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Study of CE mechanisms by square wave voltammetry: Cd(II) + nitrilotriacetic acid and Cd(II) + aspartic acid systems

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Abstract

The use of square wave voltammetry (SWV) at a hanging mercury drop electrode to study a chemical reaction preceding a reversible electron transfer (CE mechanism) is reported. Two cases were analysed: cadmium(II) + nitrilotriacetic acid and the cadmium(II) + aspartic acid systems. In both situations the homogeneous reaction in buffered solutions and in the presence of an excess of ligand was considered to be first order.

Experimental data were analysed in terms of theory of SWV for kinetic systems. Rate constants of dissociation of the complexes of cadmium with nitrilotriacetic acid and aspartic acid were determined using a numerical procedure based on a one variable fit. The results obtained are in good agreement with published values where other techniques have been used, in particular cyclic voltammetry.

Keywords: CE mechanism; Square wave voltammetry

1. Introduction

Square wave voltammetry (SWV) employing large amplitudes and large potential scan rates is a modern technique with considerable analytical and mechanistic capabilities [1,2]

One of the major advantages of SWV when compared with other pulse techniques lies in its ability to achieve high effective sweep rates; this greatly reduces the time needed to measure voltammograms over a wide potential range. Also, like all pulse techniques, SWV discriminates well against charging currents. An additional advantage is that the shape of the reversible voltammetric response and its position on the potential scale are almost independent of electrode geometry [3,4]. This opens many important possibilities for new applications, such as the use of electrodes with ill-defined geometry and for diffusion perturbed by convection.

As happens with other differential techniques, the sensitivity of SWV depends on reversibility. However, this is not a handicap since the quality of the analytical signal can be improved by judicious choice of the square wave parameters [5,6].

Owing to the wide time scale available in SWV, i.e. the frequency range, kinetic information can be extracted from systems complicated by electrode kinetics or by homogeneous chemical reactions coupled to the redox reaction.

The theory of SWV has been described for the first order kinetic cases involving slow electron transfer, preceding and following chemical reactions and catalytic chemical reactions [1,7]. The case of slow heterogeneous electron transfer was examined experimentally using the redox couple Zn(II)/Zn(Hg) as the electrochemical system [8,9]. The pseudo-first order catalytic process was tested by determination of rate constants for $Tl^{3+} + NH_2OH$, $Tl^{3+} + ClO_3^-$ and $Fe^{2+} + NH_2OH$ redox catalytic systems [10].

The theory of SWV was also extended to include the ECE mechanism and used to obtain the first order rate constants for the chemical step of the reduction of *p*-nitrosophenol [11].

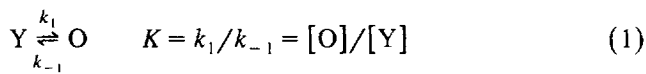
In this work we report the use of SWV at a hanging mercury drop electrode (HMDE) to study a chemical reaction preceding a reversible electron transfer, i.e. a CE mechanism. Two cases were analysed: the cadmium(II) + nitrilotriacetic acid (NTA) and the cadmium(II) + aspartic acid (ASP) systems. The former has been widely studied as an example of a CE mechanism since the pioneering

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work of Koryta [12,13] by cyclic voltammetry [14] and recently by differential pulse polarography [15]. The cadmium(II) + ASP system was previously studied by cyclic voltammetry [16,17], and illustrates the situation of the existence of two complexes in solution in equilibrium. In both cases the homogeneous reaction was considered to be pseudo-first order by operating in buffered solutions and using an excess of ligand.

2. Theoretical considerations

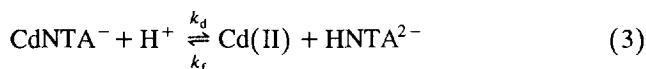
The following generalised model for a CE mechanism was used:



where Y and O are in chemical equilibrium in solution defined by the equilibrium constant K , k_1 and k_{-1} being the first order rate constants of the forward and backward reactions respectively. The species O undergoes a reversible reaction at the electrode and R is its reduced form.

2.1. Cadmium(II) + NTA

As is well known [13–15], in Cd(II) + NTA solutions two parallel homogeneous reactions take place: a direct dissociation of the CdNTA complex and a much faster acid-assisted path described by

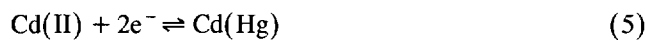


with an equilibrium constant K_{eq} given by

$$K_{\text{eq}} = [\text{Cd(II)}][\text{HNNTA}^{2-}]/[\text{CdNTA}^-][\text{H}^+] \quad (4)$$

k_d and k_f being the rate constants of dissociation and formation respectively.

Reduction of free cadmium from the dissociation of the complex occurs reversibly at a mercury electrode



being influenced by the preceding chemical reaction.

Working in buffered solutions and with an excess of ligand, we can define the constant

$$K = [\text{Cd(II)}]/[\text{CdNTA}^-] \quad (6)$$

which can be expressed as

$$K = [\text{H}^+]/\beta K^{\text{H}} \alpha [\text{NTA}] \quad (7)$$

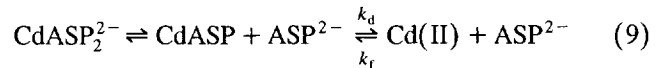
where β is the formation constant of the CdNTA⁻ complex, K^{H} is the dissociation constant of HNNTA²⁻, α is the fraction of NTA in the form of HNNTA²⁻ and $[\text{NTA}]$ is the concentration of NTA not complexed with Cd(II).

The pseudo-first order rate constants of dissociation and formation are then respectively

$$k_1 = k_d[\text{H}^+] \text{ and } k_{-1} = k_f[\text{HNNTA}^{2-}] \quad (8)$$

2.2. Cadmium + ASP

Two types of cadmium complex are formed with ASP: the 1:1 and 1:2 species with formation constants β_1 and β_2 respectively. While the dissociation of the 1:2 species is very fast, a slow step with a rate constant k_d is associated with the dissociation of the 1:1 complex [16,17]:



the reduction $\text{Cd(II)} + 2e^- \rightarrow \text{Cd(Hg)}$ being affected by the slow step.

In the presence of an excess of ligand where $[\text{CdASP}_2^{2-}] + [\text{CdASP}] > [\text{Cd(II)}]$ one has [17,18]

$$K = \frac{[\text{Cd(II)}]}{[\text{CdASP}_2^{2-}] + [\text{CdASP}]} = 1/\beta_1[\text{ASP}^{2-}] + \beta_2[\text{ASP}^{2-}]^2 \quad (10)$$

where the pseudo first order rate constant of dissociation is given by

$$k_1 = k_d \beta_1[\text{ASP}^{2-}]/\beta_1[\text{ASP}^{2-}] + \beta_2[\text{ASP}^{2-}]^2 \quad (11)$$

and the pseudo-first order rate constant of formation is

$$k_{-1} = k_d \beta_1[\text{ASP}^{2-}] \quad (12)$$

2.3. SWV

In SWV the net current at the peak ΔI_p is expressed by [1]

$$\Delta I_p = nFAc(D/\pi t_p)^{1/2} \Delta \psi_p \quad (13)$$

where $\Delta \psi_p$ is the dimensionless net current function at the peak and t_p is the pulse width. The square wave period τ is equal to twice the pulse width or equal to $1/f$, f being the square wave frequency.

For a reversible system, $\Delta \psi_p$ is constant for a given set of values of the square wave amplitude E_{SW} and the step height ΔE_s . For a kinetic system, $\Delta \psi_p$ is no longer a constant, being a function of a dimensionless kinetic parameter; in the case of a CE mechanism this means that $\Delta \psi_p$ is a function of $K[(k_1 + k_{-1})\tau]^{1/2}$ [1,7].

3. Experimental

3.1. Chemicals and solutions

All reagents were of pro-analysis grade, and the solutions prepared with distilled and deionized water from a MilliQ-Water purification system.

In the experiments with NTA the medium was 1.0 M KNO_3 and 0.1 M acetate buffer, the total metal concentration $[M]_t$ was 5.0×10^{-5} M, and the total NTA concentration $[NTA]_t$ was 5.0×10^{-3} M and 5.6×10^{-3} M.

In the experiments with ASP the medium was 0.70 M in NaClO_4 and the pH was adjusted in the range 7.5–8.5 with a borate buffer (5.0×10^{-2} M H_3BO_3 + 5.0×10^{-3} M NaOH). The total metal concentration was kept at 1.0×10^{-4} M while the total ASP concentration $[\text{ASP}]_t$ changed between 5.0×10^{-3} and 3.0×10^{-2} M.

The solutions were always purged with U-type nitrogen, and all experiments were carried out at $25 \pm 0.2^\circ\text{C}$.

3.2. Instruments

The square wave voltammograms were collected by using an EG&G-PAR potentiostat/galvanostat Model 273A controlled via the 270 software.

A square-wave amplitude of 25 mV and a step height of 5 mV were used for all experiments. The frequency of the square wave was varied in the range 50 to 3000 Hz. Three voltammograms were recorded, at least, for each set of experimental parameters.

The HMDE working electrode was from Metrohm. A platinum wire was used as the counter electrode and a saturated calomel electrode (SCE) as reference.

4. Results and discussion

4.1. Cd(II) reduction in the absence of ligand

The reduction of Cd(II) alone was analysed as a function of frequency in both media and in the range 50 to 3000 Hz.

Above 2500 Hz completely distorted curves were obtained with no resemblance at all to conventional square

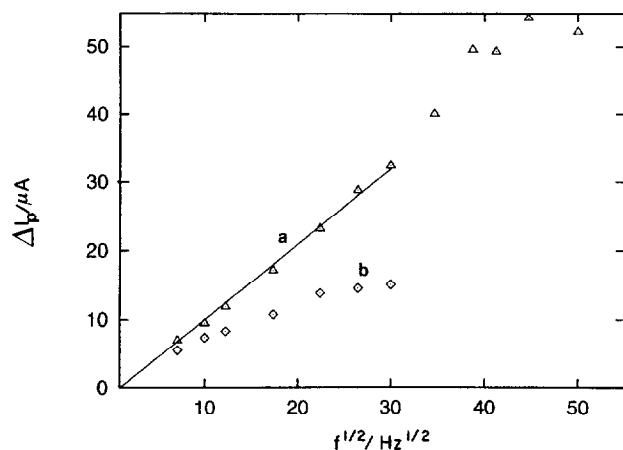


Fig. 1. Cd(II) + ASP system: variation of the net peak current with $(f)^{1/2}$ due to Cd(II) reduction in 0.7 M NaClO_4 , pH = 8.03 (borate buffer), $T = 25 \pm 0.2^\circ\text{C}$, $\Delta E_S = 5$ mV, $E_{\text{SW}} = 25$ mV: (a) $[M]_t = 1.0 \times 10^{-4}$ M and $c_L = 0$; (b) $[M]_t = 1.0 \times 10^{-4}$ M and $[\text{ASP}]_t = 1.00 \times 10^{-2}$ M.

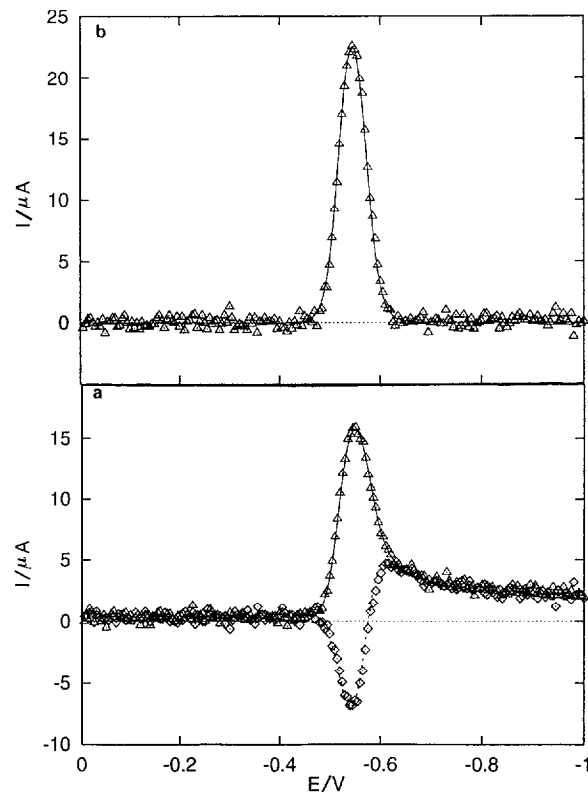


Fig. 2. Experimental (Δ \diamond) and theoretical (—) square wave voltammograms for Cd(II) reduction (10^{-4} M) in 0.7 M NaClO_4 , pH = 8.08 (borate buffer) $T = 25 \pm 0.2^\circ\text{C}$, $\Delta E_S = 5$ mV, $E_{\text{SW}} = 25$ mV and $f = 500$ Hz: (a) forward and reverse currents; (b) net current.

wave voltammograms. In the range 1000 to 2500 Hz, though the voltammetric curves look like conventional voltammograms, the net current at the peak ΔI_p is no longer a linear function of the square root of the frequency; this behaviour was quite consistent in both media, as can be seen for example in Fig. 1, curve (a). The values in the range 50 to 1000 Hz were those used further, since good linear relationships ($r > 0.999$) with a zero intercept (cf. Eq. (13)) were obtained for the variation of ΔI_p as a function of the square root of frequency.

The reversibility of Cd(II) reduction at the HMDE can also be observed in Fig. 2, where the experimental voltammograms are compared with theory. The theoretical voltammograms were obtained following the work of Ref. [1]. The current on the j th half-cycle I_j was calculated by

$$I_j = nFAc(D/\pi t_p)^{1/2} \sum_{m=1}^j \frac{Q_{m-1} - Q_m}{\sqrt{j-m+1}} \quad (14)$$

where

$$Q_m = \frac{\varepsilon_m}{1 + \varepsilon_m} \quad \text{with} \quad \varepsilon_m = \exp \left[\frac{nF(E_m - E_{1/2})}{RT} \right] \quad (15)$$

In the above relations $E_{1/2}^r$ is the reversible halfwave potential and the potential E in the half cycle m is given by

$$E_m = E_i - \left[\frac{m+1}{2} \right] \Delta E_S + (-1)^m E_{SW} \quad (16)$$

Then in each cycle, if we consider j odd, the forward difference is given by

$$\Delta I_j = I_j - I_{j+1} \quad (17)$$

The constant $nFAc(D/\pi)^{1/2}$ was calculated from the slope of the relationship of ΔI_p vs. \sqrt{f} (Eq. (13)). The value used for $\Delta\psi_p$ was 0.9281 since $E_{SW} = 25$ mV and $\Delta E_S = 5$ mV [1]. As can be seen in Fig. 2, the forward and reverse currents as well as the net current agree with theory, showing that the system is well behaved even for amalgam formation. These results agree with those obtained by Turner and co-workers [19,20].

4.2. Cadmium reduction in the presence of NTA and ASP

As can be seen in Fig. 1, curve (b), as the frequency increases there is less time for the dissociation of the complexes to occur and so the current due to Cd(II) reduction from the dissociation of the complexes decreases, which means that $\Delta\psi_p$ is no longer a constant. For a given frequency, in the range studied, the net peak current due to Cd(II) reduction in the presence of ASP or NTA is always smaller than the net current due to Cd(II) reduction in the absence of ligand. No peak position shift was observed with frequency; only the peak potential shifts due to the formation of the complexes were observed (Fig. 3).

As is well known, for both systems the reduction of the complexes CdNTA and CdASP can occur directly on the electrode according to the reactions

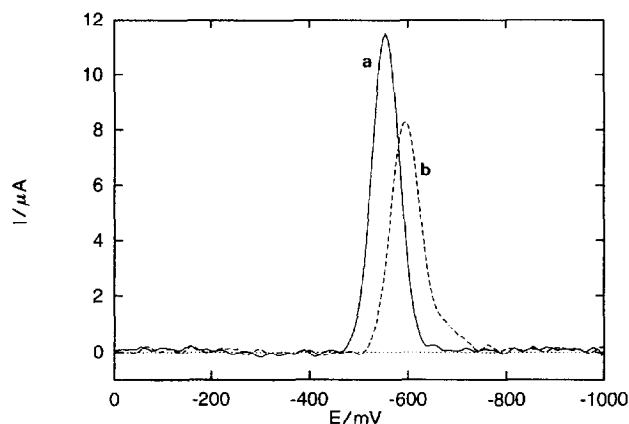
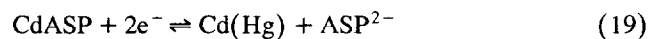
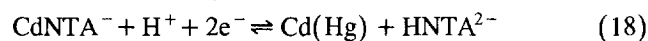


Fig. 3. Cd(II) + ASP system: experimental net square wave voltammogram for Cd(II) reduction in 0.7M NaClO₄, pH = 8.03 (borate buffer), $T = 25 + 0.2^\circ\text{C}$, $\Delta E_S = 5$ mV, $E_{SW} = 25$ mV and $f = 150$ Hz: (a) $[M]_i = 1.0 \times 10^{-4}$ M and $[\text{ASP}]_i = 0$; (b) $[M]_i = 1.0 \times 10^{-4}$ M and $[\text{ASP}]_i = 1.00 \times 10^{-2}$ M.

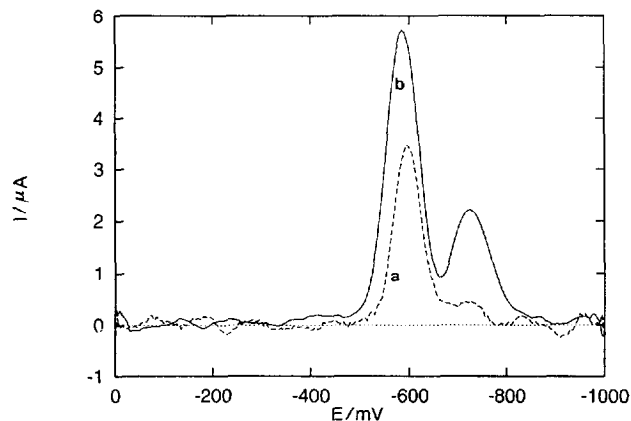


Fig. 4. Cd(II) + NTA system: experimental net square wave voltammogram for Cd(II) reduction in 1.0M KNO₃, pH = 3.20 (acetate buffer), $T = 25 + 0.2^\circ\text{C}$, $\Delta E_S = 5$ mV, $E_{SW} = 25$ mV, $[M]_i = 5.0 \times 10^{-5}$ M and $[\text{NTA}]_i = 5.60 \times 10^{-3}$ M: (a) $f = 50$ Hz; (b) $f = 500$ Hz.

These reactions occur at potentials more negative than those corresponding to Cd(II) reduction from the dissociation of the complexes. For our experimental conditions, a second reduction peak was clearly seen for the higher frequencies used, as can be observed in Fig. 4 for Cd + NTA complexes. However, only the peak due to the reversible reduction of 'free' cadmium was used to obtain kinetic information.

4.3. Determination of the rate constants

O'Dea and co-workers have demonstrated the use of SWV combined with non-linear least squares methods for estimating kinetic parameters [9,11,21].

In this work we have determined the rate constant k_1 from the experimental value of the net current at the peak, $\Delta I_{p,exp}$. This has been done as follows:

(1) first we translate $\Delta I_{p,exp}$ into the dimensionless net current at the peak $\Delta\psi_{p,exp}$ according to Eq. (13) where $nFAc(D/\pi)^{1/2}$ is known from the slope of ΔI_p vs. $(f)^{1/2}$ for Cd(II) reduction in the absence of ligand. Note that according to the molar masses of the ligands, the complexes should have the same diffusion coefficients as the metal ion, within an error of 10%, which corresponds to an error of 5% in $D^{1/2}$, this inaccuracy being within the experimental errors;

(2) next, the calculation of the rate constant is carried out using for the dimensionless current an approximate solution of the integral equation of $\psi(t)$ vs. E [1]. To obtain such a solution every half cycle of duration, t_p is divided in s subintervals; then, if we have M cycles the total number of subintervals is

$$N = Ms \quad (20)$$

The dimensionless current in any subinterval $n = 1, \dots, N$ is given approximately by [1]

$$\psi(n) = \left\{ \frac{K_2 \pi \sqrt{k\tau}}{K_2 + 1} - \frac{\sqrt{\pi}}{K_2 + 1} \sum_{i=1}^{n-1} \psi(i) R_j - \sqrt{\frac{2k\tau}{s}} \right. \\ \times \left[\frac{K_2}{K_2 + 1} + \varepsilon(n) \right] \sum_{i=1}^{n-1} \psi(i) S_j \left. \right\} \\ \times \left\{ \sqrt{\pi} R_1 (K_2 + 1) \right. \\ \left. + \sqrt{\frac{2k\tau}{s}} \left[\frac{K_2}{K_2 + 1} + \varepsilon(n) \right] \right\}^{-1} \quad (21)$$

where

$$j = n - i + 1$$

$$S_j = \sqrt{j} - \sqrt{j-1}$$

$$R_j = \sqrt{\operatorname{erf}\left(\frac{jk\tau}{2s}\right)} - \sqrt{\operatorname{erf}\left(\frac{(j-1)k\tau}{2s}\right)}$$

The constant k is related to the rate constant k_1 through the expression

$$k = k_1(1 + 1/K) \quad (22)$$

Note that K is a well-known quantity since it depends on known thermodynamic data and experimental pH and total ligand concentration;

(3) then, for a given set of experimental conditions, such as E_{SW} , ΔE_S , K and f values, we have an approximate expression for the dimensionless current at any time $\psi(t)$ as a function of k_1 . Because for each k_1 we can determine the value of the dimensionless net current at the peak one has

$$\Delta\psi_p = \psi_p^{\text{forward}} - \psi_p^{\text{reverse}} = \Delta\psi_p^{\text{exp}} \quad (23)$$

The idea is then to find the value of k_1 for which

$$\Delta\psi_p^{\text{exp}} = \Delta\psi_p(k_1) \quad (24)$$

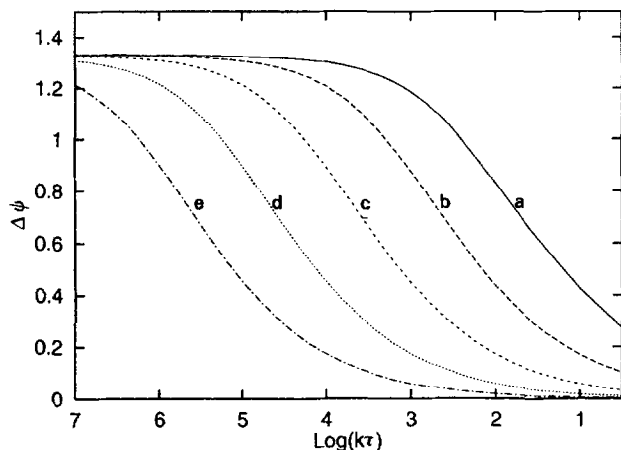


Fig. 5. Variation of the dimensionless net current at the peak $\Delta\psi_p$ with $\log k\tau$ for $\Delta E_S = 5\text{ mV}$, $E_{SW} = 25\text{ mV}$ and various values of $-\log(K)$: (a) 1.0; (b) 1.5; (c) 2.0; (d) 2.5; (e) 3.0.

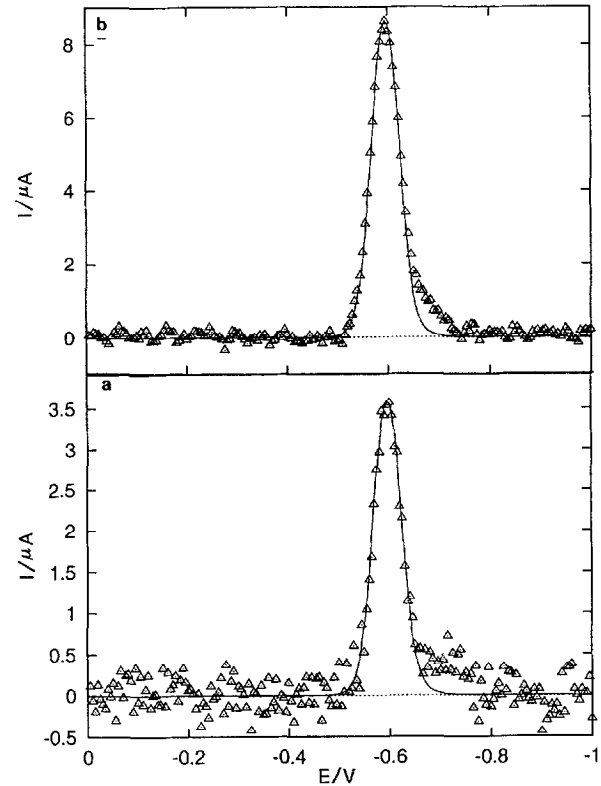


Fig. 6. (a) Cd(II)+NTA system: experimental (Δ) and theoretical (—) square wave net voltammograms for Cd(II) reduction in 1.0 M KNO_3 , pH = 3.20 (acetate buffer), $f = 50\text{ Hz}$, $[M]_t = 5.0 \times 10^{-5}\text{ M}$ and $[\text{NTA}]_t = 5.60 \times 10^{-3}\text{ M}$; (b) Cd(II)+ASP system: experimental (Δ) and theoretical (—) square wave net voltammograms for Cd(II) reduction in 0.7 M NaClO_4 , pH = 8.03 (borate buffer), $f = 150\text{ Hz}$, $[M]_t = 1.0 \times 10^{-4}\text{ M}$ and $[\text{ASP}]_t = 1.00 \times 10^{-2}\text{ M}$. $T = 25 \pm 0.2^\circ\text{C}$, $\Delta E_S = 5\text{ mV}$, $E_{SW} = 25\text{ mV}$.

The problem with the last equation is that $\Delta\psi_p(k_1)$ is a very complicated function of k_1 , as can be seen from Eq. (21). To understand the method we used to find k_1 it is important to look at the form of the function $\Delta\psi(k_1)$ vs. $\log(k\tau)$, where k is given in Eq. (22). This is shown in Fig. 5 for various values of K .

The first thing to notice is that $\Delta\psi_p$ is a decreasing function of $\log(k\tau)$. The second is that from the curves in Fig. 5 we can have an order of magnitude for k_1 . Then we can solve the equation

$$\Delta\psi_p^{\text{exp}} - \Delta\psi_p(k_1) = 0 \quad (25)$$

numerically using an iterative procedure and taking as the initial value of k_1 the estimate that we get from Fig. 5. This iterative procedure turns out to converge rather quickly due to the behaviour of the function $\Delta\psi_p$ between the two plateaux. In practice, if we are in the part of the curve where $\Delta\psi_p$ varies linearly with $\log(k\tau)$, for $s \geq 10$ subintervals the variation of the calculated $\Delta\psi_p$ values is smaller than 0.1%. In this region the whole procedure for one experimental point takes about 25 s with a 486PC.

Fig. 6 shows the experimental and theoretical voltammograms. The theoretical curves were computed using the

Table 1

Pseudo-first order dissociation rate constant k_1 of CdNTA complex at $T = 25^\circ\text{C}$ in 1.0 M KNO_3

pH	$-\log K$	$10^3 c_L / \text{M}$	f / Hz	k_1 / s^{-1}
3.20	1.00	5.60	50–500	$(2.3 + 0.3) \times 10^2$
3.61	1.40	5.00	50–300	$(8 + 2) \times 10$

values determined for k_1 for a given set of experimental conditions, as discussed. As can be seen the agreement is very good. Note in particular the good agreement between experimental and theoretical results around the peak potential. The small tail noticed in the experimental curves for potential values after the peak potential reflects the direct reduction of the complexes that can occur, as mentioned before.

In Tables 1 and 2 a summary of the results obtained for the pseudo-first order rate constants of dissociation for both systems are presented. In the computation of K the following values for the thermodynamic constants were used: $\log \beta = 9.78$ and $\log K_H = 9.65$ [22], and $\log \beta_1 = 4.537$ and $\log \beta_2 = 8.220$ [17].

Note that each k_1 value (for a given set of pH and c_L values) is an average of at least 20 values (three for each frequency used). Averaging over a reasonable set of k_1 values enables us to estimate the errors of the rate constants of dissociation.

Our method of calculation requires the measurement of the experimental current in the complete absence of kinetic effects in order to get the factor $nFAc(D/\pi)^{1/2}$. This is not particularly troublesome and enables us to have a precise idea of the useful range of frequencies to be used.

Since K is a well-known quantity, we perform a one-variable fit; this is a desirable situation, avoiding the risk of obtaining meaningless physical parameters when too many variables have to be fitted.

The dissociation rate constants can now be computed easily using Eq. (8) and Eq. (11).

While CdNTA dissociation is a proton-assisted reaction [14], there is no influence of pH on the reaction of dissociation of the CdASP complex, the results obtained for k_d being the same, within the experimental error, in the pH range studied (Table 2).

In Table 3 a summary of the results obtained in this

Table 2

Pseudo-first order dissociation rate constant k_1 of 1:1 CdASP complex at $T = 25^\circ\text{C}$ in 0.7 M NaClO_4

$-\log K$	pH	$10^2 c_L / \text{M}$	f / Hz	$10^{-3} k_1 / \text{s}^{-1}$
1.330	7.47	3.19	200–700	$5.2 + 0.6$
1.403	7.47	3.19	300–900	$6 + 2$
1.260	7.97	1.00	150–900	$8 + 2$
2.057	8.25	1.50	50–400	$3.8 + 0.9$
1.456	8.38	1.50	300–900	$4.5 + 0.8$
2.033	8.42	1.00	50–400	$4.4 + 0.8$

Table 3

Dissociation rate constants k_d at $T = 25^\circ\text{C}$ for the CdNTA complex in 1.0 M KNO_3 and the 1:1 CdASP complex in 0.7 M NaClO_4

$k_d / \text{M}^{-1} \text{s}^{-1}$	Technique	Reference
<i>CdNTA</i>		
3.9×10^5	SWV	This work
4.1×10^5	CV	[14]
2.9×10^5	DPP	[15]
<i>CdASP</i>		
$(1.5 + 0.3) \times 10^4$	SWV	This work
$(3 + 1) \times 10^4$	CV	[16]

work for k_d is presented and compared with literature values.

5. Conclusions

As far as we know there is nothing in the literature concerning the application of SWV to studies of a CE mechanism.

As can be seen from Table 3, the results obtained by SWV for the dissociation rate constants agree quite well with literature values, especially with those from cyclic voltammetry (CV), a technique well established for studying kinetic systems [23].

For both techniques a time window is available for the determination of kinetic parameters. The higher frequencies and scan rates in SWV and CV respectively, are capable of being used to place a limit on the shortest useful times and hence an upper limit for the rate constants. The lower limit depends on the longest available times that are often constrained by spherical diffusion and sometimes convection.

The following comparison can be made.

Technique	SWV	CV
Time parameter	$t_p = 1/2f$	RT/Fv
Usual range [1,24]	$f = 10$ to 1000 Hz	$v = 0.02$ to 100 V s^{-1}
Time window/s	5×10^{-4} to 5×10^{-2}	3×10^{-4} to 1
Interval of k/s^{-1}	20 to 2×10^3	1 to 3.3×10^3

So both techniques are useful for the study of first order reactions with rate constants in the range 10 to 10^3 s^{-1} ,

Since in SWV much of the background current is eliminated due the differential current measurement, low detection limits can be achieved. This enables the technique to be used to do physical–chemical studies at a micromolar concentration level; a situation not accessible to CV due to the onset of charging currents.

An additional advantage of SWV in the study of kinetic systems is that since a significant concentration range is available, the kinetics can be studied in a large interval of concentrations.

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