A Mechanistic Electrochemical Study of *bis*-(Azaferrocene-15-crown-5-ether) at a Glassy Carbon Electrode

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Summary. The work described in this paper concerns the electrochemical behaviour of *bis*-(azaferrocene-15-crown-5-ether) at a glassy carbon electrode using CV, CA, and CP techniques. On sweeping to positive direction, a one electron quasi-reversible oxidation wave coupled with a following chemical reaction is observed. Values of the chemical rate constant k_c, the rate constant of heterogeneous electron transfer k^0, the half-wave potential $E_{1/2}$, the transfer coefficient α, and the diffusion coefficient D of the depolarizer species are determined and discussed.

Keywords. Cyclic voltammetry; Mechanistic study; *bis*-(Azaferrocene-15-crown-5-ether).

Mechanistische elektrochemische Untersuchung von *bis*-(Azaferrocen-15-Krone-5-Ether) an einer Glaskohlenstoffelektrode

Zusammenfassung. Die vorliegende Arbeit beschäftigt sich mit dem elektrochemischen Verhalten von *bis*-(Azaferrocen-15-Krone-5-Ether) an einer Glaskohlenstoffelektrode; die Untersuchungen wurden mittels CV-, CA- und CP-Techniken durchgeführt. Bei einem sweep in positiver Richtung beobachtet man eine quasi-reversible Einelektronen-Oxidationswelle, gekoppelt mit einer darauffolgenden chemischen Reaktion. Die folgenden Parameter wurden bestimmt: Geschwindigkeitskonstante der chemischen Reaktion (k_c), Geschwindigkeitskonstante des heterogenen Elektronentransfers (k^0), Halbwellenpotential $(E_{1/2})$, Transferkoeffizient (α) und Diffusionskoeffizient (D).

Introduction

With a view of chemical sensor technology, modelling electron transfer processes in biological systems, and producing new redox catalysts, considerable interest is focused on the syntheses of redox-active macrocyclic molecules that contain a redox center in close proximity to a host binding site [1, 2]. The ferrocene crown ether compound examined electrochemically in the present work ($C_{36}H_{56}N_2O_{12}Fe$) is of importance in this respect. We here report the electrochemical and kinetic parameters of $C_{36}H_{56}N_2O_{12}Fe$, using the various modern electrochemical techniques often combined with digital simulation treatments. A comparison of parameters measured by various techniques serves to emphasize the correct applicability of a mechanistic scheme.
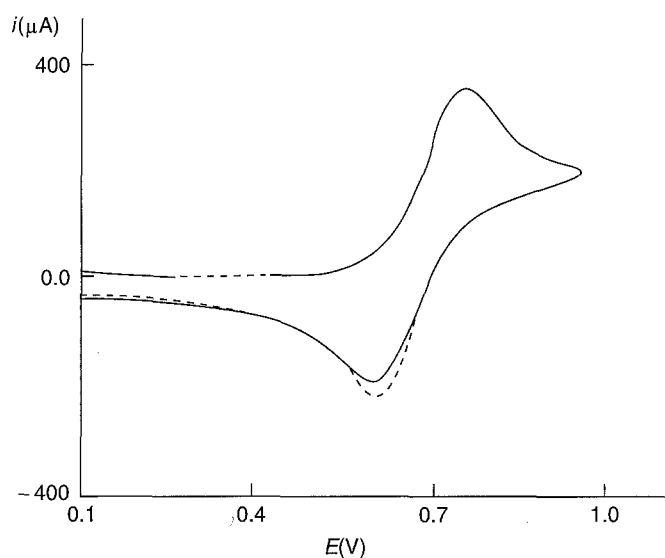
Fig. 1. Voltammograms for C_{36}-$H_{56}N_2O_{12}Fe$ at a glassy carbon electrode; —— experimental, --- theoretical (simple ET reaction); sweep rate: 50 mV/s; $T = 17\,^{\circ}C$

Results and Discussion

Direct comparison of experimental and simulated cyclic voltammograms

Figure 1 shows a cyclic voltammogram encompassing the oxidation process of a $1 \times 10^{-2}\,M$ $C_{36}H_{56}N_2O_{12}Fe$ solution at a glassy carbon electrode in CH_2Cl_2 in presence of $0.1\,M$ $TBAP$ at a temperature of $17\,^{\circ}C$ and a sweep rate of $50\,mV/s$ after applying background substraction and correction for uncompensated resistance. A digitally simulated voltammogram for a simple electron transfer process is superimposed on this. The excellent initial overlay of the experimental and digitally simulated voltammograms contrasts with the slight discrepancy of the return wave. At this stage, the latter may be tentatively ascribed to a following chemical reaction [3–6] (the experimental return peak height is slightly reduced).

The quasi-reversible electron transfer of the oxidation process of $C_{36}H_{56}N_2O_{12}Fe$ was substantiated by the peak to peak separation (ΔE_p) between the forward and backward scans [7]. The ΔE_p values given here are substantially shifted from the *Nernst*ian processes [7] ($59\,mV$ at $17\,^{\circ}C$); e.g., $\Delta E_p = 165.7$ and $241.6\,mV$ at 50 and $200\,mV/s$, respectively (Table 1).

Simulating the above situation for an EC_{irrev} reaction gave an almost perfect fit with experimental results for $k_c = 2 \times 10^{-2}\,s^{-1}$ this is a direct validation of the parameters, noting at present that the electron transfer is quasi-reversible (Fig. 2).

Convolution and deconvolution treatments

Convolution techniques provide a more segmented alternative parameter assessment to the direct comparison of experimental with simulated cyclic voltammograms of the compound under investigation. This is shown in the following:

i) The convoluted current I_1 diagrams at sweep rates of 50 and $200\,mV/s$ show nearly constant limiting values I_{lim}^A at the end of the forward sweep (Fig. 3). This

Table 1. Cyclic voltammetry and convolution data obtained for the oxidation process of $C_{36}H_{56}N_2O_{12}Fe$ at a glassy carbon electrode at $17\,°C$

Sweep Rate (mV/s)	ΔE_p (mV)	k^0 (m/s)	$I_{lim} \times 10^5$ $(As)^{1/2}$	$D_A \times 10^9$ (m^2/s)
20	125.2	1.67	5.86	0.97
50	165.7	1.68	5.91	0.99
100	202.1	1.68	5.98	1.01
200	241.6	1.67	5.88	0.98
500	315.4	1.66	5.87	0.97
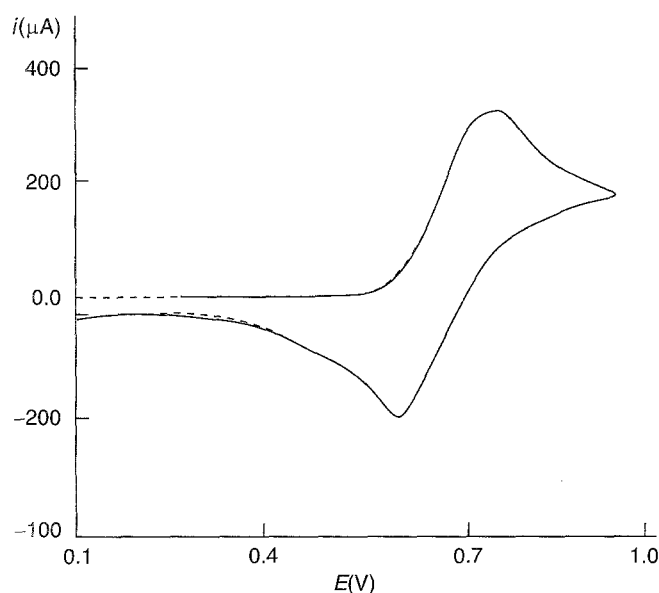
Fig. 2. Voltammograms for C_{36}-$H_{56}N_2O_{12}Fe$ at a glassy carbon electrode; —— experimental, --- theoretical (EC_{irrev} reaction); sweep rate: 50 mV/s; $T = 17\,°C$

provides a route for evaluating the diffusion coefficient of the electroactive species using the equations for diffusion controlled conditions [8]. The constancy of the limiting convoluted current is consistent with E and EC processes. Under these conditions, the concentration of the electroactive species at the electrode surface is zero [7], i.e. $[A]_{(0,t)} = 0$. Then

$$I_{lim}^A = nFa[A]^* D_A^{1/2},\qquad(1)$$

where n is the number of electrons transferred in the electrochemical reaction, F is *Faraday*'s constant, $[A]^*$ is the concentration of electroactive species in the bulk of the solution, a is the electrode area, and D_A is the diffusion coefficient of the species. Hence, the mean value of the diffusion coefficient $(0.98 \pm 0.05 \times 10^{-9}\,m^2/s)$ was evaluated from the recorded I_{lim}^A using Eq. 1.

ii) I_1 does not return to zero on the reverse half of the sweep. This again is consistent with EC behaviour [6], in which case the diffusional fields of both reactant and electrochemical product are affected by the chemical reaction. This in turn reflects
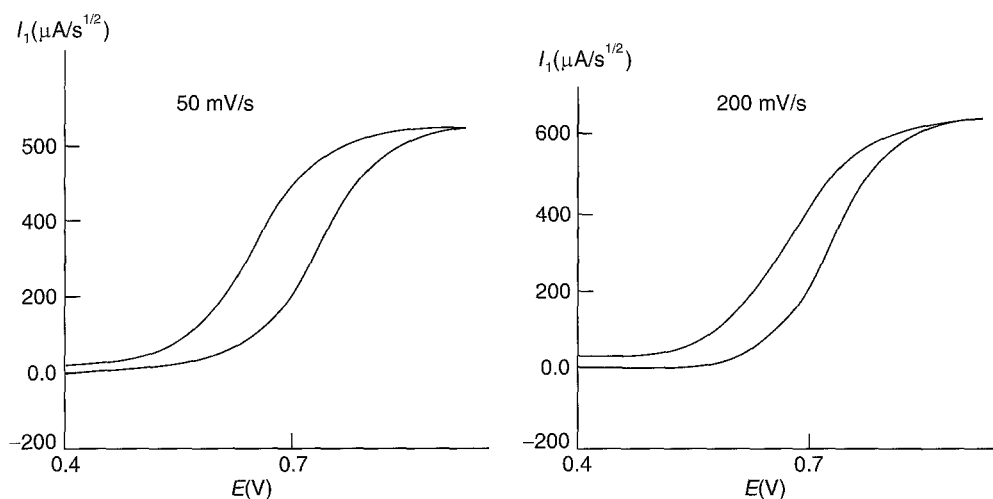
Fig. 3. Convoluted currents for $C_{36}H_{56}N_2O_{12}Fe$ at a glassy carbon electrode (sweep rates: 50 and 200 mV/s; $T = 17\,°C$)

a relative lowering of their concentrations at the electrode surface on returning the potential to the starting value. The electrochemical product is directly related to the failure of I_1 to return to an initial (zero) value at the end of a sweep. The following equation shows that $[A]_{(0,t)}$ (concentration of electroactive species at electrode surface) does not approach $[A]^*$ under the above condition.

$$[A]_{(0,t)} = [A]^* - \frac{I_1}{nFaD_A^{1/2}}$$ (2)

iii) The gap in I_1 between the sweep halves becomes wider at higher sweep rates, consistent with a quasi-reversible electron transfer [6]. The value of the standard heterogeneous rate constant k^0 is evaluated using the current function of Nicholson [9]. Assuming an equality of the diffusion coefficients of electrochemical species, the value of D is obtained from the limiting convoluted current as described in equation 1; the values of k^0 were calculated at different sweep rates (20 to 500 mV/s). Values of ΔE_p and the resulting k_0 are given in Table 1. A mean value of k^0 of $1.67 \pm 0.03 \times 10^{-5}$ m/s is obtained which is in approximate agreement with those obtained from a digital simulation treatment.

iv) The failure of I_1 to return to zero after the wave (Fig. 3) indicates the probability of a following chemical reaction.

Now we can consider the following scheme:

$$A \underset{k_{hb}}{\overset{k_{hf}}{\rightleftharpoons}} B + ne^- \xrightarrow{k_c} C,$$ (3)

where A and B are the electrochemical species, C is the chemical product, k_{hf} and k_{hb} are the forward and backward heterogeneous rate constants, respectively, and k_c is the electrochemical rate constant.

To evaluate the rate constant K_c in Eq. 3 we must have access to either the surface concentration $[A]_{(0,t)}$ alone or of $[B]_{(0,t)}$ alone. This is possible with the use of
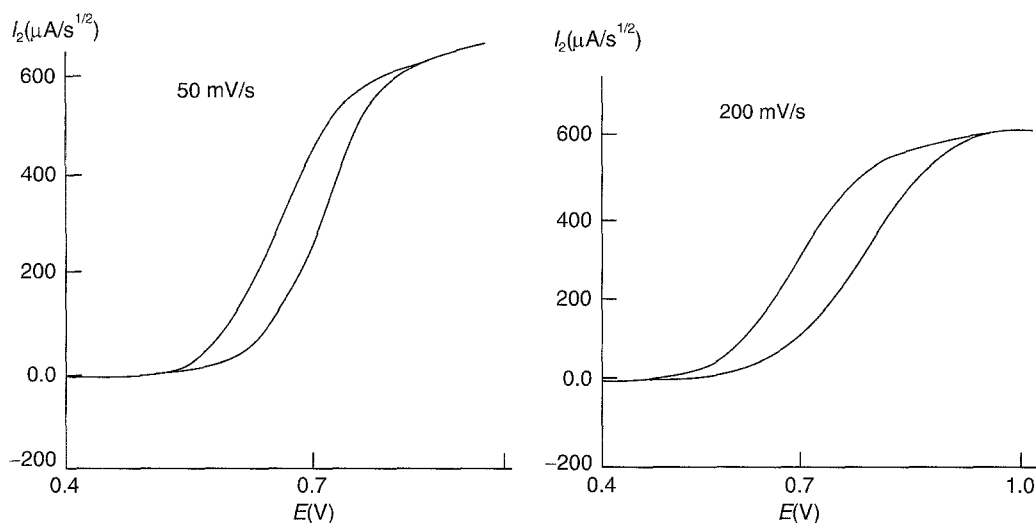
Fig. 3. Convoluted currents for $C_{36}H_{56}N_2O_{12}Fe$ at a glassy carbon electrode (sweep rates: 50 and 200 mV/s; $T = 17\,°C$)

a second integral I_2 [7]:

$$I_2 = \frac{1}{(\pi)^{1/2}} \int_0^t \frac{i(u)}{(t-u)^{1/2}}\, e^{-kc(t-u)}\, du \tag{4}$$

From Eqs. 2 and 4, we get

$$[B]_{(0,t)} = \frac{I_2}{nFaD_B^{1/2}} \tag{5}$$

The kinetic convolution I_2, however, is forced to zero [10] at the end of cyclic sweeping for an EC_{irrev} process because it is at all stages proportional to the concentration of the electroactive species B at the electrode surface. Since the chemical rate constant k_c is within the kinetic convolution, it is a reasonably simple task to calculate I_2 for a variety of test values to home in on the true value of k_c [10].

Using the digital simulation software 'CONDECON' allowed the estimation of the rate constant k_c, giving values for k_c of $2.0 \times 10^{-2}\,s^{-1}$ and $1.8 \times 10^{-2}\,s^{-1}$ for slow and fast sweeping (50 and 200 mV/s), respectively. The mean of these values $(1.9 \times 10^{-2}\,s^{-1})$ is therefore taken as the rate constant, and the relative constancy over a range of sweep rates confirms in a direct manner the EC_{irrev} mechanism [6]. The presentation of the kinetic convolution transforms is shown in Fig. 4 for two different sweep rates (50 and 200 mV/s).

Deconvoluted current data (dI_1/dt) in Fig. 5 show the expected deviation in the cathodic to anodic deconvoluted peak current ratios in a manner which varies with scan rate. The anodic deconvoluted current peak potential is located at more positive potentials than the cathodic peak. $E_{1/2}$ was estimated approximately from the mean of the peak potentials [11] $(E_{mean} = 0.68\,V)$. Digital simulation was employed at this stage to estimate the likely discrepancy between the mean of peak potential and $E_{1/2}$ for $k^0 = 1 \times 10^{-5}\,m/s$ at a variety of values of α. The other
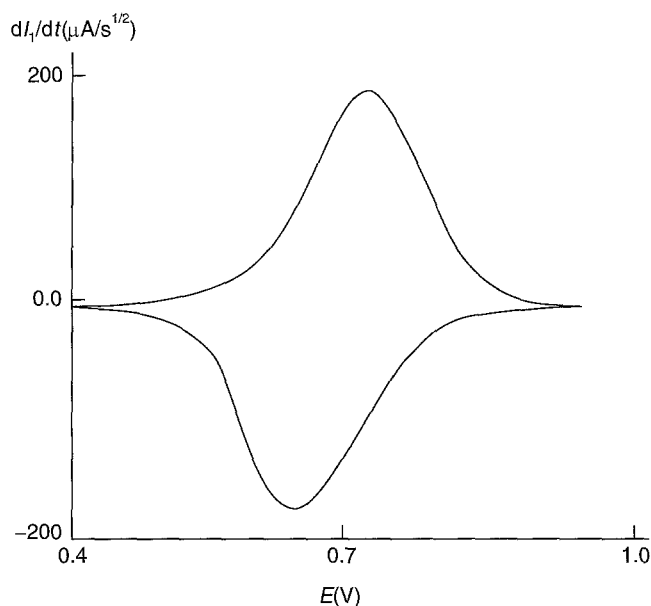
Fig. 5. Deconvoluted current for $C_{36}H_{56}N_2O_{12}Fe$ at a glassy carbon electrode (sweep rate: 50; $T = 17\,°C$)

Table 2. Digital simulated deconvoluted current data at a sweep rate of 1 V/s at different α values for $C_{36}H_{56}N_2O_{12}Fe$

α	E_{mean} (V)	ΔE (mV)
0.40	0.5335	33.5
0.44	0.5171	17.1
0.50	0.5037	3.65

parameters used were similar to those employed in the initial simulation. The obtained results at a sweep rate of 1 V/s are shown in Table 2.

The results thus indicate an overassessment of $E_{1/2}$ of 17 mV for $\alpha = 0.44$, yielding a correct value of $E_{1/2} = 0.663$. The half-peak width ($W_{1/2}$) of the forward peak deviates as expected from the theoretical value for a reversible one electron transfer process (88.09 mV at 17 °C) [3] and is a function of the sweep rate ($W_{1/2} = 146.8$ and 187.6 mV at 50 and 200 mV/s, respectively). All these observations are entirely consistent with a quasi-reversible one electron transfer followed by an irreversible chemical reaction.

On the basis of the above data, the CV oxidation wave of the compound under investigation can be represented by the following electrochemical reaction:
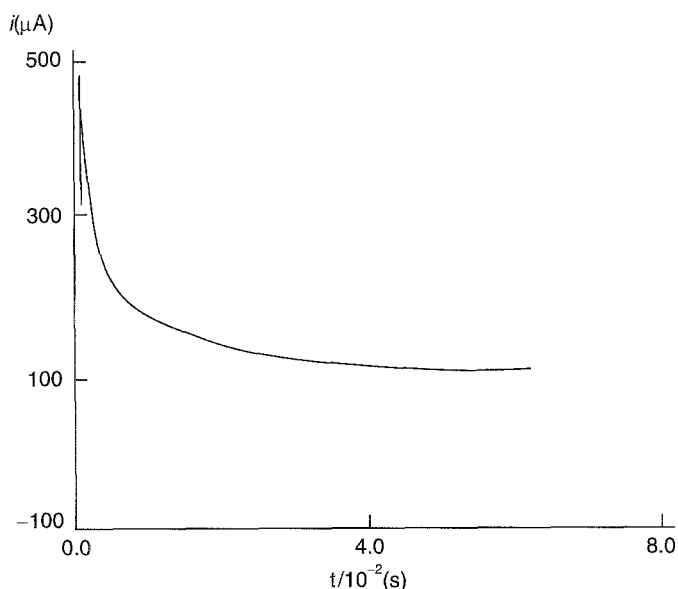
$$Fc(complex) \longrightarrow Fc^{+1}(complex) + e^{-}$$
$$\downarrow k_c$$
$$\text{Products (Electroinactive)}$$

i(μA)
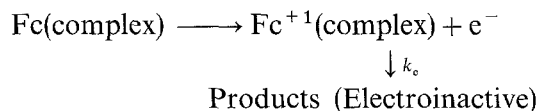
Fig. 6. Chronoamperogram for $C_{36}H_{56}N_2O_{12}Fe$ at a glassy carbon electrode ($T = 17\,°C$)

Chronopotentiometric and chronamperometric measurements

Chronoamperometric experiments at the GCE were performed to determine the charge transfer parameters and to attempt to confirm the conclusions drawn from the previous voltammetric examination. The heterogeneous rate constant k^0 and the symmetry coefficient (α) were evaluated as described below.

Chronoamperometric experiments were performed under the same conditions as the cyclic voltammetric experiments. The chronoamperogram of $C_{36}H_{56}N_2O_{12}Fe$ is shown in Fig. 6; the optimal duration of polarization was between 0.5 and 1 s. The lower limit was dictated by the logistics of collecting 500 data points, whilst the upper time limit is imposed by the increasing contribution of convection within the electrolyte to the mass transport at long measurement times. Electronic damping at the Signal Conditioning Unit was used to reduce the charging current associated with the capacitance of the electrical double layer and hence to improve the signal to noise ratio.

In case of constant potential chronoamperometry, the linearity of $i(t)$ vs. convoluted current I_1 [12] is shown in the following equation and in Fig. 7.

$$i = I_{lim}\frac{k_{hf}}{D_A^{1/2}} - I_1\frac{k_{hf}}{D_A^{1/2}} - I_1\frac{k_{hb}}{D_B^{1/2}}$$ (6)

Hence, at the intercept at $I_1 = 0$, Eq. 6 gives

$$i = I_{lim}\frac{k_{hf}}{D_A^{1/2}};$$ (7)

since $t \to 0$ as $I_1 \to 0$,

$$i = i(t = 0) = nFak_{hf}[A]^*$$ (8)

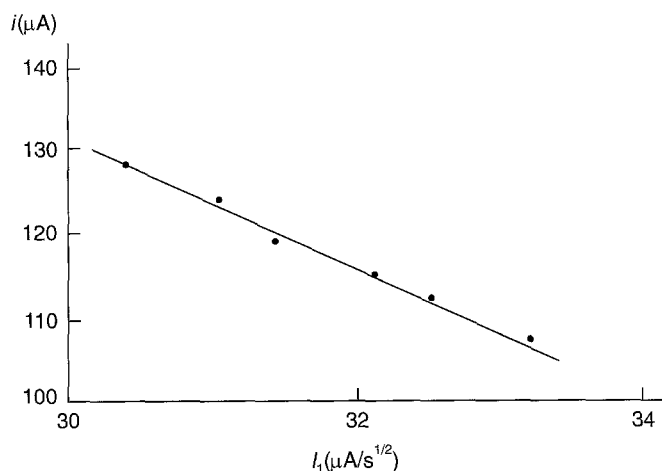Equation 8 allows the estimation of the forward heterogeneous rate constant k_{hf} of the electron transfer process.

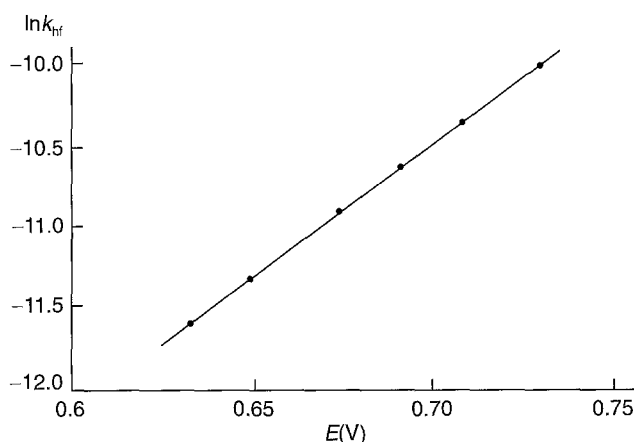**Fig. 7.** Plot of i vs. I_1 for the oxidation of $C_{36}H_{56}N_2O_{12}Fe$ at 17 °C

Fig. 8. Plot of $\ln K_{hf}$ vs. E for the oxidation of $C_{36}H_{56}N_2O_{12}Fe$ at 17 °C

The well-known following equation, equivalent to the *Butler-Volmer* relationship, is a linear relationship between $\ln K_{hf}$ and E represented in Fig. 8.

$$\ln K_{hf} = \alpha n F (E - E^0)/RT + \ln K^0 \qquad (9)$$

It yields the standard heterogeneous rate constant k^0 equal to 1.70×10^{-5} m/s at E^0, using the half wave potential of 0.663 V from the cyclic voltammetry experiment. The symmetry coefficient α (0.44) was also determined from the slope of the graph in Fig. 8. The numerical values of the standard heterogeneous rate constant k^0, the symmetry coefficient α, and the half-wave potential $E_{1/2} = E^0$ agree well with values used in the computer-generated voltammogram to give the best fit with the experimental voltammetric response.

Chronopotentiometric experiments were performed with $C_{36}H_{56}N_2O_{12}Fe$ under conditions similar to those employed with the related electrochemical techniques described above. An imposed current density of 8.8×10^{-4} A/cm^2 was used and a *Sand* time $t_s = 0.33$ s was measured from the chronopotentiogram (Fig. 9). Using the *Sand* equation [13], a diffusion coefficient of 0.93×10^{-9} m^2/s could be estimated which agrees well with the value obtained from other electrochemical techniques.
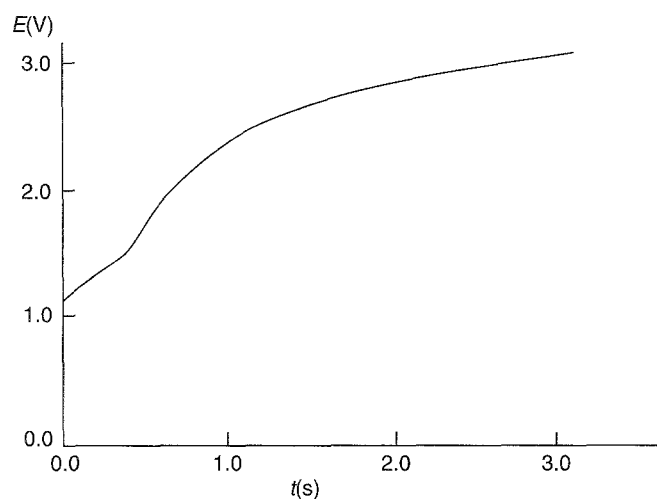
Fig. 9. Chronopotentiogram for $C_{36}H_{56}N_2O_{12}Fe$ at a glassy carbon electrode ($T = 17\,^\circ C$)

Experimental

Preparation of $C_{36}H_{56}N_2O_{12}Fe$

The condensation of 1,1-*bis*(chlorocarbonyl)-ferrocene with 2 moles of an appropriate aza crown ether in the presence of triethylamine afforded after column chromatography separation the respective *bis*(azaferrocene-15-crown-5-ether) [14]. The structure of the compound has been previously characterized by elemental analysis, mass spectroscopy, and ^1H and ^{13}C NMR spectroscopy [14].
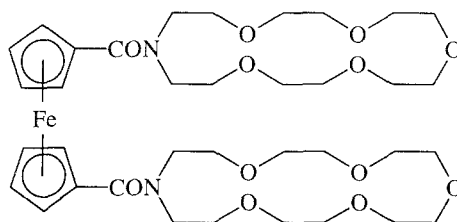
Electrochemical measurements

Cyclic sweep voltammetry, chronoamperometry, and chronopotentiometry were performed using a PAR potentiostat/galvanostat model 362 (from EG and G). An analogue-to-digital converter A/V was used to take the analogue current/potential signal from the potentiostat and to convert it into a digital signal in a form suitable for the computer. Usually 500 points were sufficient, but, if required, up to 2000 could be selected. Data were stored on disc for subsequent analysis using the CONDECON software supplied by EG and G.

The electrochemical measurements were made using a conventional three electrode cell configuration. A Metrohm inlaid glassy carbon disk electrode was used as a working electrode (geometrical surface area of about $0.2\,cm^2$). In order to obtain a reproducible electrode surface in all experiments, the working electrode was cleaned by polishing using a Metrohm polishing kit for 2 min, followed by washing in the solvent system to be used. This process was repeated when a new working solution was introduced to the cell. The reference electrode was formed from silver wire in contact with saturated lithium chloride in dichloromethane/*TBAP* systems. A $1\,cm^2$ platinum sheet auxillary electrode was used. All solutions were $0.01\,M$ in tetrabutylammonium perchlorate (*TBAP*) as the background

electrolyte. The solutions were purged with nitrogen which was maintained above the working solution during measurements. Internal resistance ohmic drop distortions were minimized by applying positive feedback compensation. The system was controlled at a potential where no electron transfer processes were observed, and the feedback resistor was adjusted until it just began to oscillate. The amount of feedback was then reduced by about ten percent to re-establish stability in the potentiostat. This degree of feedback was then used experimentally with an identical solution and cell configuration. Data obtained using the 'feedback' control of the PAR 362 Potentiostat were in excellent agreement with compensation achieved by the capture facilities of the CONDECON software compensation to be made after data collection. This additionally allows criteria for 'correct compensation' to be assessed. Accordingly, software compensation was used throughout.

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