

Journal Pre-proof

Mechanistic analysis of the cathodic stripping square-wave voltammetric response of the copper-arsenic system at a mercury electrode

Jenny Gómez Avila, Jhan Carlos Burgos Gómez, Angélica C. Heredia, Mónica E. Crivello, Fernando Garay



PII: S1572-6657(20)31062-6

DOI: <https://doi.org/10.1016/j.jelechem.2020.114833>

Reference: JEAC 114833

To appear in: *Journal of Electroanalytical Chemistry*

Received date: 18 August 2020

Revised date: 3 November 2020

Accepted date: 5 November 2020

Please cite this article as: J.G. Avila, J.C.B. Gómez, A.C. Heredia, et al., Mechanistic analysis of the cathodic stripping square-wave voltammetric response of the copper-arsenic system at a mercury electrode, *Journal of Electroanalytical Chemistry* (2020), <https://doi.org/10.1016/j.jelechem.2020.114833>

This is a PDF file of an article that has undergone enhancements after acceptance, such as the addition of a cover page and metadata, and formatting for readability, but it is not yet the definitive version of record. This version will undergo additional copyediting, typesetting and review before it is published in its final form, but we are providing this version to give early visibility of the article. Please note that, during the production process, errors may be discovered which could affect the content, and all legal disclaimers that apply to the journal pertain.

© 2020 Published by Elsevier.

Mechanistic analysis of the cathodic stripping square-wave voltammetric response of the copper-arsenic system at a mercury electrode

Jenny Gómez Avila^{a,b,c}, Jhan Carlos Burgos Gómez^a, Angélica C. Heredia^b, Mónica E. Crivello^b,

Fernando Garay^{a,*} fgaray@unc.edu.ar

^aINFIQC-CONICET, Departamento de Físico Química, Facultad de Ciencias Químicas, Universidad Nacional de Córdoba. Pabellón Argentina, Ciudad Universitaria. X5000HUA Córdoba, Argentina

^bCITeQ-CONICET, Universidad Tecnológica Nacional, Facultad Regional Córdoba, Maestro Marcelo López esq. Cruz Roja Argentina, Ciudad Universitaria, X5016ZAA, Córdoba, Argentina

^cDepartamento de Ciencias Naturales y Exactas, Facultad de Ciencias e Ingeniería, Pontificia Universidad Católica Madre y Maestra, Abraham Lincoln esq. Simón Bolívar. 10109, Santo Domingo, República Dominicana

*Corresponding author.

Abstract

Despite arsenite can be reduced to As(0) and deposited at the surface of solid electrodes such as gold, platinum, or copper, it cannot form amalgams with mercury, and so the addition of other metal ions is required for its deposition. In this manuscript, mechanistic analysis of the cathodic stripping square-wave voltammetric response of the system copper-arsenic is presented. For the analysis of experimental responses, a mathematical model is used to consider that a surface-active reagent undergoes a charge transfer step followed by a chemical reaction. The dependences of the differential peak current, and the respective peak potential and half-peak width on the square-wave frequency were used to estimate the apparent stability constant of arsenide formation and that the electrode reaction would involve the direct transfer of 2 electrons, while the simulation and fit of forward and backward voltammetric responses have been useful for inferring other parameters such as the formal charge transfer rate constant of the global electron transfer reaction, a pseudo-first order homogeneous rate constant associated with arsenide formation, and the charge transfer coefficient of the global electron transfer reaction.

Besides the values estimated for each of those parameters, all simulations indicate that the reduction of copper instead of arsenic would be taking place during the cathodic stripping scan. Accordingly, the trace-analysis reaction of arsenic in the presence of copper would be based on the surface accumulation of a metal complex, where Cu^{2+} would be the metal cation and an arsenide species the ligand. The stability of that complex at the surface of a mercury electrode would depend not only on the applied potential, but also on the ratio between copper, arsenic, and protons.

1. Introduction

Quantification of arsenic for food and environmental monitoring is particularly essential in diverse regions of our planet where high levels of this element have been found dissolved in water samples [1,2]. Therefore, the water quality resulting from filtering devices used for water treatment has to be analyzed and compared with the concentration limits of arsenic suggested by WHO [3]. Due to labor and cost associated with the spectroscopic methods such as atomic fluorescence spectroscopy, atomic absorption spectroscopy, and inductively coupled plasma-mass spectrometry, electroanalytical techniques represent a very promising approach for developing *in situ* arsenic sensors [4–8]. In this regard, *in situ* measurements are highly desirable to determine when a filtering cartridge for arsenic must be replaced. This would not only minimize errors but also avoid the collection and transportation of water samples to a centralized laboratory for analysis [1,2,4].

Electrochemical analysis is particularly useful due to its portability, relative low-cost, and its capability for speciation [9,10]. This last characteristic is quite important, considering that arsenic toxicity and bioavailability depend on the kind of prevalent chemical species [10]. As(III)

and As(V) exhibit different electrochemical behavior. While As(III) can be electrochemically reduced, As(V) is generally considered to be electroinactive [6,9–14]. Accordingly, the determination of total arsenic content requires the use of chemical reagents to reduce As(V) to As(III) [6,9–14]. Stripping voltammetric strategies of As(OH)₃ involve its reduction to As(0) and further accumulation on the surfaces of solid electrodes such as gold, platinum, or copper. However, while reduced arsenic interacts with those electrode materials and the surface must be systematically renewed to get reliable analytical signals, it was found that As(0) does not form amalgam with mercury [11]. Because of this, the deposition of As(0) on mercury electrodes requires the addition of other metal ions, typically Cu or Se. According to the literature, the reduced forms of those elements would result in intermetallic compounds that can be accumulated at the surface of a static mercury drop electrode (SMDE) [12,13]. The cathodic stripping voltammetry (CSV) with Hg as the working electrode is a classical technique for analysis of anions. Although the use of Hg as electrode material is discouraged due to its toxicity, SMDE is still recognized as one of the best electrodes for trace-analysis of various metals as well as for mechanistic studies of those reactions [14–19].

In the case of adding a salt such as CuCl₂, it has been proposed that it is formed Cu₃As_(ads) during the accumulation step [11, 13]. However, more recent publications do not specify the sort of arsenic species that is accumulated at the electrode surface neither on the kind of reaction that takes place during the stripping step [10,12]. It is not easy to study the reaction of a compound that accumulates in low concentration levels on the surface of a drop of mercury while anodic potentials are applied. With the aim of increasing the surface concentration of Cu_xAs_(ads), several researchers have varied diverse chemical characteristics of the experimental system [10,11,14,20,21]. However, irrespectively of the electrochemical technique used for the

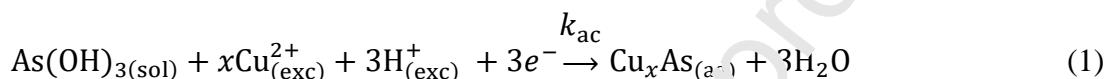
stripping scan, the dependence of cathodic peak current on the arsenic acid bulk concentration ($c_{\text{As}(\text{OH})_3}^*$) rarely shows a linear behavior that extends above 2 orders of magnitude [11,21]. Instead of this, calibration curves with 2 different slopes, the formation of peak-shoulders, and variations of peak-shapes are typical problems found during the electrochemical quantitation of arsenic species [10,21]. Because of this, diverse research groups have found that addition of extremely low amounts of small organic molecules presenting one or more thiol groups enhances the voltammetric response of arsenic [9,10,19]. Those ligands would stabilize the base line, allowing the determination of lower concentrations of arsenic [19,20,21]. However, the addition of low amounts of Na-pyrrolidine dithiocarbamate ($< 0.2 \mu\text{M}$) does not affect the average value of the half-peak width ($\Delta E_{p1/2}$) nor the shape of SW voltammograms corresponding to solutions with $c_{\text{As}(\text{OH})_3}^* > 5 \mu\text{g L}^{-1}$ and concentrations of Cu^{2+} ions between 0.1 and 1 mM [21]. Consequently, it should be considered that regardless the presence or absence of those chelating species, it is still quite unclear what kind of arsenic species prevails at the surface of a SMDE [11].

In this manuscript, it is studied the electrochemical reduction of $\text{As}(\text{OH})_3$ on a SMDE in presence of Cu^{2+} ions. The analysis is focused on simulating the response of square-wave voltammetry (SWV) corresponding to cathodic stripping scans. All simulations indicate that, during the cathodic stripping scan, the analytical signal involves the transference of 2 electrons instead of the expected 3 electrons for the reduction of arsenic to arsenide. Because of this, the expression “intermetallic compound of copper and arsenic” is not used in the following sections. Instead of this, it is inferred that a metal complex of Cu^{2+} and an arsenide species is present. As it is well-known, SWV allows the examination of reduction and oxidation currents that are obtained almost simultaneously. Thus, it is possible to evaluate the kinetics of the electrode

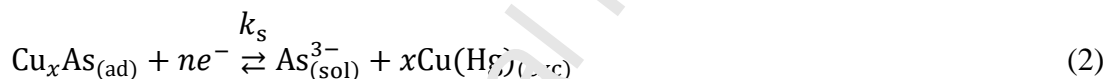
process as well as that of a following chemical reaction. The analysis of parameters associated with the differential current (ΔI) as well as the fit of voltammetric profiles of forward (I_f) and backward (I_b) currents shed new light on the studied reaction.

2. Proposed model

In presence of great excess of Cu^{2+} ions, the reduction of $\text{As}(\text{OH})_{3(\text{sol})}$ on Hg can be described according to the following expression for the accumulation step, where $E_{\text{ac}} = -0.4$ V [21,22]:



while the stripping step at the SMDE occurs for -0.95 V $< E < -0.70$ V:



At this point it will be assumed that $\text{Cu}_x\text{As}_{(\text{ad})}$ is the unique species that can be accumulated at the surface of a SMDE [10,11]. The parameter k_{ac} is the apparent rate constant for the accumulation of Cu_xAs at the mercury electrode, which results in the surface excess of Cu_xAs (Γ_{CuAs}). The value of k_{ac} depends on E_{ac} and on the bulk concentration of Cu^{2+} ions [20]. Since the reactions of Eqs (1 – 3) are typically carried out in solutions with $\text{pH} \leq 1$, it can be considered that protons and copper are in great excess with regards to arsenic species. Therefore, the constants k_1 and k_{-1} are pseudo-first order homogeneous rate constants. The latter is very

important since Eq (2) will depend solely on the concentration of arsenic, regardless of whether the charge transfer process involves the reduction of copper or arsenic. The ratio $k_1/k_{-1} = K_{eq}$.

The parameter k_s is the formal charge transfer rate constant of the global electron transfer reaction. After those considerations, Eqs (2) and (3) can be described by Fick's second law as:

$$\partial c_{CuAs}/\partial t = D(\partial^2 c_{CuAs}/\partial x^2) \quad (4)$$

$$\partial c_{As(3-)} / \partial t = D(\partial^2 c_{As(3-)} / \partial x^2) + k_1(c_{AsH3} - c_{As(3-)}K_{eq}^{-1}) \quad (5)$$

$$\partial c_{AsH3} / \partial t = D(\partial^2 c_{AsH3} / \partial x^2) - k_1(c_{AsH3} - c_{As(3-)}K_{eq}^{-1}) \quad (6)$$

Where c_{CuAs} and $c_{As(3-)}$ indicate the concentration of species that would affect Eq (2) during the stripping scan. The concentration of arsine is specified as c_{AsH3} , which is generated as product of the chemical reaction. It is assumed that all involved species have a common diffusion coefficient, $D = 4 \times 10^{-6} \text{ cm}^2 \text{ s}^{-1}$, since the ratio between the effective diffusion coefficients does not affect the shape neither the height of peak current associated with macroelectrodes in SWV [23]. Thus, the reaction scheme of Eqs (1 – 3) can be described according to the following set of boundary conditions:

$$t = 0,$$

$$x \geq 0: \quad c_{As(3-)} = 0; \quad c_{AsH3} = 0 \quad (7)$$

$$x = 0: \quad t_{ac} k_{ac} c_{As(OH)3}^* = c_{CuAs}^{ini} \quad \Gamma_{CuAs}^{ini} = K_{ad} c_{CuAs}^{ini} \quad (8)$$

in Eq (8) $K_{ad} = K'_{ad} c_{Cu(Hg)}$, is the effective adsorption constant for the compound Cu_xAs .

Concentration gradients associated with $c_{Cu(2+)}$ are not considered since it is in great excess with regards to arsenic species, $c_{Cu(2+)} \gg c_{As(OH)_3}$ [11,20].

$t > 0$,

$$x \rightarrow \infty: \quad c_{As(OH)_3} \rightarrow c_{As(OH)_3}^* \quad (9)$$

$$c_{As(3-)} \rightarrow 0 \quad c_{AsH_3} \rightarrow 0 \quad (10)$$

$$x = 0: \quad D(\partial c_{CuAs}/\partial x)_{x=0} = -I/nFA + \partial \Gamma_{CuAs}/\partial t \quad (11)$$

$$D(\partial c_{As(3-)} / \partial x)_{x=0} = I/nFA \quad (12)$$

$$D(\partial c_{AsH_3} / \partial x)_{x=0} = 0 \quad (13)$$

$$c_{As(OH)_3} \exp[nF(E_{ac} - E_1^{0''})/(RT)] = c_{CuAs} \quad (14)$$

$$\Gamma_{CuAs} = K_{ad} c_{CuAs} \quad (15)$$

Cathodic current has been defined as negative. The values of $c_{As(OH)_3}$ and c_{CuAs} are related through the Nernst expression of Eq (14) where $E_1^{0''}$ is the formal potential for the reaction given by Eq (1) [24]. Since $E_{ac} \ll E_1^{0''}$, the equilibrium represented by Eq (14) is shifted towards the formation of Cu_xAs at $x = 0$. The general form of Butler-Volmer equation is given by:

$$-I(t)/nFA = k_s e^{-\alpha\varphi(t)} \{ \Gamma_{CuAs} - c_{As(3-),x=0} e^{\varphi(t)} r_s \} \quad (16)$$

$$\varphi(t) = nF[E(t) - E_{ad}^0]/(RT) \quad (17)$$

Eq (16) is valid for multiple electron transfer reactions, where the charge transfer coefficient $\alpha = (\beta + m/\nu)/n$ [25,26]. The integers n and m indicate the number electrons of the global reaction and the number of electrons transferred before the rate determining step (rds), while ν is the number of times this step takes place [25]. The parameter β is the asymmetry factor of the rds [25]. Assuming that the electrode reaction involves the reduction of As(0) to arsine, the number $n = 3$ and the value of α could be $\beta/3$, $(1 + \beta)/3$, or $(2 + \beta)/3$ if $\nu = 1$ and the rds corresponds to the first, second, or third electron transfer step, respectively. The auxiliary constant $r_s = 1$ cm is used to unify the dimensions between Γ_{CuAs} and $c_{\text{As}(3-)}$ species in Butler-Volmer expression [18,22]. The variable $E(t)$ indicates the applied potential according to the potential function of the selected electrochemical technique, while $E_{\text{ad}}^{0'}$ is related to the formal potential of a redox reaction of soluble species [27,28]. If the potential function corresponds to SWV then the current can be normalized according to:

$$\Psi(t) = I(t) [nFA\Gamma_{\text{CuAs}}^{\text{ini}} f]^{-1} \quad (18)$$

where f is the square wave frequency and the other symbols have their usual meaning [18,22,26,28]. The differential Eqs. (4–6) can be solved according to the set of boundary conditions indicated by Eqs. (9–17) by using Laplace transforms. The resulting convolution integrals were solved by numerical integration following algebraic steps that have been detailed in a previous manuscript [22]. The explicit expression for the current corresponds to:

$$\Psi_{(m)} = \frac{\mathcal{E}_{\text{SP}(j)} + \vartheta \exp[\varphi_{(m)}] \mathcal{E}_{\text{SQ}(j)} - (\omega/f)}{(\omega/k_s) \exp[\alpha_{\text{app}} \varphi_{(m)}] + (1 + \mathbb{P}_1) + \vartheta \exp[\varphi_{(m)}] (1 + \mathbb{Q}_1)} \quad (19)$$

where $\vartheta = K_{\text{eq}}/(K_{\text{eq}} + 1)(r_s/K_{\text{ad}})$, $\Xi_{\mathbb{P}(j)} = \sum_{j=1}^{m-1} \Psi_{(j)} [S_i + \mathbb{P}_i]$ y $\Xi_{\mathbb{Q}(j)} = \sum_{j=1}^{m-1} \Psi_{(j)} [S_i + \mathbb{Q}_i]$,

$$\mathbb{P}_i = (\omega/a^2) \left\{ \exp[a^2 \delta i] \operatorname{erfc}[a\sqrt{\delta i}] - \exp[a^2 \delta (i-1)] \operatorname{erfc}[a\sqrt{\delta (i-1)}] \right\}, a = \sqrt{D}/K_{\text{ad}},$$

$$\omega = a(2\sqrt{\delta/\pi})^{-1}, i = m - j + 1, \mathbb{Q}_i = \left\{ \operatorname{erf}[\sqrt{k_{\text{chem}} \delta i}] - \operatorname{erf}[\sqrt{k_{\text{chem}} \delta (i-1)}] \right\} \omega /$$

$(aK_{\text{eq}}\sqrt{k_{\text{chem}}})$, $S_i = (\sqrt{i} - \sqrt{i-1})$, and $\delta = (50f)^{-1}$. In the following sections Eq (19) is analyzed under conditions of SWV to simulate the reduction of $\text{Cu}_{\text{xs}} \text{S}_{(\text{ad})}$ to arsine in aqueous acid media. The calculations presented in this manuscript were carried on with a FORTRAN 90 software package.

3. Experimental

Aqueous solutions were prepared with deionised (DI) water with a resistivity of 18 M Ω cm obtained from a Millipore MilliQ system. Analytical grade HCl (Merck, Argentina) was purified by sub-boiling distillation on a quartz condenser. A 50 mL stock solution of 0.0100 M As(OH)₃ was prepared by dissolving the proper amount of As₂O₃ (purity 99.99%, Sigma-Aldrich, Argentina) in DI water with some few drops of concentrated NaOH (Sigma-Aldrich, Argentina). After the complete dissolution of As₂O₃, the stock solution was acidified with HCl to pH 2 and stored at 4 °C in a dark glass bottle to prevent the oxidation of As(OH)₃. Standard arsenite solutions were prepared from the stock solution every week and stored at 4 °C.

The solutions of CuCl₂ were prepared from an analytical grade reagent (Sigma-Aldrich, Argentina). Prior to the experiments, solutions were deoxygenated bubbling Nitrogen 5.0 (Praxair, Argentina) for 20 min and keeping N₂ atmosphere during measurements.

Electrochemical measurements were carried out with a potentiostat/galvanostat Autolab PGSTAT101 (Metrohm, Switzerland), interfaced to a working electrode (VA 663 Metrohm, Switzerland) and controlled through a NOVA 1.9 software package. The working electrode was used in the mode SMDE with a surface area of 0.40 mm^2 . The counter electrode was a glassy carbon rod and all potentials are referred to a $\text{Ag}|\text{AgCl}|\text{KCl}(\text{sat})$ reference electrode. The parameters of SWV are defined as usual [15–19,22,29].

4. Results and discussion

4.1. Determining the number of exchanged electrons

Eq (1) assumes that the compound $\text{Cu}_x\text{As}_{(\text{ads})}$ was formed during the accumulation step. Although Pourbaix's diagrams involving copper and arsenic species would consider the prevalence of Cu_3As when very negative potentials are applied, there is not information about the effect of mercury in this interaction [24]. Besides, we could not find information about the kind of bounds that those species would present at the surface of a mercury drop. In this regard, it is not clear either if the compound Cu_xAs should be considered as an amalgam or a complex between copper and arsenic species. Thus, it is possible to consider that during the cathodic stripping scan may take place the reduction of $\text{As}(0)$ to $\text{As}(3-)$, the reduction of $\text{Cu}(1+)$ to $\text{Cu}(0)$, or the reduction of $\text{Cu}(2+)$ to $\text{Cu}(0)$. As a consequence of this, some researchers have proposed the presence of different compounds of copper and arsenic [11,14,21]. Regardless those assumptions increase the number of hypothetical reactions that could take place at the electrode surface, all reaction schemes point out that the charge transfer reaction is followed by a rather irreversible chemical reaction where the species AsH_3 is released as final product [11,20]. Experimentally, the presence of a following irreversible chemical reaction is evidenced by the

absence of the oxidation peak current in cyclic voltammetry or SWV [11,22,30]. According to the proposed model, the formation of a very stable species would correspond to a value of $K_{eq} \leq 10^{-4}$ [22].

In SWV, the absence of a backward peak simplifies the analysis related to the shape of the differential current (ΔI) and the values that can be observed from its corresponding half-peak width ($\Delta E_{p1/2}$) [22]. Table 1 shows the values of $\Delta E_{p1/2}$ expected for reactions with different reversibility and number of transferred electrons. Those values were calculated considering that $\alpha = 0.5$ and a set of conditions where the backward peak current is not observed. Those conditions correspond to systems with $K_{eq} \leq 10^{-4}$ and $6 \times 10^2 < k_{chem} < 6 \times 10^4$. The shape of SW voltammograms does not change for values of $K_{eq} < 10^{-4}$. On the contrary, the backward peak current increases for calculations performed with values of k_{chem} that are outside the suggested range. According to Eq (3), a value of $K_{eq} < 10^{-4}$ would indicate that the chemical reaction is shifted towards the formation of AsH_3 , which is consistent with the experimental expectations.

As it is well-known the theoretical data included in Table 1 point out that voltammetric peaks are thinner for those reactions that involve the charge transfer of higher number of electrons. However, the absence of the backward peak current simplifies the distinction between the value of $\Delta E_{p1/2}$ that corresponds to a given number of exchanged electrons. Thus, the data of Table 1 have to be compared with the experimental voltammetric profiles corresponding to the reduction of the compound Cu_xAs . Before doing this, it is important to consider that the accumulation of Cu_xAs commonly involves the variation of diverse experimental conditions with the aim of increasing the analytical response for assessing arsenite. Although it is possible to observe changes of ΔI_p , E_p , and even the presence of secondary peaks during the optimization of

the analytical signal, the value of $\Delta E_{p1/2}$ did not evidence significantly changes except for systems with high concentration of arsenic [21].

Figs. 1 and 2 show two examples of the SWV responses obtained under different experimental setups. In both cases the differential current has been divided by f , while the insets of both figures show that the values of ΔI_p depend more or less linearly with f . The respective blank signals have been subtracted from the analytical signals. As it can be observed, the responses of these two sets of experiments are quite different. In the case of Fig. 1A the normalized differential current profiles present a minimum for $f = 50$ Hz, while the peaks of $\Delta I f^{-1}$ decrease with the increment of frequency in Fig. 2A. Despite the differences in peak currents and peak potentials for the two sets of voltammograms are quite significant, all peaks have values of $\Delta E_{p1/2} = (55 \pm 5)$ mV. Those values of $\Delta E_{p1/2}$ are consistent with the presence of a quasi-reversible charge transfer reaction of 2 electrons. However, each group of voltammetric profiles shows distinctive behaviors associated with the changes introduced to its respective experimental setup. While the profiles of Fig. 1 were measured in a solution with $c_{\text{HCl}}^* = 0.3$ M and $c_{\text{Cu}(2+)}^* = 0.5$ mM, the voltammograms of Fig. 2 correspond to a solution with $c_{\text{HCl}}^* = 1$ M and $c_{\text{Cu}(2+)}^* = 1$ mM. Although the values of ΔI_p are proportional to the bulk concentration of $\text{As}(\text{OH})_3$, the sensitivity of calibration curves is highly dependent on pH and the concentration of Cu^{2+} ions. Thus, it can be observed that the sensitivity of the analytical signal is much higher with the experimental condition of Fig. 2 than with that of Fig. 1 [10,11,20,21]. Moreover, the diminution of pH increases the values of ΔI_p and changes the peak potentials towards more positive values. While it is rather simple to understand that the diminution of pH reduces the energy required for the formation of arsine, this fact would not explain why the values of ΔI_p increase with the diminution of pH [10,20,21]. Also, it is not that simple to understand how the

analytical signal depends on the amount of copper that has been accumulated at the SMDE [10,20,21].

4.2 Application of the proposed model

The comparison of experimental profiles with the data of Table 1 cannot be considered as conclusive. However, it is worth to compare the behavior observed for $\Delta I_p f^{-1}$ with a greater number of theoretical data calculated for $n = 2$ and for different values of k_s and k_{chem} . Fig. 3 shows a 3D graph where the dependence of the normalized peak current ($\Delta \Psi_p$) on the time scale of the experiment can be carried on properly [22,29]. This is because the variation of f does not only affect the apparent reversibility of the electrode process, but also the apparent lability of the chemical reaction [22,29]. Fig 3 shows the dependence of $\Delta \Psi_p$ on $\log(k_s f^{-1})$ and $\log(k_{\text{chem}} f^{-1})$.

For the analysis of Fig. 3, it is useful to describe first the behavior observed on the sides of the surface. Thus, for the case of $\log(k_{\text{chem}} f^{-1}) < -3$, it can be considered that the chemical reaction is too slow to be observed experimentally. A similar situation occurs for electrode reactions with $\log(k_s f^{-1}) < -4$, which are irreversible and thus it is not possible to observe the presence of a following chemical reaction. The values of $\Delta \Psi_p$ of systems with $\log(k_s f^{-1}) > 0$ correspond to reversible electrode reactions, while systems with $0 > \log(k_s f^{-1}) > -4$ are quasi-reversible electrode reactions. The last group of reactions shows the so-called quasi-reversible maximum (QRM) [18,22,27,28]. However, in this case the QRM can be observed only when the effect of the following chemical reaction is negligible [22]. Instead of the QRM, in the region with $0 > \log(k_s f^{-1}) > -4$, the values of $\Delta \Psi_p$ are similar to those of irreversible electrochemical reactions. More information about $\Delta \Psi_p$ and the shapes of forward and backward currents can be found in a previous manuscript [22].

Besides the different behaviors described for $\Delta\Psi_p$, the data of Fig. 3 can be used for estimating the values of k_s and k_{chem} associated with the reduction of Cu_xAs . Therefore, it is possible to match the behavior of normalized peak currents presented in Fig. 1 and Fig. 2 with some zones of the surface. To achieve this, it is necessary to multiply the values of $(\Delta I_p f^{-1})$ by a constant that would be equivalent to the parameters $nFA\Gamma_{\text{CuAs}}^{\text{ini}}$ in Eq (18). From that constant, it can be estimated that the value of $\Gamma_{\text{CuAs}}^{\text{ini}}$ ranges from $4 \times 10^{-10} \text{ mol cm}^{-2}$ to $1 \times 10^{-9} \text{ mol cm}^{-2}$ for the cases of curves 3(a) and 3(b), respectively. Despite the significant differences associated with the accumulation of Cu_xAs and the dependence of normalized peak currents on f , the values of $\Delta E_{p1/2}$ remain unchanged.

The estimation of kinetic parameters does not only require to match the dependences of $\Delta E_{p1/2}$ and ΔI_p , but also to their respective peak potentials (E_p). Fig. 4 shows how the values of E_p depend on $\log(k_s f^{-1})$ and on $\log(k_{\text{chem}} f^{-1})$. It is important to note that the values of $\Delta\Psi_p$ and E_p of Fig. 3 and Fig. 4 correspond to the same set of theoretical SW voltammograms. In the front left side of Fig. 4 it is shown the behavior of E_p for systems with irreversible charge transfer reactions. As it was mentioned above, those responses do not exhibit changes associated with the following chemical reaction. On the contrary, the dependence of E_p on $\log(k_{\text{chem}} f^{-1})$ for systems with reversible electrode reactions can be observed at the back wall that is on the right side of Fig. 4.

The data of Fig. 4 are also used for estimating the values of k_s and k_{chem} related to the experimental voltammograms presented in Fig. 1 and Fig. 2. Since the variation of f affects the apparent reversibility of both, electrochemical and chemical reactions, the surface of Fig. 4 allows associating the behavior of E_p with a theoretical pair of values for k_s and k_{chem} . Besides,

since the data of the surface have been calculated for $E^{0'} = 0$ V, the constants that allow fitting the curves to the surface would indicate the formal potentials of each reaction. Obviously, the values of k_s and k_{chem} that fit curves (a) and (b) to the surface of Fig. 3 have to be the same as those used for Fig. 4. Accordingly, this preliminary fit in which experimental curves are accommodated onto the surfaces of Fig. 3 and Fig. 4 requires the iterative evaluation of different combinations of k_s and k_{chem} as well as of $\Gamma_{\text{CuAs}}^{\text{ini}}$ and $E^{0'}$. Once the experimental data of E_p and ΔI_p match both theoretical surfaces it is possible to consider that it has been achieved a rough estimation of the values of k_s and k_{chem} . The curves 3(a) and 4(a) match the shape of respective surfaces considering that $k_s = 0.05 \text{ s}^{-1}$ and $k_{\text{chem}} = 2 \times 10^2 \text{ s}^{-1}$, while curves 3(b) and 4(b) require that $k_s = 0.02 \text{ s}^{-1}$ and $k_{\text{chem}} = 0.05 \text{ s}^{-1}$ to achieve this. On the one hand it has to be considered that, despite those values are still roughly estimated values of k_s and k_{chem} , they are clearly indicating that the following chemical reaction is slowed down by the increment of the ratio copper/arsenic at the electrode surface. On the other hand, those values are an excellent starting point for simulating and fitting the voltammetric profiles of I_f and I_b . In other words, the most important use of the surfaces presented in Fig. 3 and Fig. 4 is to provide approximated values for k_s , k_{chem} , and K_{eq} , before starting with the fit of voltammetric curves.

Fig. 5 shows with symbols a set of experimental SW voltammograms recorded at different f . Those curves are the profiles of I_f and I_b associated with the voltammograms of $\Delta I_p f^{-1}$ analyzed in Fig. 1. The curves represented with lines indicate simulated profiles calculated with Eq (19). The blank signal, associated with the reduction of free Cu^{2+} at the SMDE, has been subtracted from each voltammetric curve. Although the shapes of SW voltammetric responses

are very similar to those of systems with irreversible charge transfer, the practically flat profile of I_b points out the presence of the following chemical coupled reaction [22].

The similarity between experimental and theoretical curves is quite remarkable. As it was pointed out above, the comparison of experimental data with the surfaces of Fig. 3 and Fig. 4 provided the starting point for simulating and fitting the voltammetric profiles of I_f and I_b . Fig. 5 shows the result obtained after the fitting process, which requires numerous iterative comparisons between experimental and simulated curves [15–19,26]. Once the fitting process was finished, all experimental voltammograms were simulated considering $n = 2$ and $\alpha = 0.53$, indicating that the electrochemical responses would correspond to the reduction of copper instead of arsenic. Therefore, for $E_{ac} = -0.4$ V and a large excess of Cu^{2+} ions, $\text{As}(\text{OH})_3$ would be directly reduced to an insoluble salt of As^{3-} [31,32]. Since there is a large excess of copper species with regards to those of arsenic, the concentration gradients related to Eqs (2) and (3) will depend on the concentration of arsenic species, while the chemical equilibria and consequently the slope of calibration curves would be proportional to the amount of both. The presence of a flat profile of I_b results not only because of the formation of AsH_3 , but also due to the impossibility of re-oxidizing copper in the absence of arsenide.

Suitable simulated curves have to resemble the shape of experimental voltammograms under different scanning conditions [15,16,19,26]. Therefore, the effect of E_{sw} on the shapes of I_f and I_b is analyzed in Fig. 6. The SW voltammograms were recorded for $f = 100$ Hz, different values of E_{sw} , and keeping other experimental conditions equal to those of Fig. 5. Again, symbols correspond to experimental responses and the lines are simulated curves obtained with the same set of parameters utilized in Fig. 5. The fits of experimental responses in this wide

range of E_{sw} values allowed us to improve the estimation of k_{chem} . Theoretical curves are very similar to experimental voltammograms. However, although the blank has been subtracted from each voltammetric curve, there is a cathodic current signal that does not belong to the Cu_xAs response. That signal of current is related to the generation of H_2 , which is an electrochemical reaction outside of the present study. It is interesting to note that for $E_{sw} > 50$ mV neither ΔI_p nor $\Delta E_{p1/2}$ exhibit relevant changes, while the value of E_p varies linearly with E_{sw} . For $E_{sw} < 20$ mV, the peak currents of I_f and I_b present negative values. This behavior indicates that the potential difference between the forward and backward pulses is not high enough to hinder the reduction of the compound Cu_xAs .

Every experimental voltammogram was properly simulated considering the direct transfer of 2 electrons and $\alpha = 0.53$. Accordingly, it is possible to assume that the electroanalytical responses would correspond to the reduction of copper instead of that of arsenic. Hence, adsorbed compounds of copper and arsenic could be considered as metal complexes where arsenide species would function as ligand. Bearing in mind the important role of protons on the accumulation and stripping steps associated with the determination of arsenic in the presence of copper, it is suggested to consider the presence of species such as $CuHAs$ at the surface of a SMDE. According to experimental data collected from literature, the peak current increases almost linearly with the bulk concentration of HCl and $\Delta E_p/\Delta pH \approx 30$ mV, both dependencies are consistent with the formation of $CuHAs$ prior to the charge transfer reaction [11,20,21]. In consequence, the stability constant of other feasible complexes and their possibility for diffusing within a mercury drop would be regulated by the ratio between copper, arsenic, and protons.

5. Conclusions

Mechanistic analysis of the cathodic stripping voltammetric response of the system copper-arsenite has been performed under SWV conditions. The study was carried out considering first the dependences of ΔI_p , E_p , and $\Delta E_{p1/2}$ on f , which was then used for simulating and fitting voltammetric profiles of I_f and I_b for different values of f and E_{sw} . The mathematical model used for the simulations considers that a surface confined reagent presents a charge transfer step followed by a chemical reaction. Although this kind of system involves several unknown parameters, the absence of the anodic peak in the response of SWV would indicate the formation of a stable non-electroactive chemical product. Therefore, it was possible to conclude first that $K_{eq} \leq 10^{-4}$ and then that $n = 2$. Since the variation of f affects the apparent reversibility of the chemical and electrochemical steps, it is essential to estimate the values of k_s and k_{chem} by comparing experimental responses with theoretical surfaces such as those of Fig. 3 and Fig. 4. Simulated curves resemble very well the shapes of experimental voltammograms when the direct transference of 2 electrons and $\alpha = 0.5$ are considered in the simulation process. Regardless that the simulation and fit of voltammetric responses have proved to be useful for inferring other parameters such as k_s , k_{chem} , α , and Γ_{CuAs}^{ini} , the precise value of those parameters should not be very relevant because they notably depend on the specific experimental conditions of scanning. On the contrary, the mechanistic analysis points out that the trace-analysis of arsenic in presence of copper could be considered as the reaction of a metal complex, in which Cu^{2+} is the metal cation and arsenide species function as ligand. The stability of those complexes at the surface a mercury electrode would depend not only on the applied potential but also on the ratio between copper, arsenic, and protons. The use of a mathematical model for simulating and fitting experimental responses has allowed us to provide a step forward on the interpretation of a

complex reaction mechanism and constitutes a valuable tool for studying other electrochemical reactions.

Acknowledgements

Financial support from the Consejo Nacional de Investigaciones Científicas y Tecnológicas (CONICET), Fondo para la Investigación Científica y Tecnológica (FONCYT) PICT-2018-3973, and Secretaría de Ciencia y Tecnología de la Universidad Nacional de Córdoba (SECyT-UNC) is gratefully acknowledged. J.G.A. and J.C.B.G. acknowledge CONICET for the granted fellowships.

CRedit-author-statement

Jenny Gómez Avila: Investigation. Software, Validation.

Jhan Carlos Burgos Gómez: Investigation. Software, Validation.

Angélica C. Heredia: Writing-Reviewing.

Mónica E. Crivello: Writing-Reviewing.

Fernando Sebastián Galay: Supervision. Software, Validation. Conceptualization. Writing-Reviewing and Editing. Project administration.

Declaration of interests

The authors declare that they have no known competing financial interests or personal relationships that could have appeared to influence the work reported in this paper.

The authors declare the following financial interests/personal relationships which may be considered as potential competing interests:

References

- [1] L. Fang, X. Min, R. Kang, H. Yu, S.G. Pavlostathis, X. Luo, Development of an anion imprinted polymer for high and selective removal of arsenite from wastewater, *Sci. Total Environ.* 639 (2018) 110–117.
- [2] L. Önnby, V. Pakade, B. Mattiasson, H. Kirsebom, Polymer composite adsorbents using particles of molecularly imprinted polymers or aluminium oxide nanoparticles for treatment of arsenic contaminated waters, *Water Res.* 46 (2012) 4111–4120.
- [3] Guidelines for Drinking-water Quality. Fact Sheet 372, (2012) <https://www.who.int/news-room/fact-sheets/detail/arsenic>
- [4] K.K. Jinadasa, E. Peña-Vázquez, P. Bermejo-Barrera, A. Moreda-Piñeiro, New adsorbents based on imprinted polymers and composite nanomaterials for arsenic and mercury screening/speciation: A review, *Microchem. J.* 150 (2020) 104886.
- [5] B. Radke, L. Jewell, J. Namieśnik, Analysis of arsenic species in environmental samples, *Crit. Rev. Anal. Chem.* 42 (2012) 162–183.
- [6] D.Q. Hung, O. Nekrassova, R.G. Compton, Analytical methods for inorganic arsenic in water: a review, *Talanta* 64 (2004) 269–277.
- [7] J.A. Cox, I.A. Rutkowska, P.J. Kulesza, Critical Review-Electrocatalytic Sensors for Arsenic Oxo Species, *J. Electrochem. Soc.* 167(2020) 037565.
- [8] Justyna Werner, Tomasz Grześkowiak, Agnieszka Zgoła-Grześkowiak, Ewa Stanisław, Recent trends in microextraction techniques used in determination of arsenic species, *TrAC Trend. Anal. Chem.* 105 (2018) 121–136.
- [9] J. Zima, C.M.G. Van den Berg, Determination of arsenic in sea water by cathodic stripping voltammetry in the presence of pyrrolidine dithiocarbamate, *Anal. Chim. Acta* 289 (1994) 291–298.

- [10] C. Núñez, V. Arancibia, M. Gómez, Determination of arsenic in the presence of copper by adsorptive stripping voltammetry using pyrrolidine dithiocarbamate or diethyl dithiophosphate as chelating-adsorbent agents. Effect of CPB on the sensitivity of the method, *Microchem. J.* 126 (2016) 70–75.
- [11] H. Li, R. B. Smart, Determination of sub-nanomolar concentration of arsenic(III) in natural waters by square wave cathodic stripping voltammetry, *Anal. Chim. Acta* 325 (1996) 25-32.
- [12] A. Profumo, D. Merli, M. Pesavento, Voltammetric determination of inorganic As(III) and total inorganic As in natural Waters, *Anal. Chim. Acta* 539 (2005) 245–250.
- [13] G. Henze, A.P. Joshi, R. Neeb, Determination of arsenic in the sub-ppb-range by differential pulse cathodic stripping voltammetry, *Fresenius' Z. Anal. Chem.* 300 (1980) 267.
- [14] D.E. Mays, A. Hussam, Voltammetric method for determination and speciation of inorganic arsenic in the environment—A review, *Anal. Chim. Acta* 646 (2009) 6–16.
- [15] F. Garay, V.M. Solis, Adsorptive Square Wave Voltammetry of metal complexes. Effect of ligand concentration. Part II: Experimental applications, *J. Electroanal. Chem.* 505 (2001) 109–117.
- [16] F. Garay, Adsorptive Square Wave Voltammetry of metal complexes. Effect of ligand concentration. Part IV: Experimental applications on Hg-ferron complexes, *J. Electroanal. Chem.* 548 (2003) 11–18.
- [17] F. Garay and V. M. Solis, Adsorptive square-wave voltammetry applied to study the reduction mechanism of Cu-sulfoxine and Cu-ferron complexes, *J. Electroanal. Chem.* 544 (2003) 1–11.
- [18] V. Mirčeski, Š. Komorsky-Lovrić, M. Lovrić, in: F. Scholz (Ed.), *Square-wave Voltammetry: Theory and Application*, Springer Verlag, Heidelberg, 2007.

- [19] M. Cuéllar, S.N. Vettorelo, P.I. Ortiz, F. Garay, Theoretical and experimental study of the catalytic cathodic stripping Square-wave voltammetry of chromium species, *J. Solid State Electrochem.* 20 (2016) 3279–3286.
- [20] R. Piech, W.W. Kubiak, Determination of trace arsenic with DDTC-Na by cathodic stripping voltammetry in presence of copper ions, *J. Electroanal. Chem.* 599 (2007) 59–64.
- [21] A.C. Heredia, J. Gómez Ávila, F. Garay, M.E. Crivello, Cathodic stripping Square-wave voltammetry for assessing As(III) removal with synthetic mixed oxides, *J. Solid State Electrochem.* 21 (2017) 3619–3629.
- [22] J. Gómez Ávila, A.C. Heredia, M.E. Crivello, F. Garay, Theory of Square-wave voltammetry for the analysis of an EC reaction mechanism complicated by the adsorption of the reagent, *J. Electroanal. Chem.* 840 (2019) 117–124.
- [23] J.M. Olmos, A. Molina, E. Laborda, I. Martínez-Ortiz, Effects of unequal diffusion coefficients and coupled chemical equilibria on square wave voltammetry at disc and hemispherical microelectrodes, *Electrochim Acta* 176 (2015) 1044–1053.
- [24] P. Priest, L.J. Pauwels, J. Neud, A lixiviation-study of copper arsenides in acid medium, *J. Inorg. Nucl. Chem.*, 36 (1974) 2493–2497.
- [25] J. O'M. Bockris, A.K. Reddy, M. Gamboa-Aldeco, *Modern Electrochemistry, Fundamentals of Electrode Processes* vol. 2A, second ed., Kluwer Academic Publishers, 2002, pp. 1183–1187.
- [26] F. Garay, M. Lovrić, V. Solis, Cathodic stripping square wave voltammetry of Cu(II)-oxine complexes. A mechanistic study, *J. Electroanal. Chem.* 478 (1999) 17–24.
- [27] M. Lovrić, Š. Komorsky-Lovric, Square-wave voltammetry of an adsorbed reactant, *J. Electroanal. Chem.* 248 (1988) 239–253.

- [28] Š. Komorsky-Lovrić, M. Lovrić, Square-wave voltammetry of quasi-reversible surface redox reactions, *J. Electroanal. Chem.* 384 (1995) 115–122.
- [29] S.N. Vettorelo, M. Cuéllar, P.I. Ortiz, F. Garay, Theory of Square-wave voltammetry for the analysis of a CE reaction mechanism complicated by the adsorption of the reactant, *J. Electroanal. Chem.* 852 (2019) 113519.
- [30] P. Salaün, B. Planer-Friedrich, C.M.G. van den Berg, Inorganic arsenic speciation in water and seawater by anodic stripping voltammetry with a gold microelectrode, *Anal. Chim. Acta* 585 (2007) 312–322.
- [31] Analytical Chemistry, Electrochemical Series, in *CRC Handbook of Chemistry and Physics*, Internet Version 2005, D.R. Lide, ed., CRC Press, Boca Raton, FL, 2005.
- [32] S. G. Bratsch, Standard Electrode Potentials and Temperature Coefficients in Water at 298.15 K, *J. Phys. Chem. Ref. Data*, 18 (1989) 1–21.

Fig. 1: (A) Experimental SWV responses of ($\Delta I f^{-1}$) obtained for a solution with $c_{As(OH)_3}^* = 50 \mu\text{g L}^{-1}$, $c_{HCl}^* = 0.3 \text{ M}$, $c_{Cu(2+)}^* = 0.5 \text{ mM}$, $E_{sw} = 50 \text{ mV}$, $dE = 5 \text{ mV}$, $E_{ac} = -0.4 \text{ mV}$, $t_{ac} = 60 \text{ s}$, $f / \text{Hz} =$ (a) 20, (b) 50, (c) 100, (d) 150, and (e) 200. (B) Dependence of ΔI_p on f .

Fig. 2: (A) Experimental SWV responses of ($\Delta I f^{-1}$) obtained for a solution with $c_{As(OH)_3}^* = 30 \mu\text{g L}^{-1}$, $c_{HCl}^* = 1 \text{ M}$, $c_{Cu(2+)}^* = 1 \text{ mM}$, $E_{sw} = 50 \text{ mV}$, $dE = 5 \text{ mV}$, $E_{ac} = -0.4 \text{ mV}$, $t_{ac} = 30 \text{ s}$, $f / \text{Hz} =$ (a) 25, (b) 50, (c) 100, (d) 150, and (e) 200. (B) Dependence of ΔI_p on f .

Fig. 3: Theoretical dependence of $\Delta \Psi_p$ on $\log(k_s f^{-1})$ and $\log(k_{chem} f^{-1})$ for $E_{sw} = 50 \text{ mV}$, $dE = 5 \text{ mV}$, $K_{eq} = 10^{-4}$, and $n = 2$. Curves (a) and (b) are experimental values of ($\Delta I_p f^{-1}$) obtained from

the data of Fig. 1 and Fig. 2, respectively. Each set of experimental data was multiplied by a constant to match the values of the surface.

Fig. 4: Theoretical dependence of E_p on $\log(k_s f^{-1})$ and $\log(k_{chem} f^{-1})$ for $E_{sw} = 50$ mV, $dE = 5$ mV, $K_{eq} = 10^{-4}$, and $n = 2$. Curves (a) and (b) are experimental values of E_p obtained from the data of Fig. 1 and Fig. 2, respectively.

Fig. 5: (Symbols) Experimental SWV responses of $I_f f^{-1}$ and $I_b f^{-1}$ obtained for a solution with $c_{As(OH)_3}^* = 50 \mu\text{g L}^{-1}$, $c_{HCl}^* = 0.3$ M, $c_{Cu(2+)}^* = 0.5$ mM, $E_{ac} = -0.4$ V, $t_{ac} = 60$ s. (Lines) Theoretical fits performed with Eq 19 considering $\alpha = 0.53$, $n = 2$, $K_{ad} = 1$ cm, $K_{eq} \leq 10^{-4}$, $k_s = 0.05$ s $^{-1}$ y $k_{chem} = 1 \times 10^3$ s $^{-1}$, $E^{o'} = (0.75 \pm 0.01)$ V, and $\Gamma_{CuAs} = (4.1 \pm 0.5) \times 10^{-10}$ mol cm $^{-2}$. In both cases $E_{sw} = 50$ mV, $dE = 5$ mV, $f / \text{Hz} =$ (A) 5, (B) 30, (C) 75 y (D) 150.

Fig. 6: (Symbols) Experimental SWV responses of $I_f f^{-1}$ and $I_b f^{-1}$ obtained for a solution with $c_{As(OH)_3}^* = 50 \mu\text{g L}^{-1}$, $c_{HCl}^* = 0.3$ M, $c_{Cu(2+)}^* = 0.5$ mM, $E_{ac} = -0.4$ V, $t_{ac} = 60$ s. (Lines) Theoretical fits performed with Eq (19) considering $f = 100$ Hz, $dE = 5$ mV, $\alpha = 0.53$, $n = 2$, $K_{ad} = 1$ cm, $K_{eq} = 10^{-4}$, $k_s = 0.05$ s $^{-1}$ and $k_{chem} = 1 \times 10^3$ s $^{-1}$, $E^{o'} = (0.741 \pm 0.006)$ V, $\Gamma_{CuAs} = (4 \pm 1) \times 10^{-10}$ mol cm $^{-2}$, and $E_{sw} / \text{mV} =$ (A) 10, (B) 20, (C) 50, (D) 75, and (E) 150.

Table 1: Values of $\Delta E_{p1/2}$ measured from theoretical SW voltammograms calculated with Eq (19) for systems with different n and k_s . Relevant scan parameters are $E_{sw} = 50$ mV, $dE = 5$ mV, and $f = 100$ Hz. The informed errors depend on the value of dE .

n	Reversible ($k_s = 10^3$ s $^{-1}$)	Quasi-reversible	Irreversible ($k_s = 10^{-4}$ s $^{-1}$)

1	$(65 \pm 3) \text{ mV}$	$70 \leq \Delta E_{p1/2} / \text{mV} \leq 120$	$(125 \pm 3) \text{ mV}$
2	$(32 \pm 3) \text{ mV}$	$35 < \Delta E_{p1/2} / \text{mV} \leq 60$	$(65 \pm 3) \text{ mV}$
3	$(23 \pm 3) \text{ mV}$	$25 < \Delta E_{p1/2} / \text{mV} < 40$	$(42 \pm 3) \text{ mV}$

Highlights

- Mechanistic analysis of the CS-SWV response of the system copper-arsenic is presented.
- This would be the first time that a mathematical model of this complexity has been used for simulating this kind of experimental responses.
- The simulation and fit of the experimental curves are step by step described.
- All simulations indicate that the reduction of copper instead of arsenic is taking place during the cathodic stripping corresponding to the electrochemical detection of arsenic.
- Changes in the scan-rate simultaneously affect the apparent reversibility of all involved kinetic constants.