Single pulse voltammetry at constant sphericity

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Abstract

Single pulse voltammetry (SPV) has been applied to the study of a charge transfer reaction at a static mercury drop electrode (SMDE) under constant sphericity conditions. Amalgam formation for both a reversible and a slow electrode process has been considered. The use of constant sphericity allows us, on the one hand, to discriminate between kinetic and curvature effects and, on the other, to reduce the undesirable effects from the uncompensated IR drop. Methods for determining heterogeneous kinetic parameters are also proposed and experimental examples of fast and slow electrode processes under constant sphericity conditions in normal pulse voltammetry (NPV) are presented.

Keywords: Normal pulse voltammetry; Amalgamation; Spherical diffusion; Charge transfer kinetics

1. Introduction

Single pulse voltammetry (SPV) has been largely used in kinetic electrochemical studies. The theoretical development of this technique has been carried out for both plane and spherical electrodes [1–11].

The experimental design and the necessary theoretical background are well established when a kinetic study with plane electrodes is performed. Thus, in general, the use of dimensionless parameters is preferable for theoretical developments or for numerical calculations, and is imperative if working curves for analysis of experimental results have to be generated. In order to obtain dimensionless time and distance parameters, it is necessary to use a reference time ($t_R$) and a reference distance ($x_R$), usually expressed as $x_R = \sqrt{D_A t_R}$, where $D_A$ is the diffusion coefficient of the electroactive species initially present in the electrolyte solution. In techniques where the perturbation is dependent on time, it is easy to find a characteristic time related to the experimental time scale, which can be used as the reference time. For example, in linear sweep voltammetry the reference time can be appropriately obtained from the quotient between the potential sweep amplitude and the sweep rate.

A particularly simple and fruitful situation for obtaining working curves, which are useful for kinetic studies, appears when the applied perturbation is independent of time (as occurs in chronoamperometry or in the collection of chronoamperometric experiments which gives rise to a single pulse voltammogram). Under these conditions, if a kinetic process (either homogeneous or heterogeneous) is present, the reference time can be taken from the relevant kinetic parameter. Thus, if a first order homogeneous chemical reaction coupled to the electrode process is present, $t_R$ can be chosen as $t_R = 1/k_1$, where $k_1$ is the first order rate constant; if the homogeneous chemical reaction is a second order one, then $t_R = C_A^\infty/k_2$, where $C_A^\infty$ is the bulk concentration of the electroactive species initially present in solution and $k_2$ the second order rate constant; and so on. Similarly, if the kinetic behavior is a consequence of a slow heterogeneous charge transfer reaction, $t_R$ may be taken as $t_R = D_A/k_2^*S$, where $k_2^*$ is the standard heterogeneous rate constant for the charge transfer reaction. By making the appropriate changes in the diffusion and kinetic equations, it is easily shown that for each dimensionless potential (with the rest of the relevant parameters, like the ratio between diffusion coefficients and the electron transfer coefficient, remaining
constant) the quotient $I/I_d$ (where $I$ is the measured current at a given potential and time and $I_d$ is the diffusion current at the same time) is an exclusive function of a dimensionless parameter $\gamma$ that contains both the electrolysis time and the kinetic parameter. $I/I_d$ vs. $\gamma$ working curves can be obtained in this way. Thus, by carrying out measurements at different time-values, a lot of experimental points can be placed on the same working curve, and reliable values of the kinetic parameter can be found by adjusting the $\gamma$-values, obtained from the working curve, with the experimental time-values, such that a linear relationship is found.

However, this very desirable situation disappears when spherical electrodes are used. Spherical electrodes are commonly used in SPV because mercury electrodes (mainly the static mercury drop electrode (SMDE)) are the most appropriate under the experimental conditions required in this technique, in which each pulse is applied after re-establishment of initial equilibrium conditions. However, for numerical calculations in these electrodes, it is necessary to consider a new distance-related parameter: the dimensionless electrode radius. When the electrode radius is converted into a dimensionless parameter as $R_0 = r_0/x_R$, the working curves generated (the construction of one of these curves implies that this new parameter is kept constant) are useless because the kinetic parameter and the dimensionless electrode radius are both unknown. Hence, the easy and reliable method of the working curves becomes worthless.

An alternative that allows us to use working curves (and to take some points in the same curve in order to obtain the respective kinetic parameter by means of linear fitting) is to work at constant sphericity. Constant sphericity has been introduced in linear and triangular sweep voltammetry for mercury electrodes [12,13] and is based on a simple principle: the electrode radius and the reference time have to be changed simultaneously in order to keep $R_0$ constant. This implies the selection of a reference time independent of the kinetic parameters and chosen by the user (a good selection in SPV may be the duration of the kinetic study in this paper to the heterogeneous charge transfer reaction can be obtained. In order to show how to work at constant sphericity, we have restricted the kinetic study in this paper to the heterogeneous charge transfer process, but very similar procedures can be applied to homogeneous chemical reactions coupled to electrode processes.

2. Experimental

Experiments were carried out with a computer driven potentiostat and pulse generator designed and constructed by QUICELTRON (Spain). The experimental electrochemical ensemble was constructed so that analogue to digital converters were placed very near to the electrochemical cell. Thus, the transmission of the data to the computer was carried out in digital format, which greatly reduced the noise of the signals measured. All computer programs for user interface, pulse generation, data acquisition and data transformation were written in our laboratory using Borland C++ Builder. A static mercury drop electrode was constructed using a dropping mercury electrode, EA 1019-1 (Metrohm), to which a homemade valve was sealed. Depending on the DME used, the mercury pressure and the length of time the valve was open, electrode radii in the range 0.006–0.05 cm were obtained. For a given DME and mercury pressure the range was slightly lower. A saturated calomel electrode and a platinum electrode were used as reference and auxiliary electrodes. Chemicals were analytical grade from Merck and were used as received. In all experiments, the temperature was kept constant at $25 \pm 0.2 \, ^\circ C$. For calculations, we have used literature values for the diffusion coefficients: $D_{Cd^{2+}} = 7.2 \times 10^{-6} \, cm^2 \, s^{-1}$ [12], $D_{Cd(Hg)} = 1.6 \times 10^{-5} \, cm^2 \, s^{-1}$ [12], $D_{Zn^{2+}} = 6.7 \times 10^{-6} \, cm^2 \, s^{-1}$ [14] and $D_{Zn(Hg)} = 1.9 \times 10^{-5} \, cm^2 \, s^{-1}$ [14].

3. Theory

For the charge transfer reaction

$$A + ne^- \rightarrow B$$

the mass transport to the SMDE and the boundary value problem associated with this process, where the
product B is soluble either in solution or in the electrode, is defined by
\[ \delta_A c_A = \delta_B c_B = 0 \]  
(1)

\[ t = 0, \quad r \geq r_0 \]  
\[ t > 0, \quad r \to \infty \]  
: \[ c_A = c_A^* \]  
(2)

\[ t = 0, \quad r \geq r_0 \]  
\[ t > 0, \quad r \to \infty \]  
: \[ c_B = 0 \]  
(SOLUBLE) \hspace{1cm} (3a)

\[ t = 0, \quad r \leq r_0 \]  
: \[ c_B = 0 \]  
(AMALGAM) \hspace{1cm} (3b)

\[ t > 0, \quad r = 0 : \quad D_B \frac{\partial^2 c_B}{\partial r^2} = 0 \]  
(AMALGAM) \hspace{1cm} (3c)

\[ I(t) = D_A \left( \frac{\partial c_A}{\partial r} \right)_{r_0} = D_B \left( \frac{\partial c_B}{\partial r} \right)_{r_0} \]  
(4)

\[ I(t) = k_A c_A (r_0, t) - k_B c_B (r_0, t), \]  
(5)

where the operator \( \hat{\delta} \) (i = A, B) in Eq. (1) is given by
\[ \hat{\delta} \equiv \frac{\partial}{\partial t} - D \left( \frac{\partial^2}{\partial r^2} + \frac{2}{r} \frac{\partial}{\partial r} \right). \]  
(6)

The upper sign in Eq. (4), where two signs appear, refers to a solution soluble product and the lower one to the amalgam formation.

The heterogeneous rate constants \( k_t \) and \( k_b \), which depend on the potential applied, are defined by
\[ k_t (E) = k_t \exp \left( \frac{-z n F}{R T} (E - E^0) \right), \]  
(7)

\[ k_b (E) = k_b \exp \left( \frac{(1 - z) n F}{R T} (E - E^0) \right), \]  
(8)

where the potential \( E \) remains constant for each potential step.

For the purposes of simulation and construction of working curves, it is appropriate to normalize the variables using the expressions
\[ C_i = \frac{c_i}{c_A^*} \quad (i = A, B), \]  
(9)

\[ \Omega = \frac{t}{t_R}, \]  
(10)

\[ R = \frac{r}{\sqrt{(D_A t_R)}}, \quad R_0 = \frac{r_0}{\sqrt{(D_A t_R)}}, \]  
(11)

\[ G = \frac{R_0^{1/2}}{n F A D_A^{1/2} c_A^*}, \]  
(12)

\[ K_S = \frac{k_{t R}^{1/2}}{D_A^{1/2}}, \]  
(13)

\[ \eta = \frac{n F}{R T} (E - E^0), \]  
(14)

where \( t_R \) is a chosen experimental reference time, which for convenience we have made coincident with the duration of each potential pulse. Thus, in a given pulse, the normalized time, \( \Omega \), runs between 0 and 1.

The differential equations system corresponding to the diffusion are then
\[ \frac{\partial c_A}{\partial \Omega} = \frac{\partial^2 c_A}{\partial R^2} + \frac{2}{R} \frac{\partial c_A}{\partial R}, \]  
(15)

\[ \frac{\partial c_B}{\partial \Omega} = \frac{1}{\gamma^2} \left( \frac{\partial^2 c_B}{\partial R^2} + \frac{2}{R} \frac{\partial c_B}{\partial R} \right) \]  
(16)

and the normalized boundary conditions become
\[ \Omega = 0, \quad R \geq R_0 \]  
\[ \Omega > 0, \quad R \to \infty \]  
: \[ c_A = 1 \]  
(17)

\[ \Omega = 0, \quad R \geq R_0 \]  
\[ \Omega > 0, \quad R \to \infty \]  
: \[ c_B = 0 \]  
(SOLUBLE) \hspace{1cm} (18a)

\[ \Omega = 0, \quad R \leq R_0 : \quad C_B = 0 \]  
(AMALGAM) \hspace{1cm} (18b)

\[ \Omega > 0, \quad R = 0 : \quad \left( \frac{\partial C_B}{\partial R} \right)_{r=0} = 0 \]  
(AMALGAM) \hspace{1cm} (18c)

\[ \Omega > 0, \quad R = R_0 : \quad G = \left( \frac{\partial C_A}{\partial R} \right)_{r_0} = \gamma^2 \left( \frac{\partial C_B}{\partial R} \right)_{r_0} \]  
(19)

\[ G = K_s \left( C_A (R_0, \Omega) e^{-\gamma} - C_B (R_0, \Omega) e^{(1-\gamma) \gamma} \right), \]  
(20)

where
\[ \gamma = \left( \frac{D_A}{D_B} \right)^{1/2}. \]  
(21)

The numerical calculations in this paper were carried out with the Crank–Nicolson method [15], with implicit calculations for surface concentrations. The application of the method to this process is described in [12], where we find a recursive relationship that allows us to carry out numerical calculations for surface concentrations, which are applicable for obtaining theoretical curves for SPV at a SMDE. It is well known that the Crank–Nicolson method can give rise to numerical solutions showing oscillations connected with the initial conditions [16,17]. However, in our calculations we have used dimensionless time intervals of amplitude 0.00025 and dimensionless distance intervals of amplitude 6/1000 in
the electrolyte solution and \( R_0 \) into the electrode. Under these conditions, both concentration profiles and dimensionless current were monitored and no appreciable oscillations were observed. Moreover, numerical results are indistinguishable from those obtained with smaller intervals. Programs were written in C++ using Borland C++ Builder 5.0 using double precision arithmetic and running under Windows 2000.

4. Results and discussion

There is an extensive theoretical background in the literature on the behavior of electrode processes in the several variants of SPV. However, in order to make appropriate use of the boundary condition (3c), or its dimensionless equivalent (18c), we have calculated the theoretical curves using digital simulation procedures, more specifically, the Crank–Nicolson method, with implicit calculations for surface concentrations.

The degree of sphericity for calculated or experimental curves is given by the value of \( R_0 \). Usual values of \( R_0 \) are in the range 2–25. The influence of \( R_0 \) on the experimental curves is always important for both fast and slow processes as well as when the electrode process product is soluble in the electrolyte solution or in the electrode. As a representative example of this influence, Fig. 1 shows the \( G–\Omega \) curves calculated at two values of the dimensionless potential, \( \eta \), in the case of a slow charge transfer reaction and for an amalgam-forming system. As can be seen, the influence of \( R_0 \) is large and cannot be ignored.

As is well known, the main tool in any kinetic study is the appropriate choice of the experimental time scale. If this change is made keeping the electrode radius constant, it is found that the dimensionless variable \( R_0 \) varies from one experiment to another (according to Eq. (11)), which prevents us from working with a series of experimental data on the same working curve. An easy alternative is to keep \( R_0 \) constant, i.e., to work at constant sphericity. This can be achieved experimentally by simultaneously modifying the electrode radius and the time-scale of the experiment in such a way that the product \( R_0^{1/2} \) remains constant.

Note that for a reversible (fast) heterogeneous charge transfer reaction, if we carry out a series of experiments for a given system in which the variable \( R_0 \) is kept constant, the resulting experimental curves will be superimposed if the current is normalized to the dimensionless variable \( G \) (see Eq. (12)). Moreover, if the experiments correspond to a series of single pulse voltammograms, in which a diffusion controlled current \( (I_d) \), in turn proportional to the electrode area, can frequently be obtained, then an alternative way for normalizing the current \( I \) (preventing errors proceeding from electrode area determination) is by dividing \( I \) by \( I_d \). This is the alternative chosen in Fig. 2, in which we have selected two series of SPV experiments carried out at constant sphericity for two values of the dimensionless time \( \Omega \), corresponding to the system \( \text{Cd}^{2+}/\text{Cd}(\text{Hg}) \). The influence of \( R_0 \) on the voltammograms depends on the behavior of the reduction product (if amalgamation takes places or a solution soluble product is obtained); it depends also on the reversibility of the charge transfer reaction and on the value of the parameter \( \gamma \). The influence of sphericity on the voltammograms is maximum when amalgamation takes place, even in the case using normalized currents. This is why we have selected the system \( \text{Cd}^{2+}/\text{Cd}(\text{Hg}) \) to construct Fig. 2. In each chronoamperogram constituent of the normal pulse voltammogram, the dimensionless time, \( \Omega \), changes from 0 to 1. By taking several values of \( \Omega \), we are working in several time scales in the same experiment. Although the IR drop effect may give rise to important distortions in the normal pulse voltammograms [18], this effect disappears under constant sphericity conditions. Thus, the curves obtained for a reversible system are superimposed very well and no apparent kinetic behavior of the heterogeneous process is noted by the IR drop effect. This is not surprising, considering that we are working at constant sphericity: for a given reversible process at fixed values of \( \Omega \) and \( \eta \), the value of \( G \) obtained is also fixed. Consequently, under these conditions, \( I \) is proportional to \( R_0^{1/2} \) (according to Eq. (12)). Moreover, taking into account that the uncompensated ohmic resistance depends linearly on \( R_0^{-1} \) [19], it is found that the product IR remains constant under fixed \( R_0^{1/2} \) conditions. In short, the IR drop acts in the same way on all the curves.

\[ \Omega \]

**Fig. 1.** Effects of electrode sphericity on the chronoamperometric response for a slow charge transfer reaction and an amalgam-forming system. \( k = 0.3, \gamma = 0.5, \gamma = 1 \). The values of \( R_0 \) are: (1) 2, (2) 5, (3) 25. The \( \eta \)-values are shown on the curves.
In Fig. 3, which corresponds to a system in which amalgamation takes place, we have plotted the $G/G_d$ vs. $g$ curves (equivalent to $I/I_d$ vs. $g$ curves) calculated for several $K_S$-values and two $\Omega$-values. As is to be expected, the corresponding voltammograms move away from the reversible behavior as $K_S$ decreases, and more so for the lower $\Omega$-value (taking into account that lower $\Omega$-values correspond to shorter electrolysis times). This is the behavior expected for a system characterized by a slow charge transfer reaction when an experimental series of voltammograms is obtained under constant sphericity conditions but for different pulse durations, i.e., by changing the experimental time scale. The large dependence of the voltammograms on $K_S$ noted under these conditions can be very useful in determining experimentally the $K_S$-value corresponding to a given experimental system. Appropriate working curves can be constructed from which, for a fixed potential, we can associate a given $I/I_d$-value with a $K_S$-value.

Fig. 4 shows an example of these working curves obtained at different values of the dimensionless potential for the two possible types of behavior of the product: amalgamation and solution in the electrolyte. As is evident, a total coincidence of the curves for both cases is noted as $K_S$ reaches very low values, whereas the differences between the two kinds of behavior of the product appear for increasing $K_S$-values. They are maximal, therefore, when the charge transfer reaction behaves as reversible.

If a good experimental design is achieved, it will be possible to obtain simultaneously a set of normal pulse voltammograms corresponding to many $X$-values (i.e., by measuring the current at the selected pulse duration and at shorter time-values in each potential step). In this

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**Fig. 2.** Experimental $I/I_d$ vs. $E$ curves obtained at a SMDE for a 1 mM Cd$^{2+}$ solution in 0.1 M KNO$_3$. $n_f g^{1/2} = 0.0289$ cm s$^{-1/2}$, $t_R$ (s): 0.049, 0.081, 0.157, 0.241, 0.445, 0.719, 1.195 and 1.503. The $\Omega$-values chosen are shown on the curves.

**Fig. 3.** Dependence of the $G/G_d$ vs. $g$ curves on $K_S$ for an amalgam-forming system. $R_0 = 5$, $\gamma = 1$ and $\lambda = 0.5$. The values of $K_S$ are: (1) 0.2, (2) 0.5, (3) 1. The curve corresponding to a reversible process (curve 4) is also included. The $\Omega$-values chosen are shown on the curves.
way, different time scales in the same experiment can be obtained, and, consequently, responses near to or far from reversible behavior. An illustrative example of how the $X$-value selected gives rise to different working curves is shown in Fig. 5, generated for two $X$-values ($X = 0.05$ and 1) and different values of the dimensionless potential. Note that a given charge transfer reaction behaves as more irreversible as $\Omega$ decreases, since for a fixed $K_S$-value ($K_S \leq 1$) the corresponding $I/I_d$-value is smaller. This situation is reversed when the charge transfer reaction behaves as reversible (fast electrode process) and the dimensionless potential applied is not that corresponding to the cathodic diffusion current in question.

For the determination of heterogeneous kinetic parameters from experimental data, we have to take into account the simultaneous influence of $x$ and $k_S$ on the intensity of the current. However, this influence varies greatly, depending on the selected potential. As is well known, and is evident from Eqs. (20) and (12)–(14), the current-value for a quasi-reversible charge transfer reaction is independent of the kinetic parameter $a$ when the potential applied is equal to $E^0$ (i.e., $\eta = 0$). It is also evident that the influence of $x$ (in the kinetic region of the working curves) is larger, the further the potential is from the formal potential of the system. This behavior is illustrated in Fig. 6.

Given the above, a good procedure for determining the kinetic parameters may begin by the determination of $k_S$ using a potential which is close to the formal potential of the system, where the dependence on $x$ is very weak. For this purpose, we need (unless we already know) the value of the formal potential of the system under our experimental conditions. Fig. 7 is useful for this purpose. If we can achieve electrolysis times of sufficient length to obtain reversible behavior, we can determine the $G/G_d (=I/I_d)$ value corresponding to

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**Fig. 4.** Influence of the product behavior on the working curves $G/G_d$ vs. $\log K_S$. $R_0 = 5$, $\Omega = 1$, $\gamma = 1$ and $x = 0.5$. The values of $\eta$ are shown on the curves for the following cases: (A) solution soluble product; (B) amalgamation of product.

**Fig. 5.** Effects of $\Omega$ on the working curves $G/G_d$ vs. $\log K_S$ for an amalgam-forming system. $\Omega$-values are: (a) 0.05; (b) 1.0. $R_0 = 5$, $\gamma = 1$ and $x = 0.5$. The values of $\eta$ are shown on the curves.

**Fig. 6.** Influence of $x$ on the working curves $G/G_d$ vs. $\log K_S$. $x$-values are: (1) 0.3, (2) 0.5, (3) 0.7. $\Omega = 1$. The values of $\eta$ are shown on the curves. Other conditions as in Fig. 5.
for given values of $R_0$ and $c$, and from this, the formal potential using the experimental single pulse voltammogram. Finally, the heterogeneous kinetic parameter $\alpha$ may be evaluated from working curves \( G/G_d \) plotted in Fig. 8, for a given $K_S$-value, $R_0$ fixed and different values of $\eta$. As is clear, each curve corresponding to a different $\eta$-value provides us with information concerning the $\alpha$-value and may be used for kinetic determination purposes. However, we can also use other potentials to determine $K_S$, by selecting the $\alpha$-value that gives rise to the best fit to experimental data. This is equivalent to the simultaneous determination of both parameters. In any case, a large amount of kinetic data can be obtained from a constant sphericity series of normal pulse voltammograms.

In order to show the above-described procedure, we have carried out a series of constant sphericity experiments for the system $\text{Zn}^{2+}/\text{Zn(Hg)}$ in 1 M KNO$_3$ in which the heterogeneous charge transfer reaction is slow. Fig. 9 (very similar to Fig. 3) has been obtained for a pulse duration of between 49 ms and 1.50 s. These experimental data can also be presented in a similar way to that shown in the working curves $G/G_d$ vs. $\log K_S$, fixing the potential and plotting the ratio $I/I_d$ vs. $\log \tau_R$. Note that $\eta$ and $K_S$ are related by Eq. (13). This is done

\begin{align*}
\eta = 0 & \text{ for given values of } R_0 \text{ and } \gamma, \text{ and from this, the formal potential using the experimental single pulse voltammogram. Finally, the heterogeneous kinetic parameter } \alpha \text{ may be evaluated from working curves } G/G_d \text{ plotted in Fig. 8, for a given } K_S \text{-value, } R_0 \text{ fixed and different values of } \eta. \text{ As is clear, each curve corresponding to a different } \eta \text{-value provides us with information concerning the } \alpha \text{-value and may be used for kinetic determination purposes. However, we can also use other potentials to determine } K_S, \text{ by selecting the } \alpha \text{-value that gives rise to the best fit to experimental data. This is equivalent to the simultaneous determination of both parameters. In any case, a large amount of kinetic data can be obtained from a constant sphericity series of normal pulse voltammograms.}

& \text{In order to show the above-described procedure, we have carried out a series of constant sphericity experiments for the system } \text{Zn}^{2+}/\text{Zn(Hg)} \text{ in 1 M KNO}_3 \text{ in which the heterogeneous charge transfer reaction is slow. Fig. 9 (very similar to Fig. 3) has been obtained for a pulse duration of between 49 ms and 1.50 s. These experimental data can also be presented in a similar way to that shown in the working curves } G/G_d \text{ vs. } \log K_S, \text{ fixing the potential and plotting the ratio } I/I_d \text{ vs. } \log \tau_R. \text{ Note that } \eta \text{ and } K_S \text{ are related by Eq. (13). This is done}
\end{align*}
The points corresponding to a given potential and corresponding to the rising part of the voltammograms in Fig. 10, in which we have selected a set of potentials 
values obtained for value can be used on the same working curve, and the 
values applied are in the range between 

-0.973 (curve 1) to -1.096 V (curve 28). The \( \Omega \)-values chosen are shown on the curves.

in Fig. 10, in which we have selected a set of potentials corresponding to the rising part of the voltammograms. The points corresponding to a given potential and \( \Omega \)-value can be used on the same working curve, and the values obtained for \( K_S \) can be plotted vs. \( t_R^{1/2} \), giving rise to a linear dependence. From the corresponding slope, the \( K_S \)-value is easily obtained.

The value of the potential corresponding to \( E^0 \) can be evaluated following the procedure described above, and it is an intermediate value to those corresponding to the curves 9 and 10 in Fig. 10. The curve corresponding to \( E^0 \) was evaluated by linear interpolation using curves 9 and 10. The 95\% confidence interval for \( K_S \) at this potential was \( 4.28 \pm 0.16 \times 10^{-3} \) cm s\(^{-1} \). Moreover, using this \( K_S \)-value and the procedure previously described, an \( x \)-value equal to \( 0.270 \pm 0.005 \) was obtained when \( n \)-values applied are in the range between -2 and -5. Very similar results are obtained using other values of the potential and when selecting the \( x \)-value that gives rise to the best fit.

It is well known that the apparent kinetic parameters for the heterogeneous electrochemical reduction of \( \text{Zn}^{2+} \) are strongly dependent on the supporting electrolyte conditions. Our kinetic results are in good agreement with the literature values \([4,14,20–24]\). Literature \( x \)-values in the range 0.23–0.30 were always reported, while \( K_S \)-values of \( 4.24 \times 10^{-3} \) cm s\(^{-1} \) \([14]\) and \( 3.5 \times 10^{-5} \) cm s\(^{-1} \) \([21,22]\) for 1.0 M \( \text{KNO}_3 \), \( 3.3 \times 10^{-3} \) cm s\(^{-1} \) for 1.05 M \( \text{NaNO}_3 \) \([4]\), \( 2.8 \times 10^{-3} \) cm s\(^{-1} \) for 1.0 M \( \text{NaNO}_3 \) \([20]\), \( 2.19 \times 10^{-3} \) cm s\(^{-1} \) for 1.05 M \( \text{NaNO}_3 \) \([23]\) and \( 5.25 \times 10^{-3} \) cm s\(^{-1} \) for 1.0 M \( \text{NaClO}_4 \) \([24]\) were obtained, which are, in all cases coherent with our results.

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