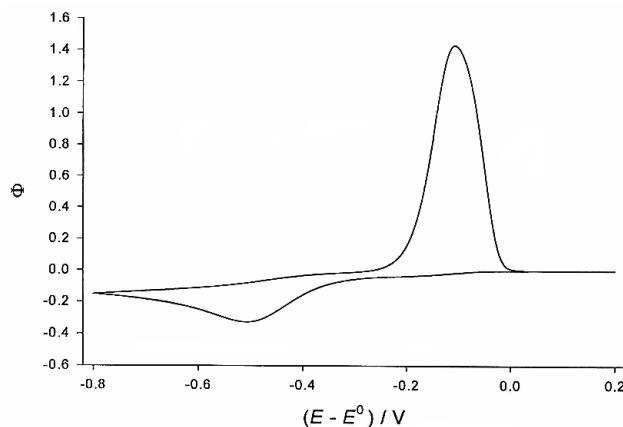


Figure 6 C

Figure 6: CV of the reaction (1) for $c_{L,tot}^* / c_{M,tot}^* = 1.6$ (A), 2 (B) and 2.5 (C). All other parameters are as in Figure 1.

The relationship between reduction peaks and the ligand concentration reflects the distribution of ions and complex in the bulk of solution. For $c_{L,tot}^* / c_{M,tot}^* = 0.2$ the peak currents and potentials are the following: $\Phi_{min,1} = -0.336$, $E_{min,1} = -0.099$ V, $\Phi_{min,2} = -0.175$ and $E_{min,2} = -0.494$ V vs. E^0 . If the ligand to metal ratio is increased to 0.8, the response becomes similar to Figure 1: $\Phi_{min,1} = -0.124$, $E_{min,1} = -0.125$ V, $\Phi_{min,2} = -0.270$ and $E_{min,2} = -0.512$ V vs. E^0 . Finally, for $c_{L,tot}^* / c_{M,tot}^* = 4$ the second peak current and potential are -0.334 and -0.507 V vs. E^0 , respectively.

CONCLUSIONS

These results show that in the anodic branch of cyclic voltammogram a single stripping peak appears at the potential which depends on the ratio of total bulk concentrations of ligand and metal, and on the rate constant of complex formation. The model developed in this paper serves to explain the second order CE mechanism. For this reason cyclic voltammograms are simulated. In this technique the minimum reactant concentration is 10^{-5} mol/L. However, the conclusions obtained in these calculations apply to the anodic stripping voltammetry as well. The latter method is used for the analysis of amalgam forming metal ions in traces. The accumulation potential must be lower than the peak potential of the reduction of complex ion and the stripping peak potential corresponds to the oxidation of amalgam into free metal ions. The signal-to-noise ratio in the stripping phase is improved by the prolonged accumulation period and the increased electrode rotation rate. The special case of anodic stripping voltammetry is pseudopolarography in which the accumulation potential is varied and its influence on the stripping peak current is monitored.

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