

Cyclic Reciprocal Derivative Chronopotentiometry with Exponential Time Currents in the Study of Slow Charge Transfer Processes between Electrodes and Redox Adsorbates

J. Gonzalez and A. Molina*

Departamento de Química Física, Facultad de Química, Universidad de Murcia, Espinardo, 30100, Murcia, Spain

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Theoretical expressions are presented corresponding to the response of adsorbed molecules which exhibit a quasi-reversible or totally irreversible charge transfer in cyclic reciprocal derivative chronopotentiometry with exponential currents (CRDEC). The higher and better defined peaks obtained in CRDEC compared with those obtained in cyclic voltammetry (CV) indicate that CRDEC could be considered as a powerful tool in the characterization of molecular films. Although reciprocal derivative chronopotentiometry with constant current (RDC) enjoys at present an extensive use in the elucidation of electrode processes, when this technique is applied to adsorbed molecules exhibiting an irreversible charge transfer, peaks are not observed. Under these conditions, RDCEC turns out to be more suitable than RDC. Furthermore, the use of programmed currents makes the selection of an appropriate range of transition times easier than does the use of constant currents. Equations for the peak currents, peak potentials, ratio between peak heights, and difference between peak potentials of successive responses corresponding to two exponential currents of opposite signs have been applied to the determination of the kinetic parameters of the experimental system azobenzene in protic media.

Introduction

At present, reciprocal derivative chronopotentiometry (RDC) with constant current, introduced by Jagner,^{1,2} enjoys extensive use in the obtainment of analytically useful data^{3–6} and in the diagnosis of electrochemical reactions,^{7–9} including the study of electrodes coated with molecular films.^{10–12}

As has been recently demonstrated,¹³ this electrochemical technique presents an identical response to that corresponding to cyclic voltammetry (CV) in the case of electrodes coated with reversible molecular films, although the analytical advantages obtained hereby are greater than those obtained in CV.^{3,13} This is fundamentally due to the need to work at high sweep rates in order to improve the sensitivity in CV, which leads to an increase in the distortion of the I/E curve which can be confused with that caused by a slow charge-transfer reaction.^{14,15} However, the analytical sensitivity in RDC increases when the applied current decreases, and therefore, the ohmic drop effects become negligible.

Despite its advantages, RDC with constant current presents a serious disadvantage when it is applied to adsorbed redox molecules exhibiting an irreversible charge transfer since in these conditions the reciprocal derivative chronopotentiogram does not present a peak.

In this work, we will demonstrate that the above disadvantage of the RDC with constant current can be overcome by using programmed currents. Thus, by following a similar theoretical procedure to that in our previous paper,¹³ in which we analyzed the behavior of a reversible molecular film in cyclic reciprocal derivative chronopotentiometry (CRDCP) with programmed currents of the form $I(t) = I_0 t^u$ and $I(t) = I_0 e^{\omega t}$, we will show here that the use of successive current time functions which vary exponentially with time, like $I(t) = I_0 e^{\omega t}$, enables us to study an electrode process between strongly adsorbed species, whatever its reversibility. This is because the reciprocal derivative exponential chronopotentiogram (CRDEC) presents a peak for any value of the rate constant of the charge transfer k^0 between the electrode and the redox adsorbate. Moreover, compared to RDC, CRDEC offers the possibility of selecting a wide range of values of I_0 and ω for the obtainment of appropriate transition times in an extensive range of surface concentrations.

To determine the $de^{\omega t}/dE$ curve, we transform the experimental E/t curve into the $E/e^{\omega t}$ curve and then its reciprocal derivative is directly calculated.

We have compared the CRDEC signal thus obtained for irreversible processes with the I/E curve corresponding to CV. The higher and better defined peaks observed in CRDEC compared to those obtained in CV indicate that CRDEC could be considered hereafter as a powerful tool in the characterization of molecular films.

We have analyzed the influence of the exponent ω in the applied current and of the kinetic parameters k^0 and α on the CRDEC curves, and we have proposed criteria for characterizing the reversibility of the process as a function of the dimensionless k^0/ω values as well as easy methods for calculating kinetic parameters of the charge-

- (1) Anderson, L.; Jagner, D.; Josefson, M. *Anal. Chem.* **1982**, *54*, 1371.
- (2) Jagner, D. *Trends Anal. Chem.* **1983**, *2*, 53.
- (3) Wang, J.; Tian, B. *Anal. Chem.* **2000**, *72*, 3241.
- (4) Wang, J.; Rivas, G.; Jiang, M.; Zhang, H. *Langmuir* **1999**, *15*, 6541.
- (5) Wang, J.; Cai, X.; Wang, J.; Jonsson, C. *Anal. Chem.* **1995**, *67*, 4065.
- (6) Tomschik, M.; Jelen, F.; Havran, L.; Trnková, L.; Nielsen, P. E.; Palecek, E. *J. Electroanal. Chem.* **1999**, *476*, 71.
- (7) Bi, S.; Yu, J. *J. Electroanal. Chem.* **1996**, *405*, 51.
- (8) Abrantes, L. M.; Molina, A.; Gonzalez, J.; Saavedra, F. *Electrochim. Acta* **1999**, *45*, 457.
- (9) Molina, A.; Gonzalez, J.; Saavedra, F.; Abrantes, L. M. *Electrochim. Acta* **1999**, *45*, 761.
- (10) Honeychurch, M. J. *J. Electroanal. Chem.* **1998**, *445*, 63.
- (11) Honeychurch, M. J.; Ridd, M. J. *Electroanalysis* **1996**, *8*, 362.
- (12) Honeychurch, M. J.; Ridd, M. J. *J. Electroanal. Chem.* **1996**, *418*, 185.
- (13) Molina, A.; Gonzalez, J. *J. Electroanal. Chem.* **2000**, *493*, 117.
- (14) Milner, D. F.; Weaver, M. J. *Anal. Chim. Acta* **1987**, *198*, 245.
- (15) Magno, F.; Lavagnini, I. *Anal. Chim. Acta* **1995**, *305*, 96.

transfer reaction k^0 and α and the surface standard potential E^0 . The above criteria have been applied to the study of the adsorption of azobenzene on mercury in aqueous media. From the measurement of the peak potentials and peak heights, we have obtained accurate values for the kinetic and thermodynamic parameters of this system.

Experimental Section

Apparatus. The computer-driven potentiostat–galvanostat was designed and constructed by QUICELTRON (Spain).

Pulse and waveform generation and data acquisition were performed using i-SBXDD4 and DAS16-330i (ComputerBoards, USA) boards, respectively. All computer programs were written in our laboratory.

In the cyclic chronopotentiometric experiments, the switch of the current was performed when the potential attained a prefixed (cathodic or anodic) value at which we suppose that the transition time has been already reached. The necessary comparison was carried out by means of an interrupt service routine which uses the clock of the personal computer after convenient reprogramming.

Data acquisition and waveform generation were independent tasks which have been carried out using two different time scales and different but connected routines. For waveform generation, we have used an interrupt service routine programmed for this purpose and triggered by the 8254 counter in the personal computer. Data acquisition was under the control of the on-board pacer which usually runs at the maximum sampling rate, and data were stored in the on-board FIFO buffer. The interrupt service routine was called a variable number of times in each potential step and was responsible for changes in the potential values and for reading of the acquisition counter and status. Hence, the use of appropriate programming techniques allows large data oversampling (highly useful in digital filtering) and almost complete versatility in the selection of time and amplitude for potential pulses with a very good acquisition synchronization.

Electrodes. A three-electrode cell was employed in the experiments. A static mercury drop electrode (SMDE, electrode radius $r_0 = 0.044$ cm, electrode area $A = 0.0239$ cm²) served as the working electrode. The SMDE was constructed using a DME, EA 1019-1 (Metrohm), to which a homemade valve was sealed. Different opening times in this valve allowed the use of mercury drops of radii varying from 0.01 to 0.05 cm. The electrode radius of the SMDE was determined by weighing a large number of drops. The standard deviation in each series of radius determination was always lower than 0.5%. The counter electrode was a Pt foil, and the reference electrode was a Ag|AgCl|KCl 1.0 M electrode.

Signal Processing. Experimental E/t curves were smoothed by applying the moving average smoothing procedure proposed by Savitzky and Golay¹⁶ and converted into the $E/e^{\omega t}$ curves. These curves were then fitted with a sigmoidal regression by using the SigmaPlot program¹⁷ and were numerically differentiated by using a finite differences formula of fifth degree¹⁸ to give the $de^{\omega t}/dE$ curves.

Chemical Reagents. K₂HPO₄, KH₂PO₄, KNO₃, ethanol (Merck, reagent grade), and azobenzene (Aldrich, reagent grade) were used as received without further purification. Azobenzene was dissolved in a small amount of ethanol and then diluted with water until the final proportion of ethanol was 1% (azobenzene concentration was 3×10^{-6} M). K₂HPO₄ and KH₂PO₄ were used to fix the pH at 6.6 (with KNO₃ 0.1 M as supporting electrolyte). Azobenzene was adsorbed at the mercury surface at a potential of 0.0 V during 60 s prior to the measurements.

Water was bidistilled, and nitrogen gas was passed through solutions for deaeration for 15 min prior to the measurements.

Theory

When several successive and alternating in sign programmed currents of the form $I(t_i) = (-1)^{i+1} I_0 e^{\omega t_i}$ for any

value of ω are applied to a coated electrode with a molecular film of an electroactive irreversible redox couple in such a way that the Langmuir isotherm is obeyed and the coverage is smaller than the unit, then the potential time response can be given by¹⁹

$$\frac{I(t_i)}{nFAk^0} = (-1)^{i+1} (\Gamma_A(t_i)\eta^{-\alpha} - \Gamma_B(t_i)\eta^{(1-\alpha)}) \quad i = 1, 2, 3, \dots \quad (1)$$

where

$$\eta = \exp\left[\frac{nF}{RT}(E - E^0)\right] \quad (2)$$

The expressions of the surface concentrations of the oxidized ($\Gamma_A(t_i)$, in mol cm⁻²) and reduced ($\Gamma_B(t_i)$, in mol cm⁻²) species for the i th (cathodic if i is odd or anodic if i is even) current applied can be easily deduced by integrating the equation

$$\frac{d\Gamma_A}{dt_i} = \frac{(-1)^{i+1} I_0 e^{\omega t_i}}{nFA} \quad (3)$$

from $t_i = 0$ to $t_i = t_i$ and taking into account that

$$\Gamma_T = \Gamma_A(t_i) + \Gamma_B(t_i) = \Gamma_{A,0} + \Gamma_{B,0} \quad (4)$$

So we deduce

$$\left. \begin{aligned} \Gamma_A(t_1) &= \Gamma_{A,0} - \frac{I_0}{nFA\omega} (e^{\omega t_1} - 1) \\ \Gamma_A(t_i) &= \Gamma_T - \frac{I_0}{nFA\omega} (e^{\omega t_i} - 1) \quad \text{for } i \text{ odd or cathodic currents} \\ \Gamma_A(t_i) &= \frac{I_0}{nFA\omega} (e^{\omega t_i} - 1) \quad \text{for } i \text{ even or anodic currents} \end{aligned} \right\} \quad (5)$$

$$\Gamma_B(t_i) = \Gamma_T - \Gamma_A(t_i) \quad (6)$$

E^0 is the surface standard potential, k^0 is the heterogeneous rate constant of the electrochemical reaction (s⁻¹), $\Gamma_{A,0}$ and $\Gamma_{B,0}$ are the initial values of the surface concentrations of the oxidized and reduced species, respectively, Γ_T is their constant sum, A is the electrode area (cm²), α and $1 - \alpha$ are the charge-transfer coefficients of the cathodic and anodic surface reactions, respectively, and n , F , R , and T have their usual meanings. Moreover, t_i is the time during which the i th exponential current $(-1)^{i+1} I_0 e^{\omega t_i}$ is applied ($0 \leq t_i \leq \tau_i$), whereas the transition time (time for which $\Gamma_A(\tau_i) = 0$ for any cathodic current (i odd) or $\Gamma_B(\tau_i) = 0$ for any anodic one (i even)) is given by

$$e^{\omega \tau_1} - 1 = \frac{nFA\omega \Gamma_{A,0}}{I_0} \quad (7)$$

$$e^{\omega \tau_i} - 1 = \frac{nFA\omega \Gamma_T}{I_0} \quad i \geq 2 \quad (8)$$

By introducing eqs 5–6 and 7–8 in eq 1, we deduce

(19) Laviron, E. In *Electroanalytical Chemistry*; Bard, A. J., Ed.; Marcel Dekker: New York, 1982; Vol. 12.

(16) Savitzky, A.; Golay, M. J. E. *Anal. Chem.* **1964**, *36*, 1627.

(17) Sigma Plot for Windows, version 5.0; Jandel Scientific: Corte Madera, CA, 1999.

(18) Maron, M. J. *Numerical Analysis: a practical approach*; Collier: McMillan: London, 1982.

$$\left. \begin{aligned} \frac{\omega}{k^0} e^{\omega(t_1 - \tau_1)} \eta^\alpha &= 1 - e^{\omega(t_1 - \tau_1)} - \eta \left(e^{\omega(t_1 - \tau_1)} - e^{-\omega \tau_1} + \frac{\Gamma_{B,0}}{\Gamma_{A,0}} (1 - e^{-\omega \tau_1}) \right) \\ \frac{\omega}{k^0} e^{\omega t_i} \eta^\alpha &= e^{\omega \tau_i} - e^{\omega t_i} - \eta (e^{\omega t_i} - 1) \\ \frac{\omega}{k^0} e^{\omega t_i} \eta^\alpha &= -(e^{\omega t_i} - 1) + \eta (e^{\omega \tau_i} - e^{\omega t_i}) \end{aligned} \right\} \quad (9)$$

for cathodic η/t curves, $i = 3, 5, 7, \dots$
for anodic η/t curves, $i = 2, 4, 6, \dots$

In the following, we will suppress the subindex i and we will use only the terms “cathodic” and “anodic” to denote whether we are applying a cathodic or anodic programmed current, respectively, since the results obtained depend solely on the sign of the current applied and not on the number of currents applied.

For a totally irreversible process, eqs 9 are simplified to the following form:

$$\left. \begin{aligned} \eta^\alpha &= (e^{-\omega(t-\tau)} - 1) \frac{k^0}{\omega} \quad \text{cathodic} \\ \eta^{-(1-\alpha)} &= (e^{-\omega(t-\tau)} - 1) \frac{k^0}{\omega} \quad \text{anodic} \end{aligned} \right\} \quad (10)$$

which can be written in a logarithm form,

$$E - E^0 = \frac{RT}{\alpha n F} \ln \left(\frac{k^0}{\omega} \right) + \frac{RT}{\alpha n F} \ln (e^{-\omega(t-\tau)} - 1) \quad \text{cathodic} \quad (11)$$

$$E - E^0 = - \frac{RT}{(1-\alpha)nF} \ln \left(\frac{k^0}{\omega} \right) - \frac{RT}{(1-\alpha)nF} \ln (e^{-\omega(t-\tau)} - 1) \quad \text{anodic} \quad (12)$$

Equations 10 for the $\eta/e^{\omega(t-\tau)}$ responses can also be written as explicit expressions of $e^{\omega(t-\tau)}$,

$$\left. \begin{aligned} e^{\omega(t-\tau)} &= \frac{1}{1 + (\omega/k^0) \eta^\alpha} \quad \text{cathodic} \\ e^{\omega(t-\tau)} &= \frac{1}{1 + (\omega/k^0) \eta^{-(1-\alpha)}} \quad \text{anodic} \end{aligned} \right\} \quad (13)$$

From eqs 13, we easily deduce the following analytical expressions corresponding to the curve $de^{\omega(t-\tau)}/dE$ versus E (CRDEC response) for a totally irreversible cathodic, y_c , or anodic, y_a , process:

$$y_c = \left(\frac{de^{\omega(t-\tau)}}{dE} \right)_{\text{cathodic}} = - \frac{\alpha n F}{RT} \frac{(\omega/k^0) \eta^\alpha}{(1 + (\omega/k^0) \eta^\alpha)^2} \quad (14)$$

$$y_a = \left(\frac{de^{\omega(t-\tau)}}{dE} \right)_{\text{anodic}} = \frac{(1-\alpha)nF}{RT} \frac{(\omega/k^0) \eta^{-(1-\alpha)}}{(1 + (\omega/k^0) \eta^{-(1-\alpha)})^2} \quad (15)$$

The expressions for the peak heights and peak potentials corresponding to the cathodic (y_c vs E) and anodic (y_a vs E) curves are shown in Table 1.

From eqs 7–8 and 14–15 and those of Table 1, it can be deduced that the necessary condition for the existence of a peak in the CRDEC curves is that $(nFA\Gamma_{A,0}\omega)/I_0 > 1$.

For a totally irreversible process, it is fulfilled that (see eqs 14–15 and eqs 1 and 3 in Table 1)

$$\frac{y_c}{y_{c,\text{peak}}} = \frac{4(\omega/k^0) \eta^\alpha}{(1 + (\omega/k^0) \eta^\alpha)^2} \quad (16a)$$

$$\frac{y_a}{y_{a,\text{peak}}} = \frac{4(\omega/k^0) \eta^{-(1-\alpha)}}{(1 + (\omega/k^0) \eta^{-(1-\alpha)})^2} \quad (16b)$$

whereas for a reversible electrode process we have previously deduced the y/y_{peak} response (see eq 38 in ref 13), which is given by

$$\frac{y}{y_{\text{peak}}} = 4 \frac{\eta}{(1 + \eta)^2} \quad \text{cathodic and anodic} \quad (17)$$

If we compare eqs 16a and 16b with eq 17, we can see that for a reversible process (eq 17) it is fulfilled that the response obtained is identical to that corresponding to cyclic voltammetry, which is dependent only on η (see eq 38 in ref 13). In contrast, for quasi-reversible and totally irreversible processes the ratios $y_c/y_{c,\text{peak}}$ and $y_a/y_{a,\text{peak}}$ depend on η and also on the values of α , k^0 , and the exponent of time ω .

By comparison of eqs 17 and 16, corresponding to reversible and totally irreversible processes, respectively, it can be concluded that with this technique equations for the ratios $y_c/y_{c,\text{peak}}$ and $y_a/y_{a,\text{peak}}$ corresponding to a totally irreversible process behave in the same sigmoidal way as those for a reversible process which transfers αn (eq 16a) or $(1-\alpha)n$ (eq 16b) electrons instead of n electrons and for which the variable η must be substituted by $\eta_c = (\omega/k^0) \eta^\alpha$ (eq 16a, cathodic) or $\eta_a = (\omega/k^0) \eta^{-(1-\alpha)}$ (eq 16b, anodic).

Thus, for a reversible process, both peak potentials are ideally equal to E^0 (and therefore $\Delta E_{\text{peak}} = 0$, see eqs 15 and 18 in ref 13), whereas for totally irreversible processes, the peak potentials and also the difference between them depend on the value of ω and on the kinetic parameters of the surface charge transfer. Moreover, in reversible processes it is fulfilled that $|y_{c,\text{peak}}/y_{a,\text{peak}}| = 1$, whereas for totally irreversible processes the following is fulfilled: $|y_{c,\text{peak}}/y_{a,\text{peak}}| = \alpha/(1-\alpha)$.

The use of programmed current in general is of great interest in the study of irreversible processes with derivative chronopotentiometry since when a constant current ($I(t) = I_0$) is used, peaks are not obtained, as is easily appreciated by making $\omega = 0$ in eqs 14 and 15 or eqs 2 and 4 in Table 1. Within programmed current, the use of an exponential current time function analyzed in this paper has some special characteristics which convert it into a highly suitable perturbation for studying the behavior of the charge transfer since the peak potential and the peak height depend in a very simple way on k^0/ω and ω , respectively (see eqs 1–4 in Table 1). We will discuss the main features of this current time function and its advantages in relation to the use of cyclic voltammetry in the following section.

Results and Discussion

(a) General Features of the CRDEC Responses.

Figure 1 shows the theoretical variation of the difference between the cathodic and anodic peak potentials of the CRDEC curves, ΔE_{peak} , with $\log(k^0/\omega)$ for $10^{-2} \leq (k^0/\omega) \leq 2 \times 10^2$, obtained by differentiating eqs 9 with respect to $e^{\omega t}$, with $\Gamma_{B,0} = 0$ and $\alpha = (1-\alpha) = 0.5$. From these data, it is possible to establish the limit values of k^0/ω for which the process behaves as totally irreversible, quasi-reversible, or reversible. Thus, we can see that a process becomes

Table 1. Peak Heights and Peak Potentials Obtained in CRDEC from Equations 14 and 15 for a Totally Irreversible Process for the Application of Two Successive and Alternating in Sign Exponential Current Time Functions $I(t) = I_0 e^{\omega t}$ and $I(t) = -I_0 e^{\omega t}$

	peak heights ^a $y_{c,peak}, y_{a,peak}$	peak potentials $E_{c,peak}, E_{a,peak}$	ratio between peak heights ^b R_y	distance between peak potentials ^c ΔE_{peak}
$I(t) = I_0 e^{\omega t}$, cathodic	$y_{c,peak} = -\frac{\alpha n F}{4RT} \quad (1)$	$E_{c,peak} = E^0 + \frac{RT}{\alpha n F} \ln\left(\frac{k^0}{\omega}\right) \quad (2)$	$R_y = \frac{\alpha}{1-\alpha} \quad (5)$	$\Delta E_{peak} = \frac{RT}{nF} \ln\left(\frac{k^0}{\omega}\right) \frac{1}{\alpha(1-\alpha)} \quad (6)$
$I(t) = -I_0 e^{\omega t}$, anodic	$y_{a,peak} = \frac{(1-\alpha)nF}{4RT} \quad (3)$	$E_{a,peak} = E^0 - \frac{RT}{(1-\alpha)nF} \ln\left(\frac{k^0}{\omega}\right) \quad (4)$		

^a $y_{x,peak} = de^{\omega(t-\tau)}/dE_{x,peak}$ with x being c for cathodic or a for anodic, respectively. ^b $R_y = |y_{c,peak}/y_{a,peak}|$. ^c $\Delta E_{peak} = |E_{c,peak} - E_{a,peak}|$.

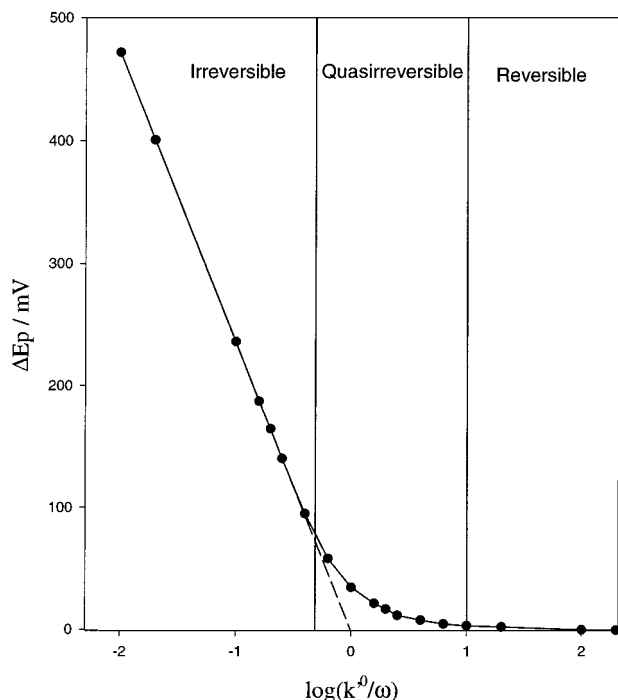


Figure 1. Theoretical dependence of ΔE_{peak} on $\log(k^0/\omega)$ in CRDEC (eqs 9) corresponding to the application of two successive and alternating in sign exponential current time functions $I(t) = I_0 e^{\omega t}$ and $I(t) = -I_0 e^{\omega t}$. $\Gamma_{B,0} = 0$, $\alpha = 0.5$, $n = 1$, $T = 298.15$ K.

more irreversible when k^0/ω diminishes (left-hand side of Figure 1) and therefore the variation of ΔE_{peak} with $\log(k^0/\omega)$ is linear in agreement with eq 6 in Table 1. For intermediate values of k^0/ω (central zone of Figure 1), the dependence of ΔE_{peak} on $\log(k^0/\omega)$ deviates from linearity. If we suppose that the sensitivity of the method in relation to the measurement of ΔE_p is of the order of 2 mV, we can consider that a deviation from the linearity (broken line) greater than 2 mV is appreciable enough to conclude that the behavior of the process is quasi-reversible, with the limit value of k^0/ω for this deviation being equal to 0.48. For values of k^0/ω greater than 10 (right-hand side of Figure 1), we can consider that $\Delta E_{peak} \approx 0$ independently of the value of k^0/ω , which is a typical feature of a reversible behavior, according to eqs 15 and 18 in ref 1. Thus, we can consider that in these conditions, a charge-transfer process between adsorbed molecules behaves as totally irreversible for values of $(k^0/\omega) \leq 0.48$ (zone Irreversible in Figure 1), whereas for values of $(k^0/\omega) \geq 10$ the process can be considered as reversible (zone Reversible in Figure 1). For intermediate values of k^0/ω , the charge transfer behaves as quasi-reversible (zone Quasireversible in Figure 1).

Figure 2 shows the CRDEC curves obtained at various values of the surface rate constant k^0 with a given value of the charge-transfer coefficient $\alpha = 0.5$ and $n = 1$. As k^0

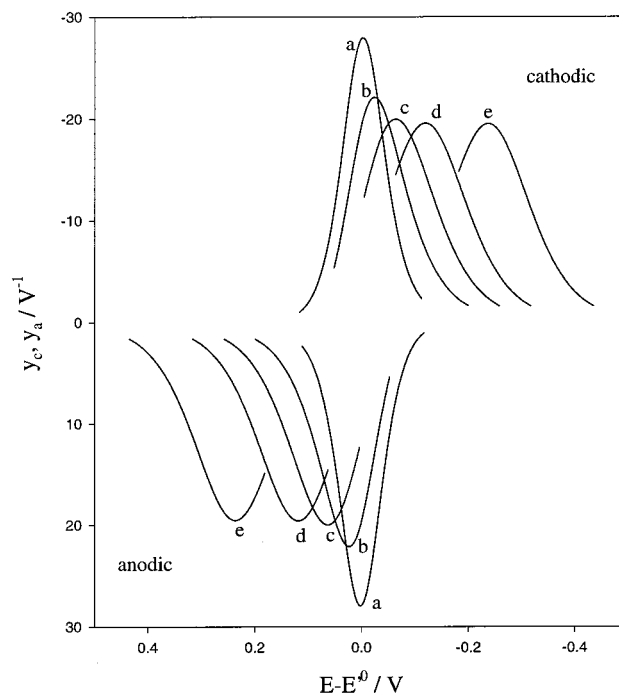


Figure 2. Theoretical CRDEC curves (y_c vs $E - E^0$ and y_a vs $E - E^0$ curves, see eqs 9) corresponding to the application of two successive and alternating in sign exponential current time functions $I(t) = I_0 e^{15t}$ and $I(t) = -I_0 e^{15t}$, $\omega = 15$ s⁻¹, $I_0/(nFA\Gamma_{A,0}) = 5.0$ s⁻¹. The values of k^0 (in s⁻¹) are (a) 150, (b) 15, (c) 4.74, (d) 1.50, and (e) 0.15. Other conditions are as in Figure 1.

decreases, cathodic and anodic curves move in negative and positive directions, respectively, and peak heights in both curves decrease to the limit values given by eqs 1 and 3 in Table 1. This type of behavior has been previously observed in differential pulse voltammetry as well as in reciprocal derivative chronopotentiometry with a diffusing species.^{8,20,21}

(b) Totally Irreversible Behavior. In Figure 3, we have shown the theoretical CRDEC curves (y_c and y_a vs $(E - E^0)$ curves, see eqs 14 and 15) obtained for a value of $k^0 = 0.1$ s⁻¹ when we applied two successive and alternating in sign exponential currents $I(t) = I_0 e^{\omega t}$ and $I(t) = -I_0 e^{\omega t}$. These curves have been obtained for three different values of ω with $I_0/(nFA\Gamma_{A,0}) = 2.5$ s⁻¹, $\alpha = 0.50$, $\Gamma_{B,0} = 0$, and $n = 1$. In all the conditions, the process behaves as totally irreversible. As is shown in these curves, an increase in the value of ω causes a shift of the cathodic and anodic peak potentials, $E_{c,peak}$ and $E_{a,peak}$, toward more negative and positive values, respectively, and therefore an increase in the value of ΔE_{peak} for a given value of k^0 . Similarly, the increase in ω causes an increase in the

(20) Kim, M. H.; Smith, V. P.; Hong, T. K. *J. Electrochem. Soc.* **1993**, *140*, 712.

(21) Birke, R. L.; Kim, M. H.; Strassfeld, M. *Anal. Chem.* **1981**, *53*, 852.

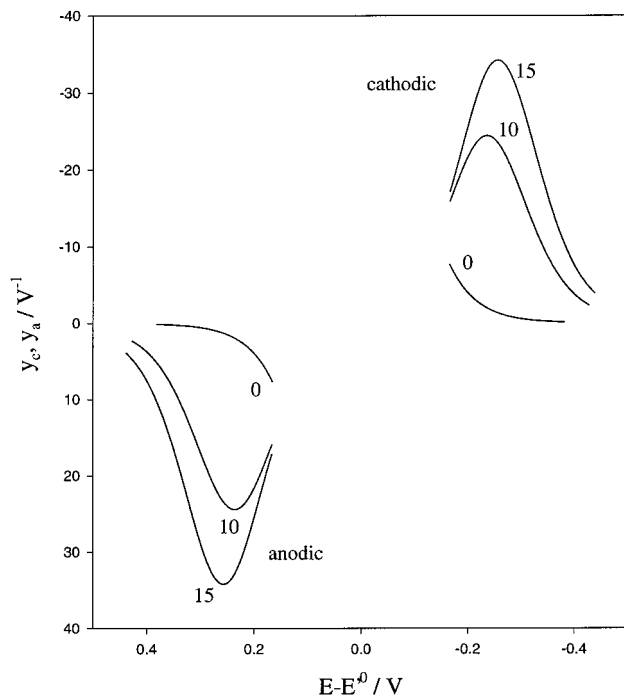


Figure 3. Theoretical CRDEC curves for a totally irreversible electrode process (y_c vs $E - E^0$ and y_a vs $E - E^0$ curves, see eqs 14 and 15). $I(t) = I_0 e^{\omega t}$ and $I(t) = -I_0 e^{\omega t}$. $I_0/(nF\Gamma_{A,0}) = 2.5 \text{ s}^{-1}$, $k^0 = 0.1 \text{ s}^{-1}$. The values of ω in s^{-1} are in the curves. The curves with $\omega = 0$ correspond to the application of two successive and alternating in sign constant currents. Other conditions are as in Figure 1.

heights of both peaks, in agreement with eqs 7–8 and eqs 1 and 3 in Table 1. The ratio between peak heights, R_y , is not affected in any case since it depends exclusively on the charge-transfer coefficients of the cathodic and anodic processes, α and $1 - \alpha$, respectively. The absence of peaks can be also observed in this figure when a constant current I_0 (curve corresponding to $\omega = 0$) is applied under these conditions.

In Figure 4, we have plotted the CRDEC curves obtained for three different values of the cathodic charge-transfer coefficient α with $\omega = 15 \text{ s}^{-1}$, $I_0/(nF\Gamma_{A,0}) = 5.0 \text{ s}^{-1}$, and $k^0 = 0.1 \text{ s}^{-1}$. From these curves, it can be shown that a decrease of α causes a decrease in the height of the cathodic peak and an increase in that of the anodic peak. Therefore, for α values smaller than 0.5 the ratio between peak heights R_y is smaller than the unit whereas its value is greater than the unit for $\alpha > 0.5$. The separation between both peaks reaches its minimum value for $\alpha = 0.5$ and increases the more α differs from this value.

From the measurements of peak heights obtained in experiments performed for different values of the ω exponent or the current amplitude I_0 , it is possible to obtain the values of the initial excess of species A and also the cathodic and anodic charge-transfer coefficients, since according to eqs 1 and 3 of Table 1 by supposing that $\Gamma_{B,0} = 0$ we obtain

$$e^{\omega\tau} y_{c,\text{peak}} = -\frac{\alpha nF}{4RT} e^{\omega\tau} = -\frac{\alpha nF}{4RT} - \frac{\alpha n^2 F^2 \Gamma_{A,0} \omega}{4RT} \quad (18)$$

$$e^{\omega\tau} y_{a,\text{peak}} = \frac{(1-\alpha)nF}{4RT} e^{\omega\tau} = \frac{(1-\alpha)nF}{4RT} + \frac{(1-\alpha)n^2 F^2 \Gamma_{A,0} \omega}{4RT} \quad (19)$$

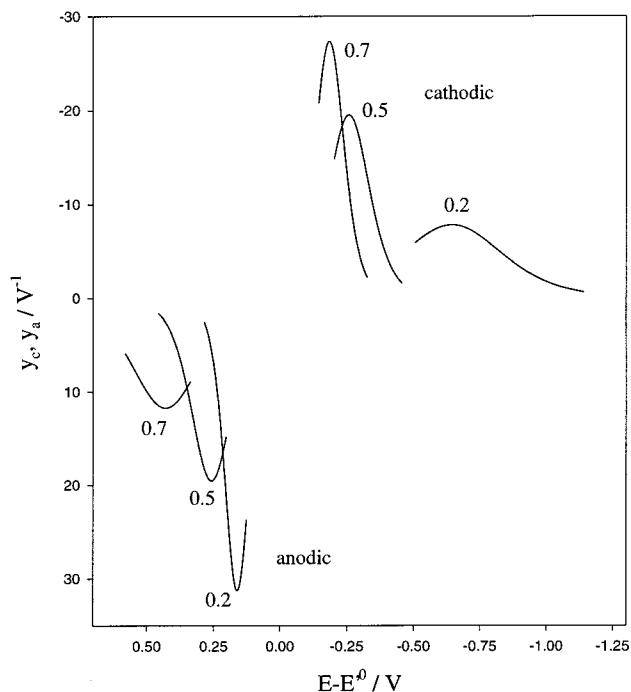


Figure 4. Theoretical CRDEC curves obtained for a totally irreversible electrode process (y_c vs $E - E^0$ and y_a vs $E - E^0$ curves, see eqs 14 and 15). $I(t) = I_0 e^{15t}$ and $I(t) = -I_0 e^{15t}$, $\omega = 15 \text{ s}^{-1}$, $k^0 = 0.1 \text{ s}^{-1}$. The values of the cathodic charge-transfer coefficient α are on the curves. Other conditions are as in Figure 2.

Therefore, the plots of $y_{c,\text{peak}} e^{\omega\tau}$ or $y_{a,\text{peak}} e^{\omega\tau}$ versus ω/I_0 for totally irreversible processes must be linear. From the intercepts and slopes of these plots, we can calculate the values of the initial excess of the oxidized species A, $\Gamma_{A,0}$, as well as those of the cathodic and anodic charge-transfer coefficients, α and $1 - \alpha$, respectively.

According to eqs 2, 4, and 6 in Table 1, the cathodic and anodic peak potentials and also the difference between them vary linearly with $\ln(k^0/\omega)$, as is shown in Figure 5, which gives the $E_{c,\text{peak}}$, $E_{a,\text{peak}}$, and ΔE_{peak} values obtained for three different values of the cathodic charge-transfer coefficient α and different values of k^0/ω . The rate constant for the surface process k^0 can be directly obtained from these work curves once the values of E^0 and of the cathodic and anodic charge-transfer coefficients are known. The determination of α and $1 - \alpha$, k^0 , and E^0 can also be easily made from the plots of $E_{c,\text{peak}}$ and $E_{a,\text{peak}}$ versus $\ln \omega$, which must be linear, according to eqs 2 and 4 in Table 1. From the intercepts of these plots with the potential axis, E^0 can be easily obtained.

In Figure 6a, we have plotted the experimental values of $E_{c,\text{peak}}$ and $E_{a,\text{peak}}$ versus $\ln \omega$ for the experimental system azobenzene $3 \times 10^{-6} \text{ M}$ in KNO_3 0.2 M ($\text{pH} = 6.6$) corresponding to CRDEC curves obtained with the application of two successive and alternating in sign exponential current time functions $I(t) = I_0 e^{\omega t}$ and $I(t) = -I_0 e^{\omega t}$, obtained for four different values of ω . The variation of the peak potentials with $\ln \omega$ is linear in agreement with eqs 2 and 4 in Table 1. From the slopes and intercepts of these lines, we have obtained the following values for the cathodic and anodic charge-transfer coefficients: $\alpha = 0.63 \pm 0.02$ and $1 - \alpha = 0.35 \pm 0.02$. We have also determined the values of the standard potential of the surface reaction and the rate constant: $E^0 = -0.336 \pm 0.001 \text{ V}$ versus $\text{Ag}/\text{AgCl}/\text{KCl}$, 1.0 M , and $\log(k^0/\text{s}^{-1}) = 0.32 \pm 0.02$. Alternatively, it is also possible to obtain k^0 , once the values of α and $1 - \alpha$ are known, from the measure-

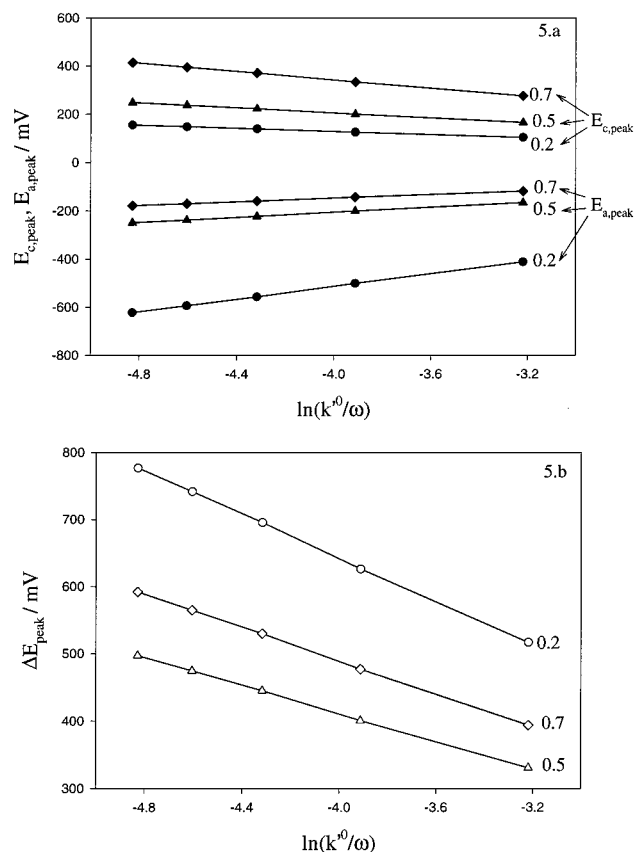


Figure 5. Theoretical variation of $E_{c,peak}$ and $E_{a,peak}$ (a) and of ΔE_{peak} (b) with $\ln(k^0/\omega)$ obtained for a totally irreversible electrode process (see eqs 2, 4, and 6 in Table 1). $I(t) = I_0 e^{\omega t}$ and $I(t) = -I_0 e^{\omega t}$. The values of α are on the curves. Other conditions are as in Figure 1.

ments of ΔE_{peak} by using the work curve shown in Figure 6b. From the experimental values of ΔE_{peak} shown in this figure (black circles), we have determined a value of $\log(k^0/s^{-1}) = 0.33 \pm 0.02$. These values are in good agreement with those previously given in the literature ($\log(k^0/s^{-1}) \approx 0.65$ in ref 22 for pH = 7.0 and $\log(k^0/s^{-1}) \approx 0.31$ in ref 23).

We have also obtained the initial excess of azobenzene on mercury on these conditions from measurements of peak heights of the CRDEC curves corresponding to $\omega = 10 \text{ s}^{-1}$ and different values of the current amplitude I_0 (see eqs 1 and 3 in Table 1): $\Gamma_{\text{azobenzene},0} = (8 \pm 2) \times 10^{-11} \text{ mol cm}^{-2}$.

These values correspond to a series of five assays. The obtained results are the mean of the five experimental values, while the error corresponds to the standard deviation.

(c) Comparison between Cyclic Voltammetry and Cyclic Reciprocal Derivative Chronopotentiometry with Exponential Currents: Totally Irreversible Behavior. The response obtained for a totally irreversible electrode process between strongly adsorbed molecules in cyclic voltammetry was deduced by Laviron in ref 24. The expressions for the cathodic ψ_c and anodic ψ_a signals (in V^{-1}) are

$$\psi_c = \frac{nF}{RT} m \eta^{-\alpha} \exp\left(\frac{m}{\alpha} \eta^{-\alpha}\right) \quad (20)$$

$$\psi_a = -\frac{nF}{RT} m \eta^{(1-\alpha)} \exp\left(-\frac{m}{1-\alpha} \eta^{(1-\alpha)}\right) \quad (21)$$

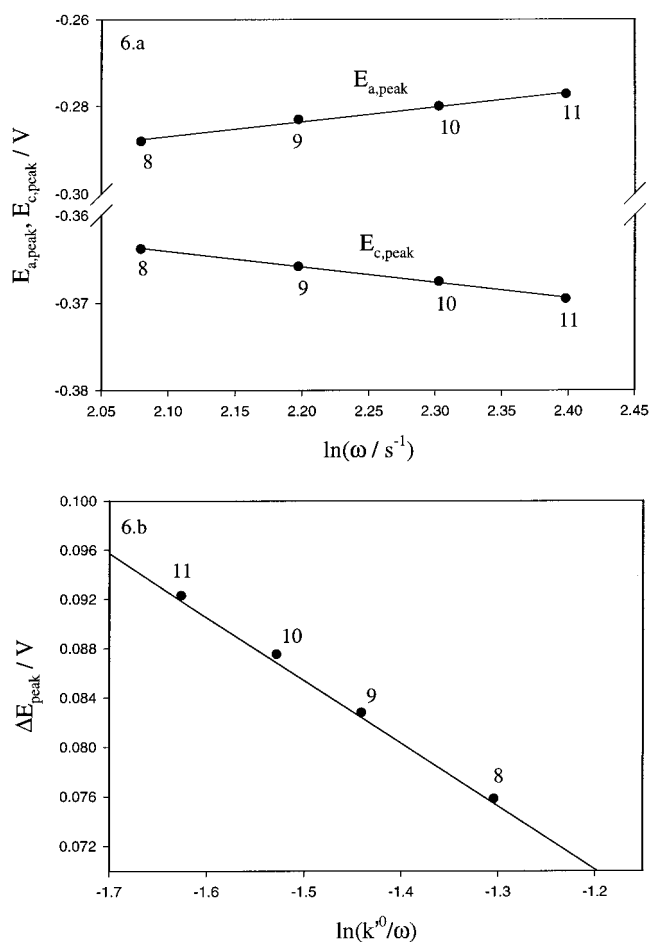


Figure 6. (a) Experimental variation of $E_{c,peak}$ and $E_{a,peak}$ with $\ln \omega$ for the azobenzene $3 \times 10^{-6} \text{ M}$ in KNO_3 0.2 M (pH = 6.6) system on a SMDE. $I(t) = I_0 e^{\omega t}$ and $I(t) = -I_0 e^{\omega t}$. (b) (solid line) Work curve calculated from eq 6 in Table 1 for $\alpha = 0.67$, $I_0/(nF\Gamma_{A,0}) = 4.06 \text{ s}^{-1}$, and $n = 2$. (black dots) Experimental ΔE_{peak} values for the system azobenzene $3 \times 10^{-6} \text{ M}$ in KNO_3 0.2 M (pH = 6.6). $I_0 = 1.5 \mu\text{A}$, $r_0 = 0.044 \text{ cm}$, $T = 290.2 \text{ K}$, $\Gamma_{\text{azobenzene},0} = 8 \times 10^{-11} \text{ mol cm}^{-2}$. The values of ω (in s^{-1}) are on the curves. We have applied a potential $E = 0.0 \text{ V}$ during 60 s prior to the application of the currents.

where

$$\psi_c = \frac{i_c}{nFv\Gamma_{A,0}} \quad \left. \begin{aligned} \psi_a &= \frac{i_a}{nFv\Gamma_{A,0}} \end{aligned} \right\} \quad (22)$$

$$m = \frac{RTk^0}{nFv} \quad (23)$$

with i_c and i_a being the voltammetric cathodic and anodic currents (in A), v being the voltammetric sweep rate (in $V \text{ s}^{-1}$), which is negative for the cathodic sweep and positive for the anodic one, and η as given by eq 2.

The expressions for the peak parameters obtained in cyclic voltammetry are given in Table 2.

If we compare the expressions for the CRDEC cathodic and anodic responses given by eqs 14 and 15 with the expressions for the CV currents given by eqs 20 and 21, we can conclude that they are not similar, contrary to what happens in a reversible electrode process, where the

(22) Komorsky-Lovric, S.; Lovric, M. *Electrochim. Acta* **1995**, *40*, 1781.

(23) Laviron, E.; Mugnier, Y. *J. Electroanal. Chem.* **1980**, *111*, 337.

(24) Laviron, E. *J. Electroanal. Chem.* **1979**, *101*, 19.

Table 2. Peak Parameters Obtained in Cyclic Voltammetry from Equations 20 and 21 for a Totally Irreversible Process^a

	peak currents ^b $\psi_{c,peak}, \psi_{a,peak}$	peak potentials $E_{c,peak}, E_{a,peak}$	ratio between peak heights ^c R_y	distance between peak potentials ^d ΔE_{peak}
cathodic sweep	$\psi_{c,peak} = -\frac{\alpha nF}{eRT} \quad (1)$	$E_{c,peak} = E^0 + \frac{RT}{\alpha nF} \ln\left(\frac{RTk^0}{nFv\alpha}\right) \quad (2)$		$\Delta E_{peak} = \frac{RT}{nF} \left[\frac{1}{\alpha} \ln\left(\frac{RTk^0}{nFv\alpha}\right) + \right.$
anodic sweep	$\psi_{a,peak} = \frac{(1-\alpha)nF}{eRT} \quad (3)$	$E_{a,peak} = E^0 - \frac{RT}{(1-\alpha)nF} \ln\left(\frac{RTk^0}{nFv(1-\alpha)}\right) \quad (4)$	$R_y = \frac{\alpha}{1-\alpha} \quad (5)$	$\left. \frac{1}{1-\alpha} \ln\left(\frac{RTk^0}{nFv(1-\alpha)}\right) \right] \quad (6)$

^a Reference 23. ^b e is the Euler number; $\psi_{x,peak} = i_{x,peak}/(nFA\Gamma_{A,0})$ with x being c for cathodic or a for anodic, respectively. ^c $R_y = |\psi_{c,peak}/\psi_{a,peak}|$. ^d $\Delta E_{peak} = |E_{c,peak} - E_{a,peak}|$.

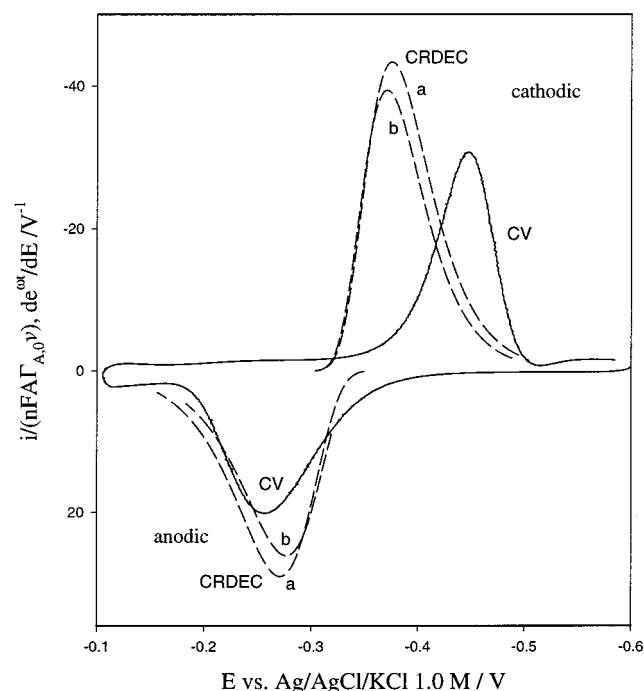


Figure 7. Curves a and b (broken lines) show experimental cyclic reciprocal derivative exponential chronopotentiograms ($(de^{\omega t}/dE)_c$ vs E and $(de^{\omega t}/dE)_a$ vs E) for the system azobenzene 3×10^{-6} M in KNO_3 0.2 M (pH = 6.6) on a SMDE. $I(t) = I_0 e^{\omega t}$ and $I(t) = -I_0 e^{\omega t}$. $I_0 = 1.5 \mu\text{A}$. The values of ω (in s^{-1}) and τ (in s) are (a) 10, 0.136 and (b) 12, 0.119. (solid line) Experimental cyclic voltammogram ($i/(nFA\Gamma_{A,0})$ vs E curve) for the system azobenzene 3×10^{-6} M in KNO_3 0.2 M (pH = 6.6) on a SMDE. Sweep rate $v = 1.5 \text{ V s}^{-1}$. $r_0 = 0.044 \text{ cm}$, $T = 290.2 \text{ K}$, $\Gamma_{\text{azobenzene},0} = 8 \times 10^{-11} \text{ mol cm}^{-2}$. In both cases, we have applied a potential $E = 0.0 \text{ V}$ during 60 s prior to the application of the current or the potential scan.

expressions of the responses obtained in both techniques are identical. Nevertheless, if we compare the expressions for the peak parameters for CV shown in Table 2 and those corresponding to CRDEC shown in Table 1, we can observe that for a totally irreversible process both voltammetric and chronopotentiometric responses present

similar dependences with $\log(RTk^0/(\alpha nFv))$ (see eqs 2 and 4 in Table 2 for CV) and with $\log(k^0/\omega)$ (see eqs 2 and 4 in Table 1 for CRDEC), and in both cases the ratio of the cathodic and anodic peak heights is equal to $\alpha/(1-\alpha)$ (see eqs 5 in Tables 1 and 2).

In Figure 7, we have plotted the experimental CRDEC responses corresponding to the application of two successive exponential currents of alternating sign $I(t) = I_0 e^{\omega t}$ and $I(t) = -I_0 e^{\omega t}$ to the system azobenzene 3×10^{-6} M in KNO_3 0.2 M (pH = 6.6). These curves have been obtained for a value of $I_0/(nFA\Gamma_{A,0}) = 4.06 \text{ s}^{-1}$ and two values of ω (10 and 12 s^{-1}). This figure also shows the CV curve obtained in the same conditions for a sweep rate $v = 1.5 \text{ V s}^{-1}$ (solid line) for which we have obtained a value of $\log(k^0/\text{s}^{-1}) \approx 0.6$. Both the voltammetric and the CRDEC curves are given in V^{-1} for comparison.

As can be clearly observed from this figure, the signals corresponding to CRDEC have greater peak heights than those corresponding to CV although in CV we have selected a sweep rate that is considerably high in order to increase the sensitivity (under these conditions, the capacitive effects and the ohmic drop can heavily distort the voltammogram). However, the work conditions chosen to obtain the cyclic derivative exponential chronopotentiograms ensure that the results obtained are highly reproducible since the ohmic drop and capacitive effects can be considered negligible ($CRT/(r^2 F^2 \Gamma_{A,0}) \approx 0.01$, with C being the double-layer capacitance in these conditions²⁵). This fact highlights the greater sensibility that CRDEC possesses compared to that of CV, a fact that has been previously pointed out by several authors in RDC with constant currents.^{3,6}

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(25) Campbell, D. J.; Herr, B. R.; Hulteen, J. C.; Van Duyne, R. P.; Mirkin, C. A. *J. Am. Chem. Soc.* **1996**, *118*, 10211.