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Short communication

Determination of kinetic parameters of 1,1′-diacylferrocene at a gold microdisc electrode

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1. Introduction

Ferrocene and its derivatives have been widely studied by various physical methods because of their key role in the stimulation of the development of organometallic chemistry and material science [1–6]. They are valuable in organic and organometallic syntheses, for example in asymmetric synthesis, catalytic hydrogenation peptide synthesis etc.. They are also potential aids to the understanding of biological electron transfer and the design of molecular electronic devices. Their redox potential and kinetic parameters are helpful for selecting donor/acceptor couples for the establishment of biomimetic membrane system.

However, the absence of straightforward and reliable procedures for the determination of kinetics of heterogeneous electron transfer reactions with rate constants above 10^{-4} m s^{-1} has long been a problem. In recent years, microelectrodes have become popular as a means of ameliorating this difficulty, especially when used in conjunction with voltammetry [1,5,7–12].

The most striking feature of microelectrodes is their extremely small surface areas which can both enhance the effective mass transport rate and reduce the potential drop in the resistive solution. In general, they exhibit sigmoidal voltammograms at slow scan rates, which offers a number of advantages over the more familiar transient voltammetry.

In this work we synthesized the ferrocene derivatives FcX_2; the substituents are generally bonded to the cyclopentadienyl ring through an sp^3 hybridized carbon atom ($X = -CO(CH_2)_nCH_3$, $n = 10, 12, 14, 16$). In this communication we report a study of the kinetic and redox properties of FcX_2 and also discuss the effect of the length of the alkyl chain on the electrochemical parameters.

2. Experimental

2.1. Preparation of 1,1′-diacylferrocene FcX_2

Ferrocene (0.0162 mol) dissolved in 1.0 ml of dry methylene chloride was added over a period of 15 min to a stirred mixture of 0.04 mol aluminium chloride and 0.045 mol acyl chloride ($CH_3(CH_2)_nCOCl$, $n = 10, 12, 14, 16$) in 20 ml of dry methylene chloride. The reaction was carried out in dry nitrogen atmosphere to avoid the oxidation of ferrocene. The reaction mixture was stirred for 2 h at room temperature and was then cooled, diluted with ice-water and filtered. The separated aqueous phase was extracted several times with chloroform and the extracts were washed to neutrality. The deep red organic solution was dried by distillation over a steam-bath. Recrystallization from a mixture of chloroform and hexane gave a pure product FcX_2 ($X = CH_3(CH_2)_nCO-$, $n = 10, 12, 14, 16$).

2.2. Chemicals

The acetonitrile solvent was redistilled with P_2O_5 (5 g per 100 ml) and then with K_2CO_3 and was stored over 4A molecular sieve activated at 550°C. $(Bt)_4NClO_4$ was recrystallized twice from absolute ethanol and hot doubly distilled water and was dried under a vacuum at

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80°C prior to use. All other chemicals were of reagent grade purity.

2.3. Apparatus and method

Voltammetric measurements were carried out using a three-electrode system with a gold microdisc, saturated calomel electrode (SCE) and a platinum wire as the working, reference and auxiliary electrodes respectively. The gold microdisc electrode was purchased from the BAS Co. Prior to use, the electrode was polished on successively finer grades of Al_2O_3 (1–0.05 μm) and was sonicated first in pure water and then in solvent supporting electrolyte solution for a minimum of 5 min each. A BAS model 100B electrochemical analyser was used to generate the potential applied to the electrochemical cell. The cell was located in a small aluminium box which was kept oxygen free by passing nitrogen over the solution. A preamplifier (BAS Co., USA) was used to amplify the current and to filter out noise.

3. Results and discussion

The redox properties of the substituted ferrocene FcX_2 were studied by cyclic voltammetry and linear sweep voltammetry at a gold microdisc electrode in 0.1 mol l^{-1} Bu_4NClO_4 + acetonitrile. They exhibit a one-electron reversible oxidation, which is believed to be localized mainly at the Fe(II) centre. Another commonly irreversible anodic wave may be observed, but the corresponding redox processes have not been investigated.

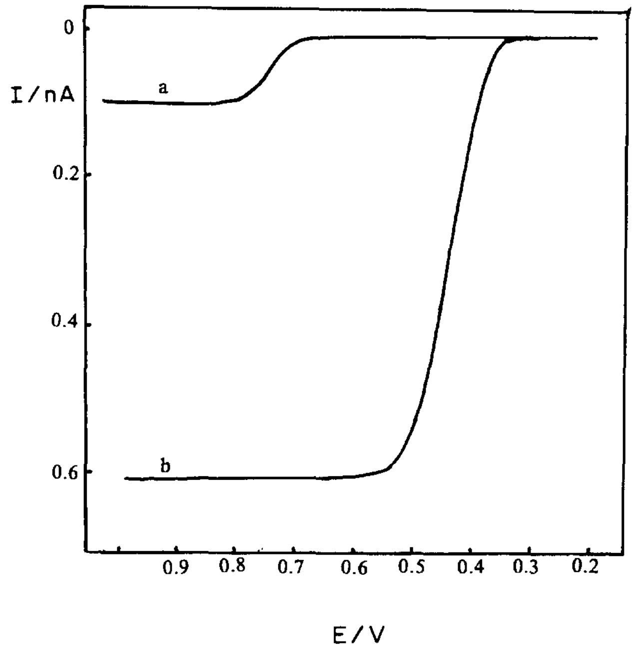

Fig. 1. Steady-state cyclic voltammograms for the oxidation of (a) 2×10^{-4} mol l^{-1} ferrocene and (b) 1×10^{-4} mol l^{-1} FcX_2 in 0.1 mol l^{-1} Bu_4NClO_4 + acetonitrile. Scan rate, 5 mV s^{-1}.

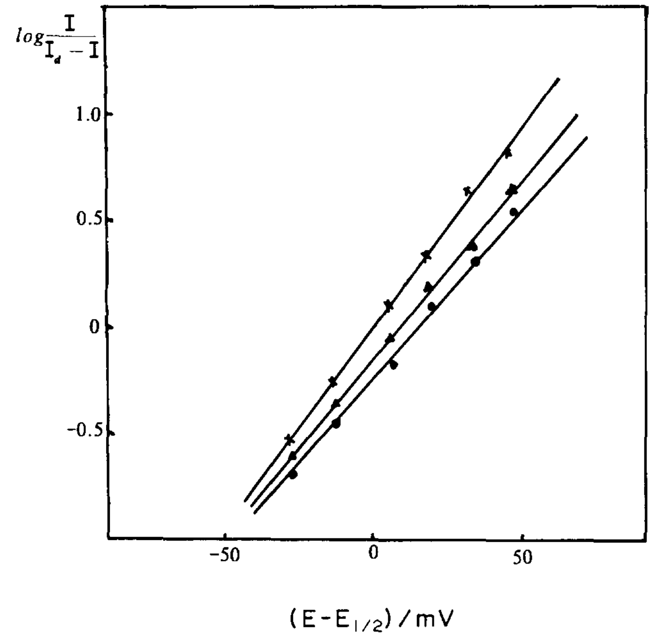

Fig. 2. Plot of $\log[I/(I_d - I)]$ vs. $E - E_{1/2}$ for steady-state voltammograms of ferrocenes **I** (×), **II** (△) and **III** (○). Scan rate, 5 mV s^{-1}.

Because of the steady-state nature of the diffusion layer at a microdisc electrode, a sigmoidal voltammogram was obtained at a slow scan rate [5]. Fig. 1 shows typical steady-state voltammograms obtained under our experimental conditions for the oxidation of 0.1 mM ferrocene (Fc) and its derivatives FcX_2. It should be noted that the voltammograms are substantially free of background current.

Fig. 1 shows that the reverse wave almost retraces the oxidation wave at an extremely slow scan rate (5 mV s^{-1}). The slopes of the plot are 57 mV, 59 mV, 60 mV and 62 mV respectively, indicating that the electrode reaction can be considered as reversible. The characteristic parameter of the voltammetric curve—the half-wave potential $E_{1/2}$—can thus be obtained from the following equations:

$$E = E_{1/2} + \frac{RT}{nF}\ln\left(\frac{I}{I_d - I}\right) \tag{1}$$

$$I_d = 4nFDcr \tag{2}$$

where all the symbol have their usual meanings. The plot of $\log[I/(I_d - I)]$ vs. $E - E_{1/2}$ shown in Fig. 2 is a straight line, and the values of $E_{1/2}$ calculated using Eq. (1) are collected in Table 1. The redox potential of each derivative FcX_2 is about 300–400 mV higher than that of ferrocene, but this value decreases with increasing the length of the alkyl chain in the molecules. This is due to the strong electron-withdrawing ability of the carbonyl inductive acceptor, so that the oxidation of FcX_2 is more difficult than that of Fc, while the long alkyl chain shows an electron-donating effect and has donor properties. However, the distance between the carbonyl group and the cyclopentadienyl ring is shorter than that between alkyl chain and Fc in FcX_2 molecules. Therefore the inductive effect may dominate the resonance effect and the ferrocene derivatives FcX_2 have a relatively high oxidation potential, which also decreased with increasing length of the alkyl chain. These results again indicate the importance of both resonance and the inductive interaction across the cyclopentadienyl ring between the substituent and the iron redox centre [6].

The diffusion coefficient D for each compound of FcX_2 can be determined using Eq. (2) and the diffusion-limiting current I_d obtained from the steady-state voltammograms at the gold microdisc electrode. The value of the effective radius is 3.1 μm, which is obtained from the voltammogram for ferrocene (the diffusion coefficient of ferrocene is 2.4×10^{-5} cm^2 s^{-1}). The diffusion coefficients of FcX_2 are summarized in Table 1. These data show that when the length of the alkyl chain attached to the cyclopentadienyl ring increases, the value of the diffusion coefficient of FcX_2 decreases.

It is well known that there are two series of equations derived using different theories, which were presented by Galus et al. [9] and Aoki et al. [13], for the voltammetric response of a quasi-reversible redox reaction under the steady-state condition at a microdisc electrode.

The first method [9] is based on the logarithmic form of Eqs. (3) and (4):

$$E - E^{\circ\prime} = \frac{RT}{(1-\alpha)nF}\ln\left(\frac{4D}{\pi k_s r}\right) - \frac{RT}{(1-\alpha)nF}\ln\left[\frac{I_d - I}{I} - \frac{I_d - I^r}{I^r}\right] \tag{3a}$$

$$\ln\left(\frac{I_d - I^r}{I^r}\right) = \frac{(E^{\circ\prime} - E)nF}{RT} \tag{3b}$$

where I^r is the calculated reversible current and I is the measured current for the kinetically controlled process at potential E and k_s is the standard heterogenous rate constant. For a given value of r, the first term on the right-hand side of Eq. (3) is constant. Therefore a plot of $E - E^{\circ\prime}$ vs. $\ln[(I_d - I)/I - (I_d - I^r)/I^r]$ should be linear with slope $RT/(1-\alpha)nF$ and intersection $[RT/(1-\alpha)nF]\ \ln(4D/\pi k_s r)$ (Fig. 3). Thus k_s of FcX_2 can be determined from the intersection, and the value of the dimensionless parameter K^0 of each ferrocene derivative can be calculated using

Table 1
Summary of half wave potential and diffusion coefficient of ferrocene and its derivatives

Compound	I	II	III	IV	V
$E_{1/2}/V$	0.43	0.84	0.82	0.73	0.71
$10^9\ D/m^2\ s^{-1}$	2.40	1.02	0.96	0.91	0.88

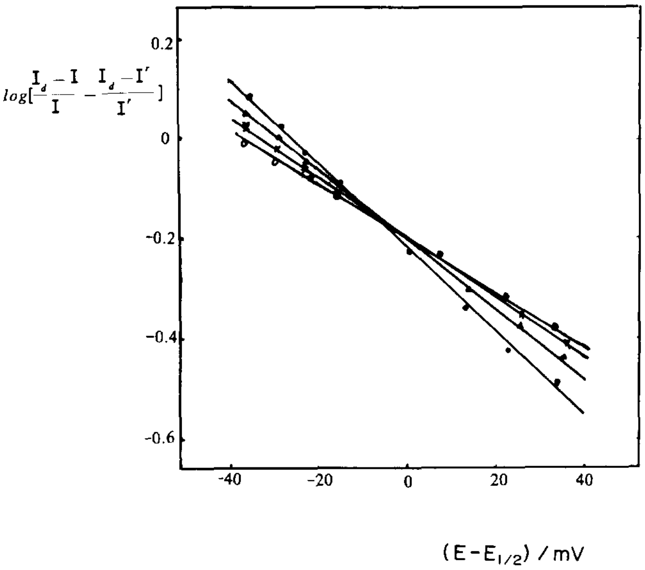

Fig. 3. Dependence of $\log[(I_d - I)/I - (I_d - I^r)/I^r]$ on $(E - E_{1/2})$ calculated from voltammograms recorded for the oxidation of 1×10^{-4} mol l^{-1} FcX_2 in 0.1 mol l^{-1} Bu_4NClO_4 + acetonitrile (scan rate, 100 mV s^{-1}): ● ferrocene **II**; △ ferrocene **III**; × ferrocene **IV**; ● ferrocene **V**.

$$K^0 = \pi k_s r/4D \tag{4}$$

The second method [13] is based on the logarithmic form of Eq. (5):

$$E = E^* - \frac{RT}{(1-\alpha)nF}\ln\left\{\left[1 - \left(\frac{I}{I_d}\right)(1 + e^{-\zeta})\right]^{1.11}\frac{I_d}{I}\right\} \tag{5a}$$

$$E^* = E^{\circ\prime} - \frac{RT}{(1-\alpha)nF}\ln\left(\frac{\pi k^{\circ\prime} r}{4D}\right) \qquad \xi = \frac{nF(E - E^{\circ\prime})}{RT} \tag{5b}$$

where k'_0 is the formal electrode reaction rate constant and ζ is the dimensionless potential. Similarly, a plot of the logarithmic term in Eq. (5) against E is a straight line with slope $RT/(1-\alpha)nF$ and intersection E^* (Fig. 4). Then $k^{0\prime}$ can be calculated from Eq. (5b) when E^0 is known.

The values of k_s, $k^{0\prime}$, $1-\alpha$ and K^0 for FcX_2 are presented in Table 2. The parameters k_s [9] and $k^{0\prime}$ [13] have the same physical meaning, which can be proved by following the reasoning developed in these papers. As can be seen from Table 2, the results determined using the two different methods are of the same order of magnitude. There is no fundamental difference between the two methods. Both k_s and k'_0

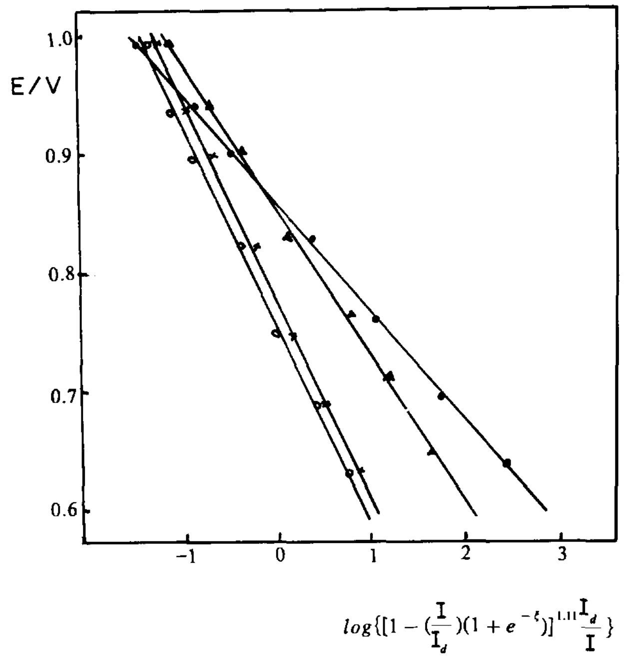

Fig. 4. Dependence of E on $\log\{[1-(I/I_d)(1+e^{-\xi})]^{1.11}(I_d/I)\}$ calculated from voltammograms recorded for the oxidation of 1×10^{-4} mol l^{-1} FcX_2 in 0.1 mol l^{-1} Bu_4NClO_4 + acetonitrile (scan rate, 100 mV s^{-1}): ● ferrocene **II**; △ ferrocene **III**; × ferrocene **IV**; ○ ferrocene **V**.

decrease with increasing length of the alkyl chain in FcX_2 molecules ($0.2 < K^0 < 20$). This means that all these electrode reactions have a usefully quasi-reversible character [14] and the reversibility of the electrode reaction also decreases with increasing alkyl chain length in FcX_2. The method due to Galus et al. [9] is simpler than that of Aoki et al. [13] and the results can be obtained more directly.

Table 2
Summary of kinetic parameters of ferrocene derivatives by two methods

Compound	II	III	IV	V
$10^4\ k_s/\text{m s}^{-1}$	6.80	6.10	5.80	5.80
$10^4\ k^{0\prime}/\text{m s}^{-1}$	2.40	2.25	1.80	1.70
$1-\alpha$	0.51	0.42	0.35	0.34
	0.66	0.48	0.36	0.38
K^0	1.6	1.5	1.6	1.6
	0.6	0.5	0.5	0.5

4. Conclusions

The present work demonstrate that both resonance and inductive effects have an important influence on the kinetic properties of 1,1′-dialkylferrocene. The effects are transmitted through the carbocyclic ring to the iron redox active centre, conforming with observations reported by others.

The long alkyl chain shows an electron-donating effect and has donor properties, while the carbonyl shows strong electron-withdrawing effect and has acceptor properties. To some extent, the longer the alkyl group, the lower are the value of $E^{0\prime}$ and D and the rate constant of electrode reaction.

The correlations help us to understand and predict the redox properties of 1,1′-dialkylferrocene and select a donor-acceptor couple for establishing a biomimetic system.

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