DETERMINATION OF THE CHARGE TRANSFER PARAMETERS OF 4,4′-(FERROCENE-1,1′-DIYLDIVINYLENE)BIS(BENZO-15-CROWN-5) AT GLASSY CARBON ELECTRODE

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Electrochemical parameters of 4,4′-(ferrocene-1,1′-diyldivinylene)bis(benzo-15-crown-5) were collected using cyclic voltammetry, chronoamperometry and chronopotentiometry at a glassy carbon electrode. One-electron quasi-reversible oxidation wave was obtained at E_{pa} of 0.532 V and E_{pc} of 0.387 V. The peak separation, ΔE_p, standard heterogeneous rate constant, k^0, and diffusion coefficient, D, of the electrochemical species have been processed by convolution and deconvolution transformations. Digital simulations using the kinetic parameters were also performed.

Key words: Electrochemistry; Cyclic voltammetry; Chronoamperometry; Glassy carbon; Ferrocenes; Crown ethers.

The convolution–deconvolution voltammetry[1,2] allows to get more qualitative informations from the cyclic voltammetric measurements *i.e.* the reaction sequence with corresponding potential regions as well as informations on (electro)chemical reversibility.

The convolution in the case of simple electron transfer (E process) is a semi-integral[1,2] of the current $i(u)$ measured at time u.

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

where t is the time at which convolution is calculated. For simple electrochemical process Ox → Red with only Ox present we find

$$[\mathrm{Ox}]_b - [\mathrm{Ox}]_e = \frac{I_1}{nFAD_0^{1/2}} \qquad (2)$$

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and

$$[\mathrm{Red}]_\mathrm{e} = I_1 \frac{D_0^{1/2}}{D_\mathrm{R}^{1/2}} \ , \qquad (3)$$

where D is the diffusion coefficient, A is the electrode area, $[\mathrm{Ox}]_\mathrm{e}$, and $[\mathrm{Ox}]_\mathrm{b}$ are the concentrations at the electrode and bulk, respectively.

In case of quasi-reversible electron transfer, the forward and backward sweeps of convoluted current I_1 are not superimposed and are functions of potential. Unlike the deconvolution of the current data $\mathrm{d}I_1/\mathrm{d}t$ shows almost symmetrical displacement of forward and backward peak values around standard electrode potential (E^0), see refs[13–16].

For many years non-substituted ferrocene is used as an internal standard[3] for electrochemical measurements. Zara *et al.*[4] calculated the standard heterogeneous rate constant (k^0) of ferrocene (Fc) on Pt from potential sweep measurements at rates between 0.5 and 5.0 V/s. The k^0 value is equal to $6.3 \pm 0.06 \cdot 10^{-5}$ m/s in dimethylformamide (DMF) with 0.06% (v/v) of water. The diffusion coefficient of ferrocene in DMF + 0.5 M $NaClO_4$ is equal to $1.1 \cdot 10^{-9}$ m^2/s. Its value diminishes when water is added to DMF and ethanol (EtOH) and increases when water is added to propylene carbonate (Pc). Crooks and Bard[5] estimated for Fc $k^0 = 2.2 \cdot 10^{-3}$ m/s (25 °C) and $D = 2.6 \cdot 10^{-10}$ m/s. They found that Fc/Fc$^+$ reference redox couple can be used for potential measurements in organic solvents at temperatures up to 275 °C. Above critical temperature of MeCN (T_c = 275 °C) the solvent more likely reacts with electrochemically generated substrates. Some derivatives of ferrocene have been used for preparation of modified electrodes[6,7]. Leddy and Bard[7] have found heterogeneous rate constant for poly(vinylferrocene) about two order of magnitude smaller than for similar species in solution, ($k^0_\mathrm{PVF} = 9.2 \cdot 10^{-7}$ m/s, $k^0_\mathrm{VF} = 1.3 \cdot 10^{-4}$ m/s), where the rate of heterogeneous charge transfer at the electrode surface is not affected by the incorporation of electroactive species into a polymer layer. The synthesis of ferrocene redox unit (Fc) bound to macrocyclic compounds containing ion selective ring (crown ether, Cr) has been subject of modelling electrontransfer processes in biological systems and new redox catalysts[8,9]. The ferrocene crown ether compound, examined electrochemically in the present work is of importance in this respect. The objective of this study is to report its electrochemical and chemical kinetic parameters evaluated by convolution–deconvolution potential sweep voltammetry and digital simulations.

EXPERIMENTAL

Synthesis

The 4,4′-(ferrocene-1,1′-diyldivinylene)bis(benzo-15-crown-5), $C_{42}H_{48}O_{10}Fe$ (FcCr) was synthesized according to ref.[10]. The structure of the compound was characterized by the elemental analysis, mass spectroscopy, and ^{1}H and ^{13}C NMR spectroscopy[10].

Electrochemical Apparatus

The potentiostat/galvanostat Model 362 (EG&G) was used for electrochemical measurements in a conventional three-electrode cell configuration. Metrohm glassy carbon disk with the geometrical surface area of 0.197 cm^2 served as a working electrode and silver wire in saturated lithium chloride in dichloromethane/TBAP as a reference electrode. The residual current was eliminated by taking the voltammogram with the same sweep rate in the blank electrolyte. The solution resistance R_u was compensated. All measurements were performed at the temperature 17 °C. The same temperature was considered in the calculations. The EG&G CONDECON software was used for the acquisition of electrochemical parameters for the compound under consideration. The electrochemical data have been processed by digital simulation software CONDESIM. Chronoamperometric experiments were performed at same conditions as cyclic voltammetry. The duration of polarization was 0.5 s and its lower limit was dictated by the time required to collect 500 data points. Its upper limit was imposed by the increasing contribution of convection within the electrolyte to the mass transport at long times. The current was filtered prior to capture to reduce the charging current associated with the capacitance of the electrical double layer to improve signal to noise ratio. Chronopotentiometric experiments were performed for FcCr under the same conditions. The current density of $7.7 \cdot 10^{-4}$ A/m^2 was imposed and the sand time t_s measured from the chronopotentiogram was 0.102 s.

RESULTS AND DISCUSSION

Direct Comparison of Simulated and Experimental Voltammograms

Figure 1 shows cyclic voltammogram corresponding to redox reaction of $1 \cdot 10^{-2}$ M FcCr as a glassy carbon electrode in CH_2Cl_2/0.1 M TBAP supporting electrolyte and a sweep rate of 100 mV/s. Dashed line displays the digital simulation for a simple electron transfer under the same conditions. The excellent degree of overlay of the experimental and the simulated voltammogram is a direct validation of the parameters involved. The evidence for the quasi-reversible electron transfer comes from the considerable difference between the peak separation ΔE_p found in our measurement from that for the Nernstian case[11]. Increasing ΔE_p for the scan rate rising from 20 mV/s to

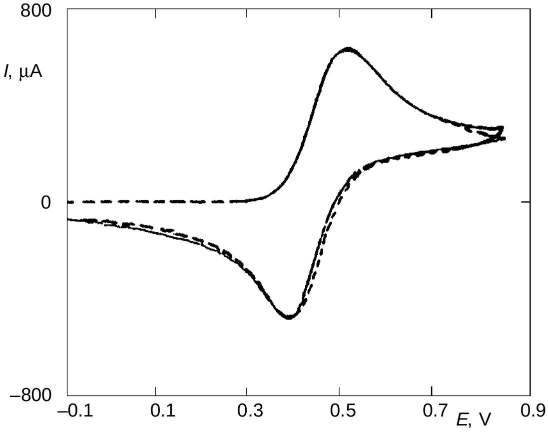

FIG. 1
Voltammograms for FcCr at the glassy carbon electrode: —— experimental, – – – – theoretical, sweep rate 100 mV/s

500 mV/s also indicated the non-Nernstian electron behaviour. The mean value of heterogeneous rate constant $k^0 = 6.44 \pm 0.08\ .\ 10^{-5}$ m/s was estimated from the peak separation at different sweep rates according to Nicholson[12] (Table I). This value is in good agreement with the simple quasi-reversible electron transfer.

Convolution and Deconvolution

Diagram of the convoluted current I_1 shows for model species Ox nearly constant limiting values I^0_{lim} at the end of sweep at rates of 50 and 500 mV/s (Fig. 2, Table I), in consistently with simple electron transfer process[16]. Constant limiting convoluted current provides an evaluation route for the diffusion coefficients of electroactive species. Equations (*2*) and (*3*) apply at potentials sufficient to reduce the concentration of elec-

TABLE I
Cyclic voltammetry and convolution data of the oxidation of FcCr at a glassy carbon electrode

Sweep rate mV/s	ΔE^0 mV	k^0 m/s	$I^0_{\mathrm{lim}}\ .\ 10^5$ A $s^{1/2}$	$D_0\ .\ 10^9$ m^2/s
20	74.1	6.85	3.76	0.40
50	81.0	6.24	3.67	0.38
100	86.9	6.77	3.72	0.39
200	93.2	6.14	3.72	0.39
500	114.5	6.21	3.79	0.41

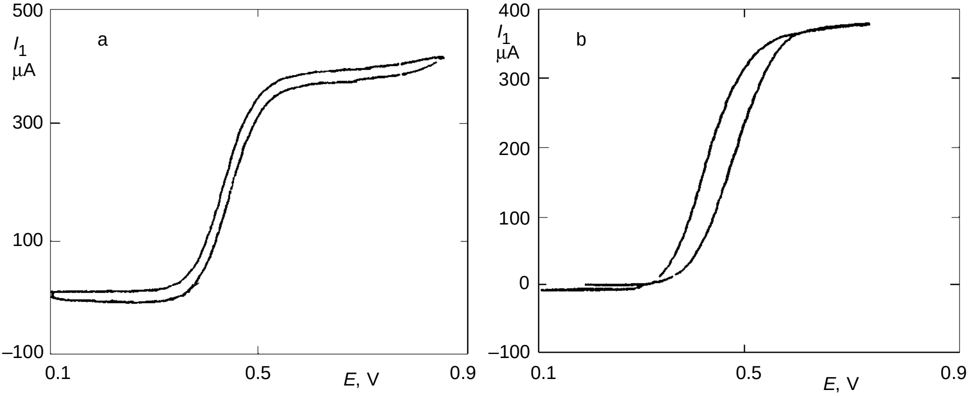

FIG. 2
Convoluted current for FcCr at the glassy carbon electrode, sweep rate: 50 mV/s (a), 500 mV/s (b)

troactive species at the electrode $[\mathrm{Ox}]_e$ to zero. The Cottrell equation[17] arises directly from the constancy of the following equation

$$I^{0}_{\mathrm{lim}} = nFAD^{1/2}_{0}\,[\mathrm{Ox}]_\mathrm{b}\ , \tag{4}$$

where n is the number of electrons transferred in electrochemical reaction, F is the Faraday constant, $[\mathrm{Ox}]_\mathrm{b}$ is the concentration of electroactive species in the bulk, A is the electrode area and D_0 is the diffusion coefficient of the species Ox. Equation (*4*) is valid, no matter which form of the potential disturbance drives its concentration to zero and there is no dependence on the rate of the electron transfer. Assuming the equality of diffusion coefficients of electrochemical species Ox, Red, the mean value of diffusion coefficient $D = 0.39 \pm 0.03\ 10^{-9}$ m^2/s was estimated from the limiting convoluted current I^{0}_{lim} recorded using Eq. (*4*).

Based upon the observation of a fixed plateau value for I_1 shown in Fig. 2, it can be stated, that on the time scale of electrochemical experiment, homogeneous chemical steps preceding or following electron transfer are absent. Additionally, I_1 returns to its initial (zero) value at the end of a sweep (Fig. 2). At low sweep rate (v = 50 mV/s) the plateau height is equal to that of the sweep end, which also confirms the simple electron transfer.

The I_1 convolution shows a distinct separation between the forward and reverse scan in the region of the half-wave potential apparently due to the lower rate of the electron transfer[16].

The deconvolutions ($\mathrm{d}I_1/\mathrm{d}t$) for FcCr at two different sweep rates 50 and 500 mV/s are shown in Fig. 3. The peaks are not aligned (non-Nernstian electron transfer)[18,19] and for deconvoluted current the anodic peak potential is more positive than the cathodic

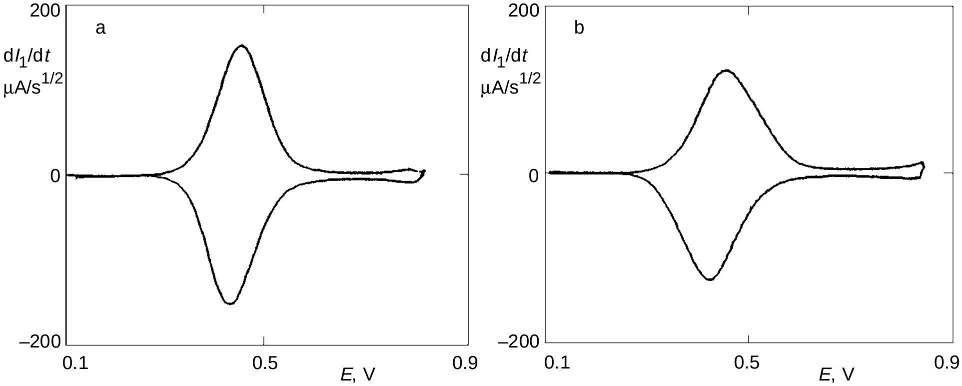

FIG. 3
Deconvoluted current for FcCr at the glassy carbon electrode, sweep rate: 50 mV/s (a), 500 mV/s (b)

peak. The calculated half-peak potential $W_{1/2}$ = 88.09 mV at 17 °C (ref.[18]) for Nernstian deconvoluted currents. The experimental values of half-peak potential, as expected, differ considerably from the Nernstian system value. Thus *e.g.* $W_{1/2}$ = 140.7 mV at 500 mV/s 105.3 mV at 50 mV/s. This difference becomes larger with increasing sweep rate as expected for the quasi-reversible behaviour of the compound[12].

The half-wave potential of FcCr was evaluated approximately from dI_1/dt plot as a mean value of the forward and reverse peak potentials. Digital simulation was employed at this stage to estimate the likely discrepancy between the mean peak potential and $E_{1/2}$ for $k^0 = 6.44 \cdot 10^{-5}$ m/s at variety of α values. The other parameters used were similar to those employed in the initial simulation. The results obtained at the sweep rate of 1 V/s are shown in Table II. The value E_{mean} = 0.45 V differs from the experimental $E_{1/2}$ value by 4.8 mV for α = 0.41, yielding an estimate of a corrected value of $E_{1/2}$ = 0.445 V. On the basis of the above data it can be concluded that FcCr undergoes one-electron reaction.

Chronoamperometric and Chronopotentiometric Measurements

Chronoamperometric curve of FcCr is shown in Fig. 4. In case of chronoamperometry, the linearity of $i(t)$ with convoluted current I_1 (ref.[20]) is shown in the following equation

$$i = I_{\mathrm{lim}} \frac{k_{\mathrm{hf}}}{D_0^{1/2}} - I_1 \frac{k_{\mathrm{hf}}}{D_0^{1/2}} - I_1 \frac{k_{\mathrm{hb}}}{D_{\mathrm{R}}^{1/2}} \quad . \tag{5}$$

Hence at the intercept at $I_1 = 0$, Eq. (*5*) gives

$$i = I_{\mathrm{lim}} \frac{k_{\mathrm{hf}}}{D_0^{1/2}} \quad . \tag{6}$$

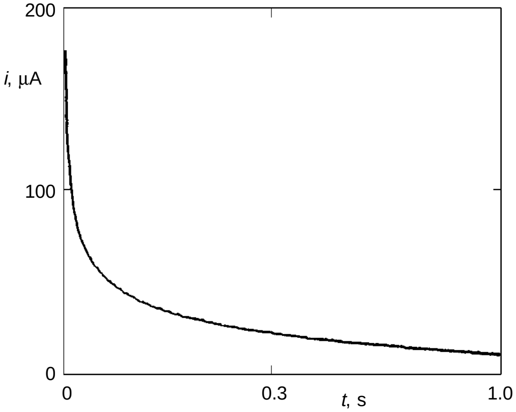

FIG. 4
Chronoamperogram for FcCr at the glassy carbon with polarization time 0.5 s

Since $t \rightarrow 0$ and $I_1 \rightarrow 0$

$$i = i(t = 0) = nFAk_{hf}[\mathrm{Ox}]_b \ . \qquad (7)$$

Equation (*7*) allows the estimation of the forward heterogeneous rate constant k_{hf}.

From Eq. (*8*) the standard heterogeneous rate constant k^0 can be calculated for potential E^0

$$\ln k_{hf} = \alpha nF(E - E^0)/RT + \ln k^0 \ , \qquad (8)$$

where k_{hf} is the forward heterogeneous rate constant and E is the electrode potential. A value of $k^0 = 6.27 \ . \ 10^{-5}$ m/s was obtained. Equality of D_0 and D_R diffusion coefficients, *i.e.* $E_{1/2} = E^0$ and using a half-wave potential $E_{1/2} = 0.445$ V, a symmetry coefficient α 0.41 was determined from the slope of Eq. (*8*). The above results from the chronoamperometric analysis are in general agreement with results obtained from cyclic voltammetry and therefore support the model of quasi-reversible electron transfer.

The chronopotentiometric technique has been used to measure the diffusion coefficient values for the compound under consideration using the Sand equation[21]. The value of diffusion coefficient D_0 was found to be $0.37 \ . \ 10^{-9}$ m^2/s which agrees well with the value obtained from cyclic voltammetry.

CONCLUSIONS

We have demonstrated that FcCr compound showed a quasireversible electron transfer behaviour in CH_2Cl_2/0.1 M TBAP at a glassy carbon electrode. The electrochemical parameters were evaluated where possible using convolution–deconvolution voltammetry, chronoamperometry and chronopotentiometry.

TABLE II
Digital simulation deconvoluted current data at sweep rate of 1 V/s at different α values for FcCr compound

α	E_{mean}, V	E, mV
0.35	0.5094	9.4
0.41	0.5048	4.8
0.50	0.5001	1.0

Based on the variation of ΔE_p with V, a mean value of $k^0 = 6.44 \pm 0.08 \cdot 10^{-5}$ m/s was estimated *via* Nicholson method. A value of $D = 0.39 \pm 0.03 \cdot 10^{-9}$ m^2/s was evaluated from the limiting convoluted current I_{lim} and agrees well with values obtained from other voltammetric techniques.

Diggle and Parker[22] report $k^0 = 4.4 \cdot 10^{-4}$ m/s for ferrocene in TBAP/MeCN, while Sharp *et al.*[23] report $2.2 \cdot 10^{-3}$ m/s for the same system. A diffusion coefficient of $2 \cdot 10^{-9}$ m^2/s has also been reported[24]. Zara *et al.*[4] reported $k^0 = 6 \cdot 10^{-5}$ m/s for potential sweep rates between 0.5 and 5.0 V/s in DMF with 0.06% (v/v) of water and a value of $D = 1.1 \cdot 10^{-9}$ m^2/s. Crooks and Bard[5] estimated k^0 $2.2 \cdot 10^{-3}$ m/s for ferrocene in acetonitrile and diffusion coefficient of $2.6 \cdot 10^{-9}$ m^2/s *via* Stokes–Einstein equation. Thus, the presence of a bulky crown ether ring bound to the ferrocene center suggests the decrease in k^0 value compared with previously published results[4–5,22–24] for unsubstituted ferrocene compounds. The D value reported for FcCr compound is in agreement with the literature data[4–5].

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