Monatshefte für Chemie 128, 1207–1217 (1997)

Monatshefte für Chemie
Chemical Monthly

Printed in Austria

Determination of Kinetic Parameters of the $FeCl_3/FeCl_2$ System *via* a Novel Treatment of Chronoamperometric Data

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Summary. Computer based methods for the processing of chronoamperometric data *via* convolutions are discussed. On the example of the quasi-reversible Fe^{3+}/Fe^{2+} couple, their application for data acquisition and determination of the heterogeneous electrochemical parameters is demonstrated. The plot of $\Delta Q/\Delta i$ *vs.* $\Delta\sqrt{t}/\Delta i$ is superior to that employing i/I_1, being less sensitive to distortions by charging currents once these have died away and by the effects of damping on the initially rapidly varying currents. Cyclic voltammetry is often combined with convolution or deconvolution, and digital simulation studies are also frequently performed to confirm the results.

Keywords. Chronoamperometry; Cyclic voltammetry; $FeCl_3/FeCl_2$ couple.

Bestimmung kinetischer Parameter des Systems $FeCl_3/FeCl_2$ mittels einer neuen Verarbeitung chronoamperometrischer Daten

Zusammenfassung. Computerunterstützte Verfahren zur Verarbeitung chronoamperometrischer Daten mittels Faltungsintegralen werden diskutiert. Am Beispiel des quasireversiblen Systems Fe^{3+}/Fe^{2+} wird die Anwendung der neuen Methoden zur Datenerfassung und zur Bestimmung der heterogenen elektrochemischen Parameter gezeigt. Der Plot von $\Delta Q/\Delta i$ gegen $\Delta\sqrt{t}/\Delta i$ ist dem von i/I_1 überlegen, da er durch Ladeströme und Dämpfung der ursprünglich stark variierenden Ströme weniger stark beeinflußt wird. Cyclische Voltammetrie wird häufig im Zusammenhang mit Konvolutions- und Dekonvolutionsmethoden angewandt; digitale Simulation zur Überprüfung der Ergebnisse wird ebenfalls oft eingesetzt.

Introduction

The potential step (chronoamperometric) experiment possesses some attractive aspects in the field of mechanistic analysis. It is simple to perform, and – because of the fixed potential at which the system is studied – there is no need to presuppose a particular potential dependence of the electron transfer rate constant. In this respect, the technique lends itself to the study of such a potential dependence and provides a means of assessing adherence to a kinetic to a model such as that of *Butler-Volmer.* A second advantage lies in the fact that after a brief initial period there is no contribution to the observed current from the charging of the electrical double layer at the electrode surface. Thus, it is considered to be an elegant method for evaluating the electrochemical parameters for the simple electron transfer in unstirred electrolyte solutions.

$$O \underset{k_{\mathrm{hb}}}{\overset{k_{hf}}{\rightleftharpoons}} R + ne^- \tag{1}$$

The electroactive species O and R may or may not be present initially in the bulk solution. k_{hf} and k_{hb} are the respective heterogeneous rate constants for the electron transfer. Various data treatments have been advocated for the current/time response following a displacement of the applied potential by a fixed amount from an initial open circuit value, including direct comparison of experimental and calculated data (Eqs. (2)–(4)) for quasi-reversible electron transfer [1–2].

$$i(\mathrm{t}) = \gamma \cdot \exp \beta^2 t \cdot \mathrm{erfc} \beta t^{1/2} \tag{2}$$

$$\gamma = I^O_{\mathrm{lim}} \cdot \frac{k_{hf}}{D_O^{1/2}} + I^R_{\mathrm{lim}} \cdot \frac{k_{hb}}{D_R^{1/2}} = i(t=0) \tag{3}$$

$$\beta = \left(\frac{k_{\mathrm{hf}}}{D_O^{1/2}} + \frac{k_{hb}}{D_R^{1/2}} \right) \tag{4}$$

In terms of the diffusion coefficients D_0 and D_{R} and the other parameters, the limiting convoluted currents, *i.e.* the values of convoluted currents I_1 [3] well past the wave in each direction are defined as follows:

$$I_1([O]^* \rightarrow 0) : I^O_{\mathrm{lim}} = nFA[O]^b D_O^{1/2} \tag{5}$$

$$I_1([R]^* \rightarrow 0) : I^R_{\mathrm{lim}} = nFA[R]^b D_R^{1/2} \tag{6}$$

$[x]^b$ and $[x]^*$ are the concentrations of the electroactive species in the bulk electrolyte and at the electrode, respectively; A is the electrode area, and F is the *Faraday* constant.

Oldham and others [4–8] have suggested an alternative in which the *semi*-integral of the current is calculated *via* relationship (7) where $i(u)$ is the current at time u prior to the time of evaluation t of I_1.

$$I_1 = I_1(t) = \int_0^t \frac{i(u)}{\pi(t-u)^{1/2}} \mathrm{d}u \tag{7}$$

under conditions of constant potential chronoamperometry, the linearity of $i(t)$ with I_1 in Eq. (8) allows the above parameters to be determined in principle in any regime of electron transfer.

$$i(t) = -\beta I_1 + \gamma \tag{8}$$

Therefore, the chronoamperometric data were explored *via* Eq. (8), where γ and β have the meanings defined above. The linear relation between i and I_1 suffers from the charging current, and damping exists in the early stages of the recorded current data, affecting the convoluted current I_1.

However, in this work we have used an alternative strategy which involves an equally exact linearization procedure which is advantageous in the treatment of experimental data and is simple to invoke in terms of computational requirements. The alternative linear expressions (9) can be utilized:

$$\frac{\Delta Q}{\Delta i} = \frac{2\gamma}{\pi^{1/2}\beta}\frac{\Delta t^{1/2}}{\Delta i} + \frac{1}{\beta^2} \tag{9}$$

The use of the algebraic difference between any two individual data points, not necessarily adjacent, which is indicated by the symbol Δ, provides an exact method for obtaining a linear relation. The charging currents – once they have decayed – do not affect the subsequent linearity of the expression, and the displacement of the points contributing to the delta function can be varied to offset the effect of noise on a particular data set. Thus, no distortion due to charging currents or damping effects occurs.

In the industrial field, acidified solutions of ferric chloride are most commonly used as chloride leachants [9–10] for the dissolution of metal ore minerals. A better understanding of the electrochemical behaviour and an accurate measurement of the heterogeneous transfer kinetic parameter of the ferrous-ferric system by modern electroanalytical techniques allows to explain of the role of this redox couple in the leaching process. In this work, an experimental determination of the heterogeneous electrochemical parameters of the quasi-reversible hydrometallurgically important system Fe^{2+}/Fe^{3+} in $0.1\,M$ aqueous HCl at a glassy carbon electrode using convolutive chronoamperometric as well as convolutive-deconvolutive cyclic voltammetric techniques is presented.

Results and Discussion

Figure 1 shows the profiles of the chronoamperometric data at overpotentials of 0.15 V and −0.15 V, respectively, for the $FeCl_3/FeCl_2$ couple for both oxidation and reduction processes. The starting potential of the chronoamperometric experiment is always set to the equilibrium potentials (open circuit potential, 0.436 V *vs.* SCE). It is obvious that the slow rise in current is due to a slight excess of damping. These results do not adhere to the *Cottrell* relationship (Eq. 10), where I_1 depends on the

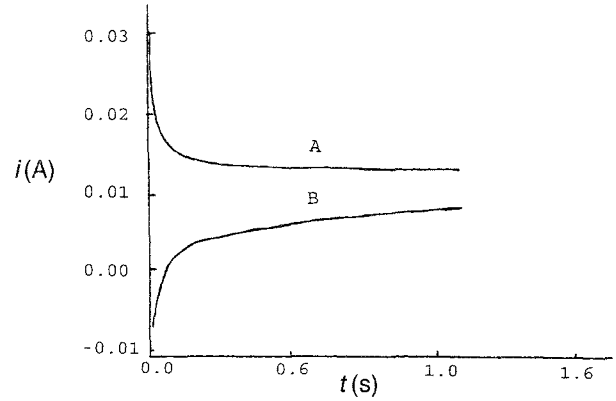

Fig. 1. Chronoamperometric data for $FeCl_3/FeCl_2$ in $1\,M$ HCl containing $10^{-2}\,M$ $FeCl_3$ and $10^{-2}\,M$ $FeCl_2$ at a GCE; $E_{eq} = 0.435\,V$ *vs.* SCE; A Oxidation, B reduction

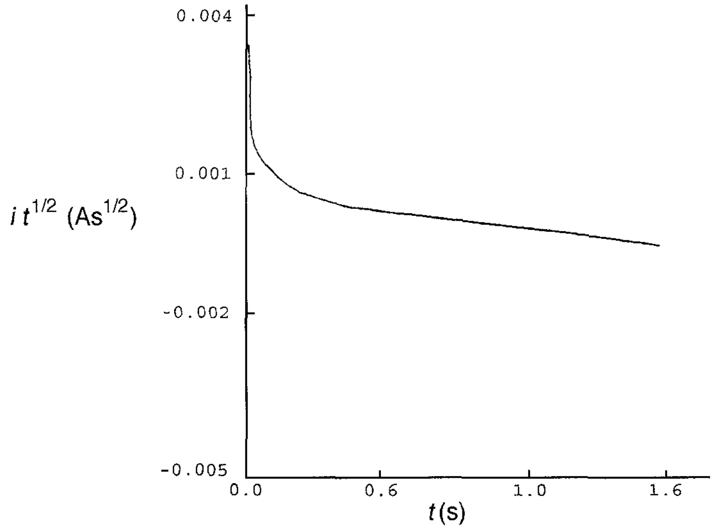

Fig. 2. Plot of $i\sqrt{t}$ *vs.* t for the $FeCl_3/FeCl_2$ system

potential, *i.e.* it is constant with time. This is demonstrated by a plot of $it^{1/2}$ *vs.* t (Fig. 2) and confirms the quasi-reversible electron transfer.

$$i(t) = I_1/(\pi t)^{1/2} \tag{10}$$

Under conditions of constant potential chronoamperometry, the linearity of $i(t)$ with I_1 in Eq. (8) allows k_{hf}, k_{hb}, D_O, and D_R to be determined in principle in any regime of electron transfer. Eq. (8) can be modified as follows:

$$i(t) = -\beta I_1 + \gamma = gI_1 + c \tag{11}$$

In the limiting case ($k_{\mathrm{hf}} > k_{\mathrm{hb}}$, *i.e.* at sufficiently large overpotentials, $[O]^*$ approaching zero), the second terms in Eqs. (3) and (4), vanish affording Eqs. (12) and (13).

$$\gamma = I^{O}_{\mathrm{lim}} \cdot \frac{k_{\mathrm{hf}}}{D_O^{1/2}} \tag{12}$$

$$\beta = \frac{k_{hf}}{D_O^{1/2}} \tag{13}$$

Therefore, a measurement of the intercept c and the gradient g $(i.e.\beta)$ yields D_O and k_{hf} (or, if $k_{\mathrm{hb}} \gg k_{\mathrm{hf}}, D_R$ and k_{hb}) from the linear relation of $i(t)$ *vs.* I_1 for both the oxidation and the reduction process. At very large overpotentials, the gradients approach negative infinity and hence indicate a trend towards *Cottrell* behaviour [11]. In this case, the potential dependent rate constant k_{hf} can be calculated from a measurement of the gradient g according to Eq. (14).

$$g = -\beta = -k_{\mathrm{hf}}/D_O^{1/2} \tag{14}$$

Additionally, the changes in the gradient values with overpotential provide a route to the standard heterogenous rate constant k^0 and the symmetry coefficient α and

Table 1. Chronoamperometric data obtained from the linear relationship $i(t) = gI_1 + C$ for $10^{-2}\,M$ $FeCl_3/FeCl_2$ at a glassy carbon electrode

E-E^0 (V)	c (V)	g (V^{-1})	$\ln k_h$
0.15	4.32×10^{-4}	−2.38	−9.777
0.14	4.31×10^{-4}	−2.32	−9.803
0.13	4.30×10^{-4}	−1.09	−10.558
0.12	4.29×10^{-4}	−0.78	−10.893
0.11	4.28×10^{-4}	−0.61	−11.138
−0.11	-4.36×10^{-4}	−4.84	−9.069
−0.12	-4.26×10^{-4}	−1.78	−10.702
−0.13	-4.27×10^{-4}	−1.15	−10.507
−0.14	-4.26×10^{-4}	−1.80	−10.059
−0.15	-4.26×10^{-4}	−2.98	−9.555

hence can be used as a test for the *Butler-Volmer* relationship. The values of intercepts c and gradients g from i/I_1 plots are given in Table 1. The diffusion coefficients $D(FeCl_2) = 5.68 \times 10^{-10} m^2/s$ and $D(FeCl_3) = 5.65 \times 10^{-10} m^2/s$ were obtained from I_{lim} $(FeCl_2) = 4.30 \times 10^{-4} As^{-1}$ and $I_{lim}(FeCl_3) = 4.29 \times 10^{-4} As^{-1}$, respectively (Table 2). The *Butler-Volmer* relationship can be written in the form of

$$\ln k_h = \alpha nF(E - E^0)/RT + \ln k^0 \tag{15}$$

where k_{hf} is the heterogeneous rate constant of the electron transfer, E is the electrode potential, and E^0 is the standard electrode potential. Eq. (15) is a linear relationship and yields the values of k^0, α_{anodic}, $\alpha_{cathodic}$ (symmetry coefficients), and $E_{1/2}$ (Table 2).

There is an alternative to using Eq. (11) which does not rely experimentally on convolution of the current-time relationships and which has the advantage of not being dependent on the charging current after its decay. The terms $\Delta Q/\Delta i$ and $\Delta t^{1/2}/\Delta i$ are functions which do not contain contributions from charging currents. Therefore, measurements of the data when the charging current has diminished should reflect the real kinetic performance of the electrode process.

Derivation of the novel chronoamperometric data plot

For a moderate electron transfer process, the current response given by Eq. (2) can be represented in the form

$$i = \gamma \cdot m(w), w = \beta t^{1/2}, m(w) = e^{w^2} \operatorname{erfc} w \tag{16}$$

where

$$\operatorname{erfc} \sigma = 1 - \frac{2}{\pi^{1/2}} \int_0^{\sigma} e^{-w^2} dw \tag{17}$$

Eq. (16) can be expressed in terms of dw (w)/dw:

$$\frac{dm(w)}{dw} = 2mw - \frac{2}{\pi^{1/2}} \tag{18}$$

Table 2. Electrochemical parameters for 10^{-2} M $FeCl_3/FeCl_2$ at a glassy carbon electrode

$D_{FeCl_2} \times 10^{10}$ (m^2/s)	5.68^a 5.61^b 5.57^c 5.60^d
$D_{FeCl_3} \times 10^{10}$ (m^2/s)	5.65^a 5.67^b 5.53^c 5.60^d
$k^0 \times 10^6$ (m/s)	3.1 ± 1.2^a 1.7 ± 0.7^b 3.0^d 3.5 ± 0.5^e
α_{anodic}	0.32 ± 0.02^a 0.43 ± 0.01^b 0.50^d
$\alpha_{cathodic}$	0.47 ± 0.04^a 0.48 ± 0.03^b 0.50^d
$E_{1/2}$ V *vs.* SCE	0.4358^a 0.4356^b 0.436^d 0.435^f

[a] $i(t) = gI_1 + c$; [b] $\Delta Q/\Delta i$ *vs.* $\Delta t^{1/2}/\Delta i$; [c] limiting convoluted current I_{lim}; [d] digital simulation; [e] cyclic voltammetry; [f] deconvolution voltammetry (dI_1/dt)

The expression for dm (w)/dw Eq. (18) leads to a suitable test for the experimental data *via* di/d$t^{1/2}$ in terms of i and t.

By integrating Eq. (18), we get the step function

$$\Delta m = \int_{w_1}^{w_2} m \cdot d(w^2) - \frac{2\Delta W}{\pi^{1/2}} \tag{19}$$

Expressing m in terms of i and w in terms of t gives

$$\frac{\Delta i}{\gamma} = \frac{\beta^2}{\gamma} \int_{t_1}^{t_2} i dt - \frac{2\beta \Delta t^{1/2}}{\pi^{1/2}} \tag{20}$$

Rearrangement of Eq. (20) affords

$$\int_{t_1}^{t_2} \frac{i dt}{\Delta i} = \frac{2\gamma \Delta t^{1/2}}{\pi^{1/2} \beta \Delta i} + \frac{1}{\beta^2} \tag{21}$$

or

$$\frac{\Delta q}{\Delta i} = \frac{2\gamma}{\pi^{1/2}\beta} \frac{\Delta t^{1/2}}{\Delta i} + \frac{1}{\beta^2} \tag{22}$$

Eq. (22) has the form of a linear relationship

$$y = gx + c \tag{23}$$

where

$$q = \int_0^t i\mathrm{d}t, y = \Delta q/\Delta i, \quad \text{and} \quad x = \Delta t^{1/2}/\Delta i \tag{24}$$

All values can easily be calculated from current/time data. The unknown values of γ and β can be calculated from the intercept

$$c = \beta^{-2}, \; i.e.\ \beta = c^{-1/2} \tag{25}$$

and the gradient

$$g = \frac{2\gamma}{\pi^{1/2}\beta} \tag{26}$$

In the limiting case ($k_{\mathrm{hf}} >> k_{\mathrm{hb}}$) one finds that Eqs. (12) and (13) can be applied; so

$$\frac{\gamma}{\beta} = I^O_{\mathrm{lim}} = nFAD_O^{1/2}[O]^{\mathrm{b}} \tag{27}$$

$$g = \frac{2}{\pi^{1/2}} \cdot I^O_{\mathrm{lim}} \tag{28}$$

Hence, D_O of the electroactive species O can be calculated from Eq. (29),

$$D_O = \left(\frac{\pi^{1/2}g}{2nFAD_O^{1/2}[O]^{\mathrm{b}}}\right)^2 \tag{29}$$

and k_{hf} can be calculated from Eq. (30):

$$k_{\mathrm{hf}} = \frac{\pi^{1/2}g}{nFAD_O^{1/2}[O]^{\mathrm{b}}} = (D_O/C)^{1/2} \tag{30}$$

The gradients of $\Delta Q/\Delta i$ *vs.* $\Delta t^{1/2}/\Delta i$ plots which are calculated from the same original data as used in the above analysis of i(t) with I_1 provide a direct route to the diffusion coefficient D_O *via* Eq. (29). The potential dependent rate constant (k_{hf}) can be calculated from the measurement of the gradient (g) and the intercept (c) and *via* Eq. (30). Table 3 shows the chronoamperometric data obtained from Eq. (22).

Cyclic voltammograms of the $FeCl_3/FeCl_2$ couple, recorded using a glassy carbon electrode, are presented in Fig. 3. At a sweep rate of 5 mV/s, $\Delta E_{\mathrm{p}} =$ 165.7 mV, whereas at a scan rate of 20 mV/s, $\Delta E_{\mathrm{p}} = 241.6$ mV. Thus, the peak separation ΔE_{p} between the forward and backward sweep is greater than that expected for a reversible one electron transfer (59.6 mV) and increases with increasing sweep rate. This results confirms the quasi-reversible nature of the electron transfer. The numerical value for the standard heterogeneous rate constant, k^0, was obtained from a measurement of the peak separation (ΔE_{p}) in cyclic voltammograms of the $FeCl_3/FeCl_2$ couple *via* the *Nicholson* method [12].

Table 3. Chronoamperometric data obtained from the function $\Delta Q/\Delta i = g\Delta t^{1/2}/\Delta i + c$ for 10^{-2} *M* $FeCl_3/FeCl_2$ at a glassy carbon electrode

E-E^0 (V)	g ($As^{1/2}$)	c (s)	$\ln k_h$
0.15	1.82×10^{-4}	0.089	−9.432
0.14	1.80×10^{-4}	0.109	−9.532
0.13	1.78×10^{-4}	0.123	−9.605
0.12	1.78×10^{-4}	0.222	−9.906
0.11	1.77×10^{-4}	0.298	−10.056
−0.11	-1.94×10^{-4}	0.062	−9.182
−0.12	-1.83×10^{-4}	0.298	−10.025
−0.13	-1.82×10^{-4}	0.219	−9.877
−0.14	-1.85×10^{-4}	0.135	−9.861
−0.15	-1.81×10^{-4}	0.078	−9.366

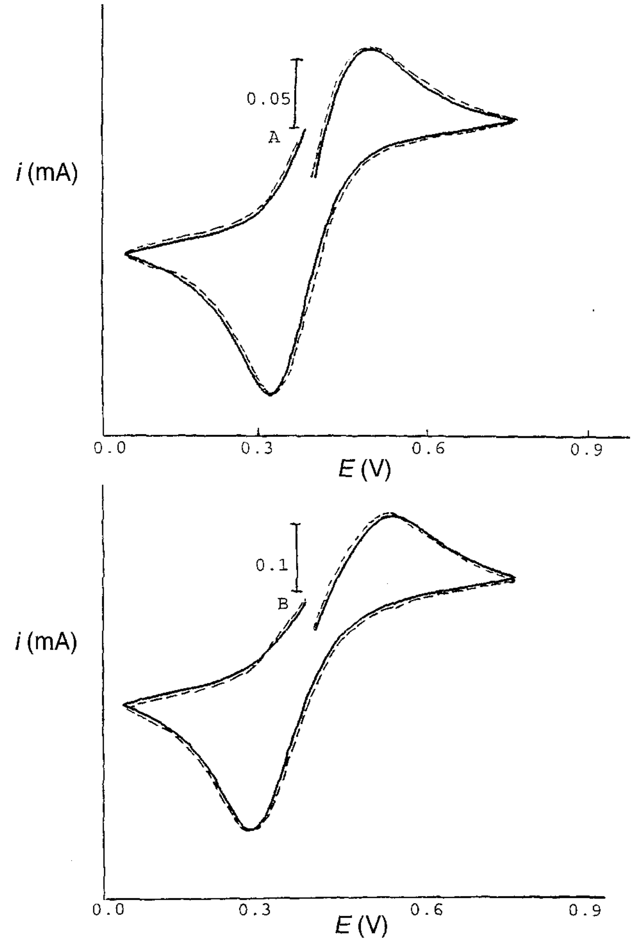

Fig. 3. Experimental (——) and simulated (- - -) cyclic voltammograms for the $FeCl_3/FeCl_2$ system in 1 *M* HCl at a GCE; A sweep rate of 5 mV/s, B sweep rate of 20 mV/s

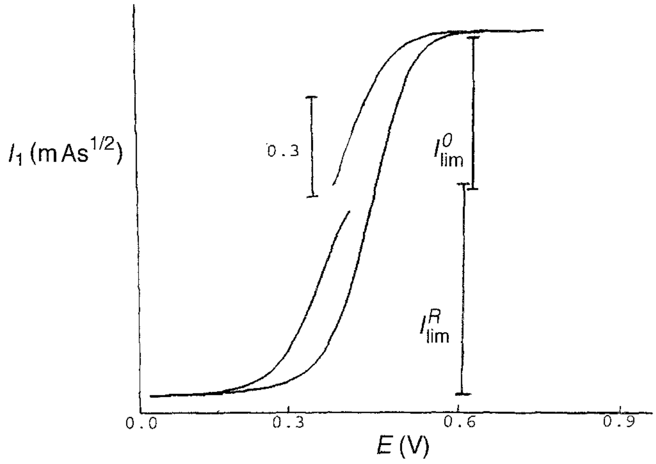

Fig. 4. I_1 convolution of cyclic voltammetry at 5 mV/s

The charge transfer parameter ψ was calculated from the following relationship:

$$\psi = \frac{k^O (D_O/D_R)^{\alpha/2}}{(\pi n F(v) D_O/RT)^{1/2}} \tag{31}$$

The variation of ΔE_p with ψ gave a mean value of $k^O = (3.5 \pm 0.5) \times 10^{-6}$ m/s, (Table 2) which is in approximate agreement with that obtained from chronoamperometric analysis in this work. The values for k^O listed in Table 2 are comparable with those obtained by others [9, 10]. *Sharma* and *Dutt* [10] have determined these parameters in 1 M HCl at 21°C on graphite, using dc polarography in flowing media. Results were as follows: $\alpha_{\text{cathodic}} = 0.59$, $k^O = 1.2 \times 10^{-6}$ m/s. From the present communication it is important to note that the values of the heterogeneous rate constant k^O determined using two different techniques and digital simulation do not coincide. Based on the above results, a digital simulated cyclic voltammogram was generated using the EG & G Condesim 300 software. The simulated data are in good agreement with experimental results obtained on the $FeCl_3/FeCl_2$ couple in 1 *M* HCl using a glassy carbon electrode. Table 2 also shows the electrochemical parameters used for generating the theoretical current-potential curve. The almost perfect fit with the experimental results shown in Fig. 3 is a direct validation of the parameters.

Figure 4 shows the I_1 convolution of cyclic voltammetry at 5 mV/s and indicates a separation between the forward and backward sweeps which confirms the quasi-reversibility of electrode reaction. The diffusion coefficients evaluated *via* I_{lim} using Eq. (5) and (6) are cited in Table 2. They compares well with the values determined from chronoamperometric techniques. Deconvoluted current data (dI_1/dt) which are simply the differential of current i are shown in Fig. 5. The diagram shows the expected deviation in the cathodic to anodic deconvoluted peak current ratios varying with the scan rate. The anodic deconvoluted current peak potential is located at more positive potentials than the cathodic peak, and $E_{1/2}$ was estimated approximately from the mean of the peak potentials [13, 14] ($E_{1/2} = 0.435$ V). The width of the deconvoluted current ($W_{1/2}$) confirms the

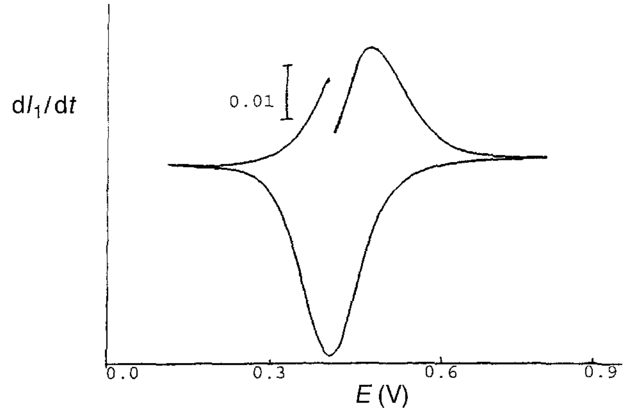

Fig. 5. Deconvoluted current data (dI_1/dt) at 5 mV/s

electron transfer behaviour of the examined system, since the calculated peak is shifted from values expected for *Nernstian* deconvoluted currents [14]. The experimental values of $W_{1/2}$, as expected, deviate considerably from the *Nernstian* system value, *e.g.* $W_{1/2} = 140.7$ mV at 5 mV/s and 105.3 mV at 20 mV/s, and the peak becomes broader upon increasing the sweep rate.

Experimental

A Princeton Applied Research (PAR) potentiostat/galvanostat model 362 (from EG & G) with a Condecon software package supplied by EG & allowed the data capture of electrochemical current data as well a convolutive-deconvolutive analysis. Condesim software, also supplied by EG & G, was used for the generation of the theoretical current-potential curve. The current was electrically damped prior to data capture using the EG & G Condecon signal conditioning unit to reduce the charging current associated with the capacitance of the electrical double layer and to improve the signal to noise ratio.

Cyclic sweep voltammetry and chronoamperometry were performed *via* a convential three electrode cell configuration. Background data were stored and subtracted from the experimental data set, minimizing side effects such as double layer charging currents. A Metrohm inlaid glassy carbon disk electrode was used as a working electrode (geometrical surface area: $1.87 \times 10^{-2} m^2$) in unstirred 1 *M* HCl solution containing the electroactive species (1×10^{-2} *M* of $FeCl_3$ and 1×10^{-2} *M* or $FeCl_2$) at 27°C. To obtain a reproducible electrode surface, the GCE was polished using a Metrohm polishing kit for 2 min. The reference electrode was a saturated calomel electrode, and a 1 cm^2 platinum sheet auxiliary electrode was used. In case of cyclic voltammetric studies, the potential was normally scanned at low rates (typically 5 or 10 $mV{\cdot}s^{-1}$) to obtaint kinetic parameters for the quasi-reversible $FeCl_3/FeCl_2$ couple. For chronoamperometric experiments, the optimal duration of polarization was between 0.2 and 0.5 s.

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Received March 11, 1997. Accepted (revised) June 2, 1997