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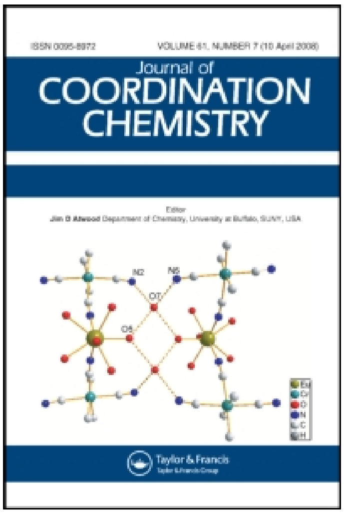

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VOLTAMMETRY OF NOVEL MONOMERIC AND DIMERIC Fe(IV) COMPLEXES OF PENTANE-2,4-DIONE*BIS*(*S*-METHYLISOTHIOSEMICARBAZONE): THE ROLE OF THE AXIAL LIGAND

Ljiljana S. Jovanović[a]; Luka J. Bjelica[a]
[a] Faculty of Sciences, Institute of Chemistry, Novi Sad, Yugoslavia

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VOLTAMMETRY OF NOVEL MONOMERIC AND DIMERIC Fe(IV) COMPLEXES OF PENTANE-2,4-DIONE*BIS*(*S*-METHYLISOTHIOSEMICARBAZONE): THE ROLE OF THE AXIAL LIGAND

LJILJANA S. JOVANOVIĆ* and LUKA J. BJELICA

Institute of Chemistry, Faculty of Sciences, Trg D. Obradovića 3, 21000 Novi Sad, Yugoslavia

(Received February 17, 1995)

Several monomeric Fe(IV) complexes of general formula [Fe(L)X] (X = Cl, Br, I, NCS, NCO) and the μ-oxo dimer $[Fe(L)]_2O$, in which L is the trianion of the quadridentate ligand pentane-2,4-dione-*bis*(*S*-methylisothiosemicarbazone) were studied by voltammetric methods on a glassy carbon electrode in DMF solution with different supporting electrolytes (tetrabutylammonium perchlorate, $LiClO_4$, LiCl). A common characteristic of solutions of the monomeric complexes is the ready occurrence of ligand-exchange: X-DMF, X-Cl and DMF-Cl; the first is especially pronounced with the reduced species. Reduction of these complexes proceeds in two one-electron steps whose characteristics are sensitive to the nature of the axial ligand. On the other hand, the dimer is reduced in three one-electron steps, the first two being *quasi*-reversible metal-centred processes, and the third taking place mostly on the ligand. Acid-base properties and monomer-dimer equilibria are discussed in detail, and a general reaction scheme is proposed.

KEYWORDS: iron(IV) complexes, axial ligand, voltammetry, monomer-dimer equilibria

INTRODUCTION

Like the majority of other related ligands, thio- and *S*-alkylisothio-semicarbazones stabilize iron in the + 3 oxidation state.[1–3] However, it has been recently shown that a template synthesis involving Fe(III) and the appropriate reactants in the presence of pyridine resulted unexpectedly in a Fe(IV) complex [Fe(L)I], in which L is the trianion of the quadridentate ligand pentane-2,4-dione*bis*(*S*-alkyl-isothiosemicarbazone).[4] In the presence of ammonia, this low-spin monomer is transformed into a diamagnetic μ-oxo dimer $[Fe(L)]_2O$.[5] The structures of the monomeric square-pyramidal complexes and the μ-oxo dimer have been determined by x-ray analysis,[4,5] and some general physicochemical characteristics of the dimer and a series of monomers have been described recently.[6]

As with the majority of complexes with a central ion in its high oxidation state, an important role in stabilization of Fe(IV) is played by (the donor properties of) the axial ligands. The present article describes in detail the voltammetric behaviour

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* Author for correspondence.

of the Fe(IV) monomeric complexes [Fe(L)X] (X = Cl, Br, I, NCO, NCS), and the $[Fe(L)]_2O$ dimer in DMF, with special emphasis on the role of the axial ligand in the electrochemical processes at a glassy carbon electrode and monomer-dimer equilibria in solution.

EXPERIMENTAL

Chemicals

The investigated complexes were synthesized in our Institute and their purity checked by elemental analysis.[6] The salts LiCl, $LiClO_4$, tetrabutylammonium perchlorate (TBAP) and tetraethylammonium chloride (TEACl) were recrystallized before use. An aqueous perchloric acid solution (0.062 mol dm^{-3}) was used to study acid-base properties of the complexes. Nitrogen for deaeration was purged by passing over copper turnings heated to 450°C and through two columns filled with 4Å molecular sieves.

Electrodes

A glassy carbon disc electrode (AMEL 493, Milan) was used as the working electrode. To ensure its proper functioning, it was polished with fine alumina suspensions (Buehler Ltd., 0.5 and 0.05 μm). A glassy carbon plate (Sigri Elektrographit 2400, dimensions 1.6 x 2.0 x 0.2 cm) served as the working electrode in controlled-potential electrolyses. The counter electrode was a Pt ring of sufficiently large surface area. An aqueous saturated calomel electrode (SCE) with an asbestos tip (Ingold 303), connected to the working solution *via* an appropriate salt bridge, served as the reference electrode.

Apparatus

An AMEL (Milan) voltammetric set-up with the possibility of iR drop compensation was employed in all electrochemical experiments. The curves were recorded on a Hewlett-Packard 7044A x-y recorder, or a Hewlett–Packard 1741A storage oscilloscope. Addition of $HClO_4$ solution was performed by means of an automatic Radiometer piston burette. Electronic spectra were recorded on a Cary 219 spectrophotometer.

General procedure

The 1×10^{-3} mol dm^{-3} solutions of the complexes in 0.1 mol dm^{-3} supporting electrolyte were prepared by weighing the dried substances and dissolving them in purified and freshly distilled DMF according to the recommended procedure.[7] Purged and presaturated nitrogen then was bubbled through the solution (stirred additionally with a magnetic stirrer) for 1 h, and afterwards left to stream over it.

All experiments were performed at room temperature, the solutions being thermostated (25 ± 0.2°C) for kinetic measurements only. Peak potentials were determined with an uncertainty of ±2 mV.

RESULTS AND DISCUSSION

Although the monomeric complexes in their crystalline states are characterized by pentacoordination of Fe(IV) with the organic ligand in the meridial and the anion X in the axial plane (square pyramid), all the findings presented below suggest that these complexes in DMF solutions acquire an octahedral configuration, in which the sixth coordination site is occupied either by a molecule of the solvent, or another monodentate ligand. On the other hand, the configuration of the dimer in the solution is most probably a square bipyramid with the oxygen atom in the centre. Analogous behaviour has been observed for similar Fe(III) complexes in DMF solution.[8–10]

MONOMERS

Perchlorate medium

A general voltammogram of the investigated complexes is presented in Figure 1, in which the set of curves A represents reduction and set B oxidation processes.

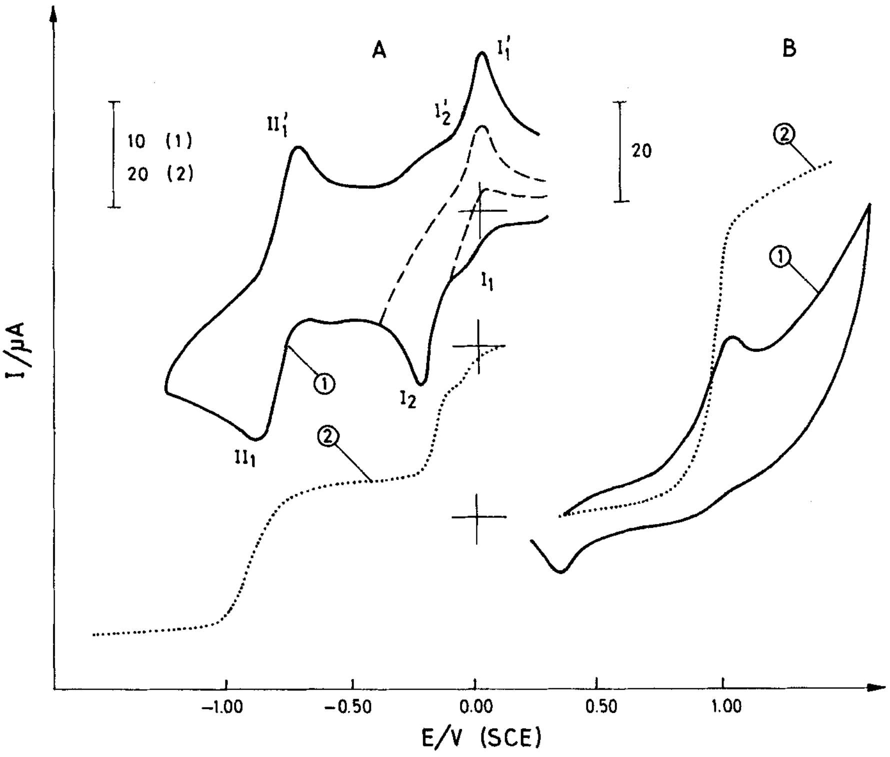

Figure 1 Voltammograms for [Fe(L)I] reduction (A) and oxidation (B); 0.1 mol dm^{-3} TBAP, 0.20 V s^{-1} (1), 600 r.p.m. (2).

Oxidation of the complexes takes place at more positive potentials than 0.5 V, and involves several mono- or multi-electron processes, which primarily depend on the nature of X^-. At $E > 1.2$ V the multi-electron, irreversible oxidation of ligand L causes complex decomposition.

The complexes are reduced in two *quasi*-reversible, one-electron processes (I and II), the first of them being represented by two close peaks I_1 and I_2. In view of the fact that potential of peak I_2 is different for each of the investigated monomeric complexes and the only structural difference is the ligand X in the axial position, it can be supposed that this peak is due to the reduction of the $[Fe^{IV}(L)(DMF)X]$ complex ("X-complex"), whereas peak I_1 relates to the reduction of the "DMF-complex" $[Fe^{IV}(L)(DMF)_2]^+$. The ratio of the heights of these two peaks for a given complex depends on sweep rate, as a decrease in v produces a relative increase in peak I_1. Similar behaviour was also observed for the anodic peaks I_1' and I_2'. These observations suggest the occurrence of the following equilibrium between the reacting species.

$$[Fe^{IV}(L)(DMF)_2]^+ + X^- \rightleftharpoons [Fe^{IV}(L)(DMF)X]^0 + DMF \qquad (1)$$

An analogous reaction can be also written for the corresponding reduced complex species, but the ratio of their equilibrium concentrations is different. This is illustrated in Figure 2. Although peak I for both the Br^- and NCO^- complex is unique, a fact which suggests a relative stability of the "X-complexes" of Fe(IV), the reduction is followed by release of X^-, and this is more pronounced in the case of the Br^- complex. The ratios of the peak currents $I_2'/(I_1 + I_2)$ allows us to estimate the relative affinity of Fe(III) towards different anions. Thus, the stability of $[Fe^{III}(L)(DMF)X]^-$ decreases in the series $NCO^- > Cl^- > Br^- \simeq I^- \simeq NCS^-$. The effect of the X^- anion on the stability of the Fe(IV) complexes can also be assessed on the basis of the ratios of peak/wave currents $I_2/(I_1 + I_2)$. Normally, the effect of equilibrium (*1*) is included, but the above sequence is retained.

Another illustration of the axial ligand effect on electrochemical behaviour of the complexes is the possibility of correlating the I_2 peak potentials with the frequency of the corresponding charge-transfer bands (Fig. 3). In view of the fact that at low v chemical complications (equilibrium (*1*)) for the less stable complexes (I^-, NCS^-, Br^-) become significant, and that at higher v the electron-transfer process becomes more irreversible, this correlation is only a qualitative one. However, for sweep rates of 0.20–0.50 V s^{-1}, where the above effects are least pronounced, the correlation of $E_p(I_2)$ with $\tilde{\nu}$ of the charge-transfer bands is linear for four complexes. The large deviation for the NCS^- complex can be explained by the assumption that the electron transfer corresponding to peak I_2 does not take place in the same molecular orbitals as those involved in light absorption.

The second reduction process (peaks II_1/II_1') takes place at the same potentials for all the complexes, which means that the same complex species, *i.e.*, $[Fe^{III}(L)(DMF)_2]^0$, is involved (see Fig. 1 A). The peaks correspond to one-electron, *quasi*-reversible processes, and their heights at lower v are approximately equal to the total current for process I. The exception is for [Fe(L)NCO] and to some extent [Fe(L)Cl] (Fig. 4), whose reduction is characterized by the appearance of additional peaks (II_2 and II_3) which can be ascribed to the corresponding Fe^{III}-X and Fe^{III}-X_2 complexes. The affinity of the Fe^{III}-complex toward NCO^- is especially pronounced, as peak II_1 appears only at $v < 0.5$ V s^{-1} (Fig. 4). With both complexes,

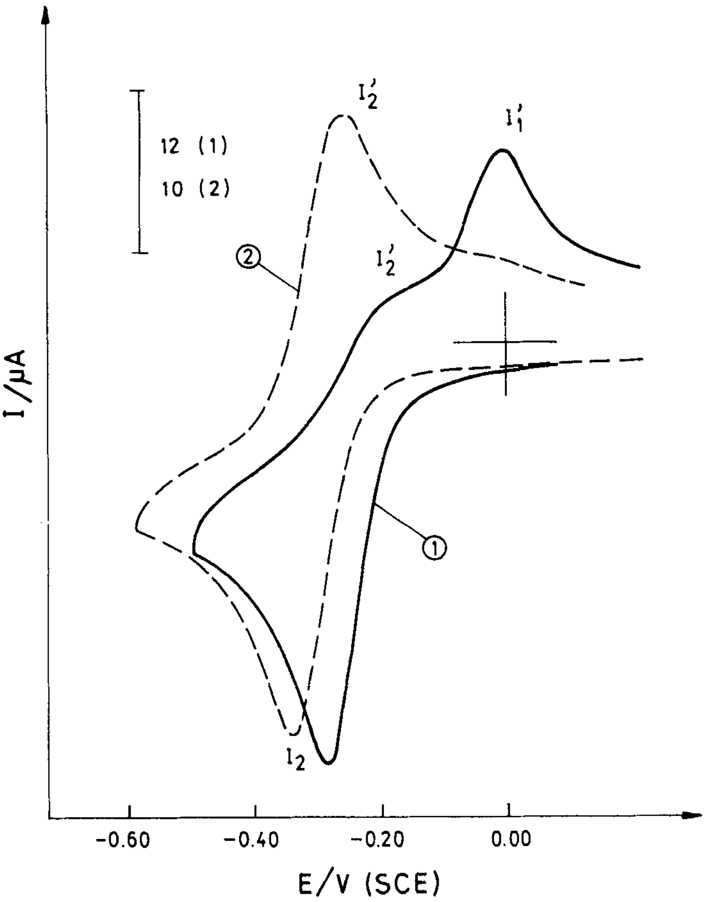

Figure 2 Cyclic voltammograms for reduction of [Fe(L)Br] (1) and [Fe(L)NCO] (2) in a narrower potential range; 0.1 mol dm^{-3} TBAP, 0.20 V s^{-1}.

however, the reduction is accompanied by a relatively fast dissociation of the coordinated X$^-$, which is manifested in a corresponding increase in the peak II_1' current.

Some of the common voltammetric characteristics of the investigated complexes obtained in perchlorate medium are presented in Table 1.

Exhaustive electrolysis at the potential of peak I_2 showed the expenditure of 1 mole of electrons per mole of the complex and 2 moles if the electrolysis is carried out directly at the potential of process II. The colour of the solution during the electrolysis changes from a dark-brown to light red (process I) and then to olive-brown (II). A short exposure of the electrolyzed solution to atmospheric oxygen results in the change of its colour to dark green, characteristic of the presence of the dimer, which can also be confirmed by recording electronic spectra and cyclic voltammograms.

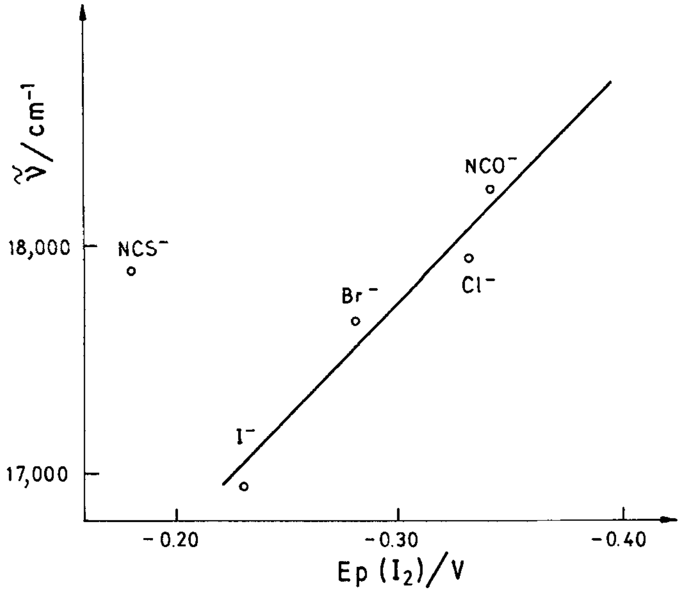

Figure 3 Correlation of $E_p(I_2)$ for monomers with the corresponding $\tilde{\nu}$ of charge-transfer bands; 0.1 mol dm^{-3} TBAP, 0.20 V s^{-1}.

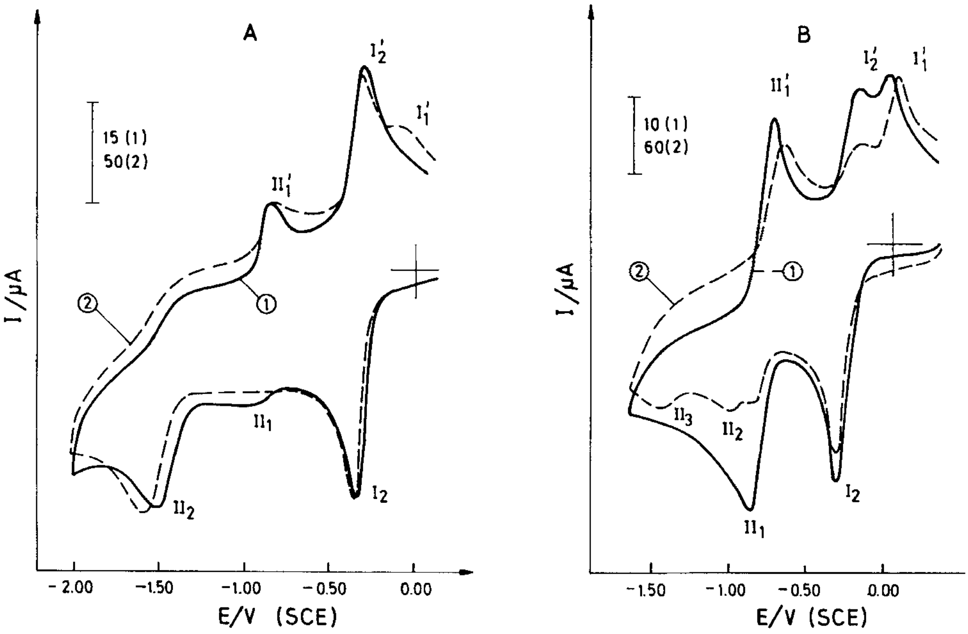

Figure 4 Cyclic voltammograms for reduction of [Fe(L)NCO], (A): 0.20 V s^{-1} (1); 2.0 V s^{-1} (2) and [Fe(L)Cl], (B): 0.20 V s^{-1} (1); 5.0 V s^{-1}; 0.1 mol dm^{-3} TBAP.

Table 1 Voltammetric data for iron(IV) complexes in 0.1 mol dm^{-3} TBAP.

Monomer	v^a	$E_p(I_2)^b$	$E_p(II_1)$	$E_p(II_2)$	$\frac{I_p(I_2)^c}{c\,v^{1/2}}$	$\frac{I_p(II_1)}{c\,v^{1/2}}$	$\frac{I_p(II_2)}{c\,v^{1/2}}$
[Fe(L)NCS]	0.02	-0.16	-0.87		32.4	47.7	
	0.20	-0.18	-0.89		33.8	40.4	
[Fe(L)I]	0.02	-0.20	-0.88		37.8	40.5	
	0.20	-0.23	-0.90		42.3	35.6	
[Fe(L)Br]	0.02	-0.24	-0.88		49.7	52.2	
	0.20	-0.28	-0.90		59.2	43.9	
[Fe(L)Cl]	0.02	-0.30	-0.88		51.9	48.6	
	0.20	-0.33	-0.90		56.7	42.4	
[Fe(L)NCO]	0.02	-0.33	-0.90	-1.47	57.1	11.8	23.6
	0.20	-0.34	-0.91	-1.50	59.2	5.6	29.6
Dimer	v	$E_p(I_D)$	$E_p(II_D)$	$E_p(III_D)$	$\frac{I_p(I_D)^d}{c\,v^{1/2}}$	$\frac{I_p(II_D)}{c\,v^{1/2}}$	$\frac{I_p(III_D)}{c\,v^{1/2}}$
$[Fe(L)]_2O$	0.02	-0.64	-0.93	-2.00	42.5	36.7	56.7
	0.20	-0.65	-0.94	-2.05	46.6	43.9	53.8

^{a}Sweep rate, in V s^{-1}. ^{b}Electrode potentials, in V *vs* SCE. ^{c}Current functions, in μA mmol^{-1} dm^3 V$^{-1/2}$s$^{1/2}$. ^{d}Concentration calculated for the dimer.

The changes occurring on the reduced complex species are reversible and, if the electrolysis is carried out strictly in the absence of oxygen (to prevent dimerization of the reduced complex), the starting monomer can be completely regenerated.

Effect of Ag^+

To investigate the stability of $[Fe(L)(DMF)_2]^+$ complexes in the absence of X^-, small volumes of $AgClO_4$ solution were successively added to the complex solution containing perchlorate up to a stoichiometric amount with X^-. As a result, the peaks I_2/I_2' on the voltammogram for [Fe(L)X] disappear, while the peak couples I_1/I_1' at + 0.10/ + 0.070 V show an increase to about 50% of the total current for this process. In additions a new reduction peak (I_D) appears at − 0.64 V, whose height is comparable to that of peak I_1. The new peak (see Fig. 7) is characteristic for the first-step reduction of the dimer, whose further reduction occurs at the potential range of peak II_1; this apparently does not shift with the addition of Ag^+. A partial dimerization of the complex in the absence of X^-, giving rise to an oxo-dimer, is probably caused by the presence of traces of water. This phenomenon is quite common in the chemistry of oxo-dimers.[11] Dimer formation is accompanied by a change in the colour of the solution (it becomes green), and was also evidenced by recording electronic spectra. As one cannot prepare an absolutely anhydrous DMF solution, in the absence of the X^- anion, a partial conversion of the monomer into the dimer will always take place.

Behaviour in LiCl

In the presence of an excess of chloride in solution, cyclic voltammograms for all the complexes are practically identical, as illustrated by Figure 5A. Peak I_2 is shifted to more negative values with a slope $\Delta E/\Delta \log [Cl^-] \simeq -30$ mV/decade (Fig. 5B, inset). In the reverse scan, peak I_1' is missing, so that all the voltammograms in this

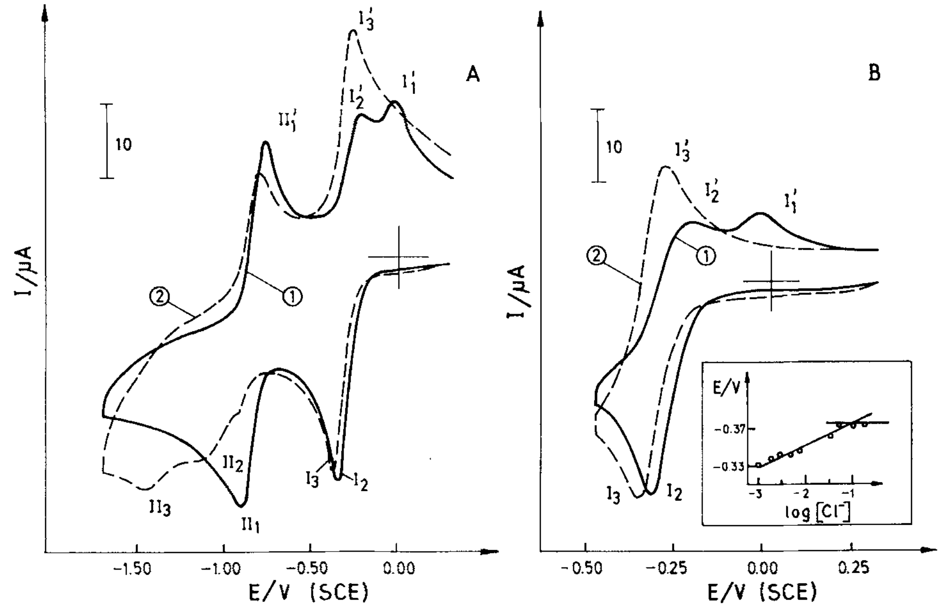

Figure 5 Cyclic voltammograms for reduction of [Fe(L)Cl] in 0.1 mol dm^{-3} TBAP (1) and 0.1 mol dm^{-3} TBAP + 0.05 mol dm^{-3} LiCl (2); 0.20 V s^{-1}. Inset: $E_p(I_2)$ *vs* log [Cl$^-$].

range of potentials have a couple of *quasi*-reversible peaks denoted by I_3/I_3'. On this basis it can be supposed that the process corresponding to peak I_3 is the reduction of $[Fe^{IV}(L)Cl_2]^-$. However, in the range of potentials of the second electron transfer at $v < 1$ V s^{-1} there are three peaks, II_1, II_2 and II_3 (Fig. 5A, curve 2) corresponding to the reduction of $[Fe^{III}(L)(DMF)_2]^0$, $[Fe^{III}(L)(DMF)Cl]^-$ and $[Fe^{III}(L)Cl_2]^{2-}$, respectively. The voltammograms recorded with RDE, as well as the cyclic voltammograms obtained at $v > 1$ V s^{-1} show that the electron transfer is characterized by a unique wave/peak at potentials close to peak II_3, a fact which indicates the species reacting at peaks II_1 and II_2 are formed by slow release of Cl$^-$ following reduction at peak I_3.

As for the second reduction step of the chloride complexes it is evident that the excess negative charge on the reduced species is most easily relaxed by release of both Cl$^-$ ions, so that even at $v = 10$ V s^{-1} the peak II_1' can be observed. The height of this peak, depending on the nature of the complex, reaches a maximum at $v = 0.20 - 0.50$ V s^{-1}, and at higher v shows a decrease accompanied by an increase in the other two peaks, especially that of II_3'. This is a consequence of different rates of Cl$^-$ release from Fe(III) and Fe(II), *i.e.*, of a lower affinity of the latter ion for Cl$^-$. On the other hand, the presence of Li$^+$ does not contribute to stabilization of Fe(II) complexes by ion pair formation, as found for some other complexes of polydentate ligands.[8,12] The same behaviour was also observed in the presence of an excess of Et_4NCl. All the species containing Fe^{III} are oxidized in the unique peak I_3' (Fig. 5A, curve 2), which means that they (because of their high affinity for chloride) have already accepted two Cl$^-$ ions in their coordination spheres.

Exhaustive electrolysis of the monomer solution at the potential of peak I_3 yielded one mole of electrons per mole of reactant. Subsequent electrolysis at the more negative peak II_3 (− 1.60 V) gave another 0.9 moles of electrons, which is approximately equal to the consumption in perchlorate medium. The reduction products, especially those obtained at peak II_3, are extremely sensitive to traces of oxygen in solution, which cause reoxidation and partial dimerization of the complex. However, effective (though not complete) reoxidation of the complex to the initial Fe(IV) state can be achieved electrochemically.

The above reduction processes are accompanied by a change in the colour of the solution from dark red to purple (after the reduction at I_3) and light brown (after II_3). In the presence of oxygen, a dark green solution is formed as a result of partial formation of the dimer.

Acid-base properties of monomers

The monomeric complexes (both in perchlorate and chloride media) exhibit relatively low sensitivity to the action of weak acids (phenol). Only the presence of a 50% excess of a strong acid ($HClO_4$, aq, $\simeq$ 5 mol H^+/mol monomer) in chloride medium can produce total decomposition of the complex and release of Fe(III). In contrast, addition of strong base (LiOH) to the monomer in perchlorate medium (in the absence of an excess of Cl^-) resulted in its partial dimerization, seen from the voltammograms and electronic spectra. Such behaviour accords well with observations of formation of oxo-dimers.[11] The probable reactions are as follows.

$$2[Fe^{IV}(L)(DMF)X] + OH^- \rightleftharpoons [Fe^{IV}(L)]_2OH^+ + 2DMF + 2X^- \qquad (2)$$

$$[Fe^{IV}(L)]_2OH^+ + OH^- \rightleftharpoons [Fe^{IV}(L)]_2O + H_2O \qquad (3)$$

Ligand-exchange reactions

As mentioned above, the complexes both in perchlorate and chloride media undergo ligand-exchange reactions DMF-X^- and X^--Cl^-. In solutions of all the complexes in perchlorate medium there are two complex species, $[Fe^{IV}(L)(DMF)X]^0$ and $[Fe^{IV}(L)(DMF)_2]^+$, linked by the kinetic equilibrium (*1*). A similar equilibrium also exists between the products of the first reduction, so that the overall process can be represented by the following scheme.

$$\begin{tikzcd}
{[Fe^{IV}(L)(DMF)_2]^+ + X^-} \arrow[r, shift left, "K_1^{IV}"] \arrow[d, shift right, "E^{0'}_{DMF} + e^-"'] & {[Fe^{IV}(L)(DMF)X]^0 + DMF} \arrow[l, shift left] \arrow[d, shift right, "+e^-"'] \\
{[Fe^{III}(L)(DMF)_2]^0 + X^-} \arrow[r, shift left, "K_1^{III}"] \arrow[u, shift right, "-e^-"'] & {[Fe^{III}(L)(DMF)X]^- + DMF} \arrow[l, shift left] \arrow[u, shift right, "-e^- \quad E_x^{0'}"']
\end{tikzcd} \qquad (4)$$

The equilibrium constants K_1^{IV} and K_1^{III} represent the ratio K_a/K_d for the reaction of Fe^{IV} and Fe^{III} complex, respectively. A quantitative characterization of these equilibria is possible only *via* calculation of the ratio K_1^{IV}/K_1^{III}; this requires a knowledge of E^0 values for $[Fe^{IV}(L)(DMF)_2]^+/[Fe^{III}(L)(DMF)_2]^0$ and $[Fe^{IV}(L)(DMF)X]^0/[Fe^{III}(L)(DMF)X]^-$ couples. As the "X-free complex" is particularly unstable and in the absence of X^- it reacts with traces of water yielding the dimer, quantitative conversion of the initial X^- complex by adding Ag^+ is not possible. Besides, the DMF-complex formed exhibits *quasi*-reversible behaviour, so that the $E^{0'}$ value, expressed as $(E_p^a + + E_p^c)/2$ corresponds only approximately to E^0. For this reason, all other constants are only of a qualitative nature. As for the X^- complexes, their relative high stability and the reversible behaviour of the I_2 peaks at $5\ V\ s^{-1} > v > 0.5\ V\ s^{-1}$ enables calculation of relatively reliable values of equilibrium constants for the complexes with Cl^-, Br^- and NCO^-. With the NCS^--complex, and especially with the complex containing I^-, the overlapping of peaks I_2' and I_1' hinders the determination of $E^{0'}$.

Introduction of the corresponding $E^{0'}$ values into equation (*5*)

$$\frac{E_x^{0'} - E_{DMF}^{0'}}{0.059} = \log\frac{K_1^{III}}{K_1^{IV}} \qquad (5)$$

resulted in the values for $K^{IV}{}_1/K^{III}$ presented in Table 2.

In a similar way we can describe equilibria involving X^--Cl^- ligand exchange reactions. In the presence of excess chloride, the first reduction step is accompanied by the following equilibria.

$$\begin{tikzcd}
{[Fe^{IV}(L)(DMF)X]^0 + 2Cl^-} \arrow[r, shift left, "K_2^{IV}"] \arrow[d, shift right, "E_x^{0'}\ +e^-"'] & {[Fe^{IV}(L)Cl_2]^- + X^- + DMF} \arrow[l, shift left] \arrow[d, shift right, "+e^-"'] & E_{2Cl}^{0'} \\
{[Fe^{III}(L)(DMF)X]^- + 2Cl^-} \arrow[r, shift left, "K_2^{III}"] \arrow[u, shift right, "-e^-"'] & {[Fe^{III}(L)Cl_2]^{2-} + X^- + DMF} \arrow[l, shift left] \arrow[u, shift right, "-e^-"'] &
\end{tikzcd} \qquad (6)$$

However, for correct calculation of the K_2^{IV}/K_2^{III} ratio it has to be taken into account that these equilibria proceed in two steps, DMF-Cl^- and X^--Cl^- exchange, resulting in $[Fe^{IV}(L)XCl]^-$, and formation of $[Fe^{IV}(L)Cl_2]^-$. In view of the existence of two simultaneous equilibria, reversible behaviour of peak I_2 for $[Fe^{IV}(L)XCl]^-$ cannot be registered, and determination of the K_2^{IV}/K_2^{III} ratio is not possible, except when $X^- = Cl^-$. In the latter case the equilibrium involves the mono- and bis-chloride complexes of Fe(IV) and Fe(III), and the values obtained are included in Table 2.

The data for K_1^{IV}/K_1^{III} presented in Table 2 indicate that the introduction of X^- into the coordination sphere produces a dramatic enhancement in stability of the Fe(IV) complexes compared to the Fe(III) cases. The observed sequence

Table 2. Values of reversible potentials[a] and equilibrium constants[b] for the first reduction process of some of the monomeric complexes.

Complex	$E_{DMF}^{0'}$	$E_x^{0'}$	$E_{2Cl}^{0'}$	K_1^{IV}/K_1^{III}	K_2^{IV}/K_2^{III}
[Fe(L)NCS]	+0.044	−0.080	−0.345	1.5×10^2	
[Fe(L)Br]	+0.045	−0.227	−0.353	3.9×10^4	
[Fe(L)Cl]	+0.044	−0.290	−0.345	4.6×10^4	8.6
[Fe(L)NCO]	+0.043	−0.314	−0.353	1.1×10^6	

[a] Expressed as $E^{0'} = (E_p^a + E_p^c)/2$, V; for complexes in 0.1 mol dm^{-3} TBAP + 1 mmol dm^{-3} Ag^+ ($E^{0'}{}_{DMF}$); 0.1 mmol dm^{-3} TBAP ($E_X^{0'}$); 0.1 mol dm^{-3} TBAP + 0.1 mol dm^{-3} LiCl ($E_{2Cl}^{0'}$) [b] For the processes defined by (*4*) and (*6*).

$NCO^- > Cl^- > Br^- \gg NCS^-$ corresponds to the conclusions derived from the I'_2 and I'_1 peak currents (see Fig. 2). On the other hand, the introduction of the second Cl^- into the coordination sphere, due to an excess of negative charge on the complex species, is not favoured either in case of Fe(IV) or Fe(III) complexes. Hence, a low value of K_2^{IV}/K_2^{III} is observed.

Reaction scheme

Figure 6 presents a general reaction scheme for the monomeric complexes in the investigated media, comprising both heterogeneous and homogeneous equilibria, and including the dimerization reaction. A common characteristic of all main reduction products obtained either in perchlorate or chloride media is their tendency to release the coordinated X^- (*i.e.*, Cl^-), and thus relax the negative charge of the complex ion.

DIMER

Perchlorate medium

In the presence of TBAP, μ-oxo dimers are reduced in three steps (peaks I_D-III_D), as shown in Figure 7. The first two steps are one-electron, *quasi*-reversible processes followed by slow monomerization of the complex. As one electron is transferred to each Fe(IV) ion, a relatively large potential difference between the two peaks (0.28 V) is probably due to the geometric and electronic asymmetry of the molecule. The

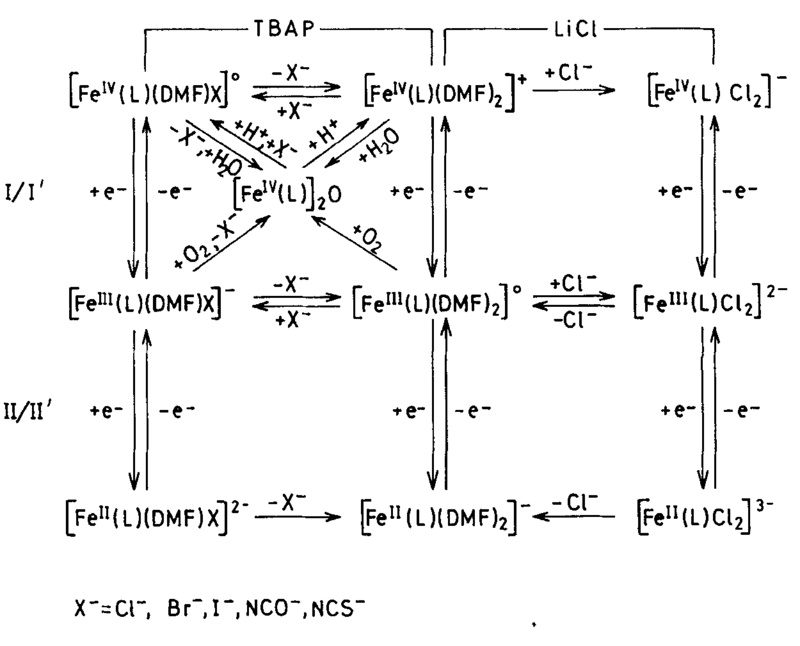

Figure 6 General reaction scheme for monomers.

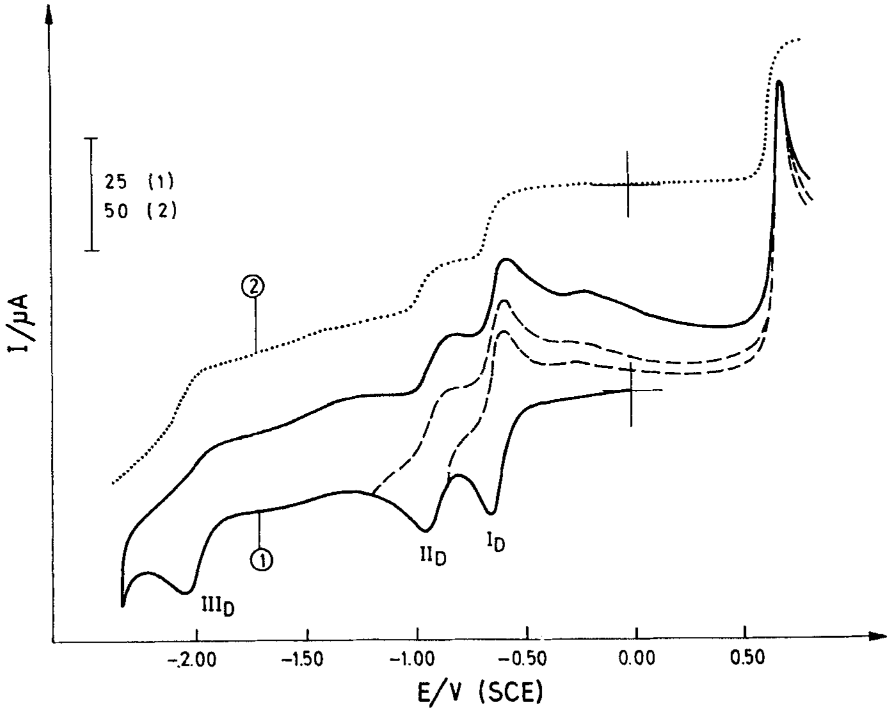

Figure 7 Voltammograms for $[Fe(L)]_2O$ in 0.1 mol dm^{-3} TBAP; 0.20 V s^{-1} (1); 600 r.p.m. (2).

third reduction takes place at substantially more negative potentials (≈ -2.0 V), which is a consequence of the species having already a double negative charge, as well as the ligand-centred nature of the process. Hence, a decrease in the corresponding oxidation peak is observed, as well as the appearance of new anodic peaks, thus indicating a partial decomposition of the complex.

The addition of Cl^- (LiCl) to a dimer solution containing perchlorate causes a positive shift of the III_D peak potential, due to the Li^+ effect described below. Furthermore, the presence of an excess of Cl^- (0.1 mol dm^{-3}) gives rise to partial decomposition (5–10%) of the dimer, and this is observed through the appearance of characteristic peaks for the monomer.

The data obtained by controlled-potential electrolysis in perchlorate media showed the expenditure of ≈ 1.0 and ≈ 0.5 moles of electrons per mole of reactant at peak I_D and II_D, respectively. The green colour became dark brown (I_D) and then light brown (II_D). Although the initial heights of I_D and II_D are approximately equal, peak II_D shows a fast decay during electrolysis, which results in the consumption of about 0.5 $e/[Fe(L)]_2O^-$. This is a consequence of a partial monomerization of the complex during electrolysis, which hinders electrochemical regeneration of the complex after its reduction.

The dimer is oxidized in two steps, the first of which (at +0.7V, Fig. 7) is an apparently two-electron process (two successive one-electron processes at close potentials) followed by fast monomerization (the corresponding reduction peak emerges only at v >1 V s^{-1}, and increases at higher v). The other one-electron peak (at + 1.1 V) is overlapped with a multi-electron peak due to ligand oxidation, observed close to the potential limit of the medium. This process is followed by fast irreversible decomposition of the complex and adsorption of the products formed. As a consequence, the electrode surface is fouled, a result which hindered a detailed investigation of the process. Basic voltammetric characteristics of the dimer in the presence of TBAP are presented in Table 1.

Effect of Li$^+$

In contrast to results for the monomeric complexes, the shapes of cyclic voltammograms recorded for the dimer in perchlorate medium is dependent of the nature of the cation present in the supporting electrolyte. The alkali metal cations form ion pairs with the reduced dimer species, as illustrated for Li$^+$ in Figure 8.

In the concentration range 10^{-3} - 10^{-2} mol dm^{-3}, the presence of Li$^+$ causes a shift of the III_D peak potential to more positive potentials with a slope of about 200 mV/decade, suggesting the reduced complex species (trianion) reacts with three Li$^+$ ions. At higher Li$^+$ concentrations (>1 x 10^{-2} mol dm^{-3}) peak II_D is shifted in a positive sense by about 45 mV/decade, indicating the involvement of one Li$^+$ ion, and the slope of peak III_D is decreased. The value of + 76 mV/decade, obtained for the Li$^+$ concentration range of 10^{-2} - 10^{-1} mol dm^{-3} corresponds to reaction

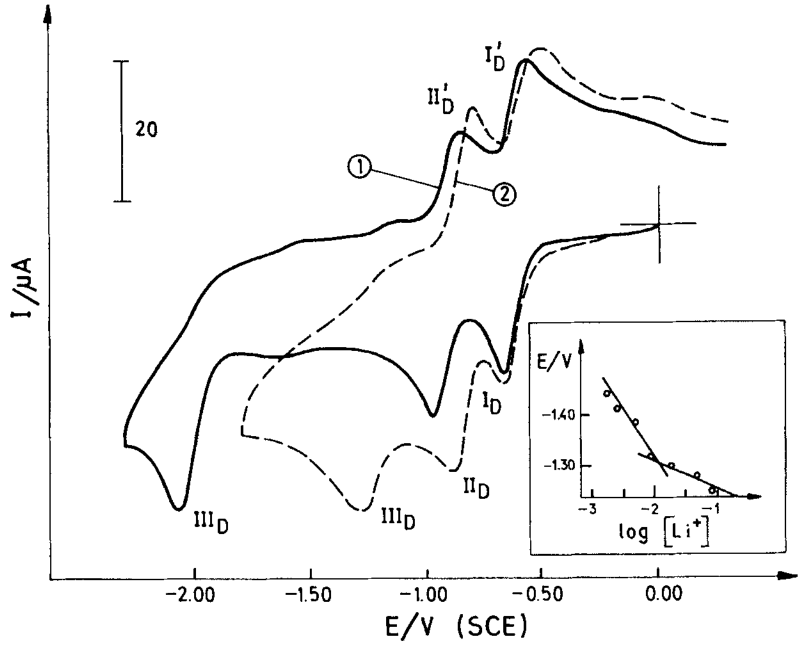

Figure 8 Cyclic voltammograms (0.20 V s^{-1}) for $[Fe(L)]_2O$ in 0.1 mol dm^{-3} TBAP (1) and 0.1 mol dm^{-3} TBAP + 0.088 mol dm^{-3} $LiClO_4$ (2). Inset: E_p (III_D) *vs* log [Li$^+$]

with $\simeq$ 1.3 Li^+ ions, indicating a considerable stability of the $[Fe^{III}(L)]_2O^{2-} \ldots (1\text{–}2)\ Li^+$ associate in solution.

The total association constant (K_{as}) calculated from the expression[13]

$$\exp\left(\frac{nF}{RT}\Delta E\right) = 1 + K_{as}\,[Li^+]^p \tag{7}$$

where $p = 3$ for the Li^+ concentration range 10^{-3} – 10^{-2} mol dm^{-3} gives a value of $\simeq 1 \times 10^{18}$ (dm^3 mol^{-1}),[3] which indicates that the product is very stable.

Acid-base properties of the dimer

As in the case of the monomer, protonation of the dimer can be achieved only by adding strong acid. Reaction with H^+ is fast and stoichiometric, especially in chloride medium (Fig. 9). At the level of 2 H^+/dimer complete monomerization of the complex is achieved; this assumes oxygen bridge disruption and stabilization of the monomer with chloride, as follows.

$$[Fe^{IV}(L)]_2O + 2H^+ \rightleftharpoons 2\,[Fe^{IV}(L)]^+ + H_2O \tag{8}$$

$$[Fe^{IV}(L)]^+ + 2\,Cl^- \rightleftharpoons [Fe^{IV}(L)Cl_2]^- \tag{9}$$

The course of these changes, monitored by measuring the corresponding peak currents, is linear and, apart from voltammetry (Fig. 9, inset), can also be confirmed by spectrophotometric measurements.

Reaction scheme

The voltammetric behaviour of the dimer in perchlorate medium can be represented by the following general scheme

$$\begin{tikzcd}
 & {[Fe^{IV}(L)]O[Fe^{IV}(L)]} \arrow[r, "H^+;\,Cl^-"] \arrow[dd, shift right, "+e^-"'] & \text{monomers} \\
I_D/I'_D & & \\
 & {[Fe^{III}(L)]O[Fe^{IV}(L)]^-} \arrow[r, "\text{slow}"] \arrow[uu, shift right, "-e^-"'] \arrow[dd, shift right, "+e^-"'] & \text{monomers} \\
II_D/II'_D & & \\
 & {[Fe^{III}(L)]O[Fe^{III}(L)]^{2-}} \arrow[r, "+\,Li^+"] \arrow[uu, shift right, "-e^-"'] \arrow[dd, shift right, "+e^-"'] & {[Fe^{III}(L)]_2O^{2-} \ldots Li^+} \\
III_D/III'_D & & \\
 & {[Fe^{II}(L)]O[Fe^{III}(L)]^{3-}} \arrow[r, "+\,2Li^+"] \arrow[uu, shift right, "-e^-"'] & {[Fe^{II}(L)]O[Fe^{III}(L)]^{3-} \ldots 3\,Li^+}
\end{tikzcd} \tag{10}$$

Successive addition of three electrons to the complex in an inert medium gives as a result an unstable trianion which undergoes decomposition to several unidentified products. On the other hand, depending on the nature of the medium, the initial dimer, as well as some electrode reaction products can participate in side reactions with either H^+ or Cl^-, yielding monomers. An opposite effect is the ion

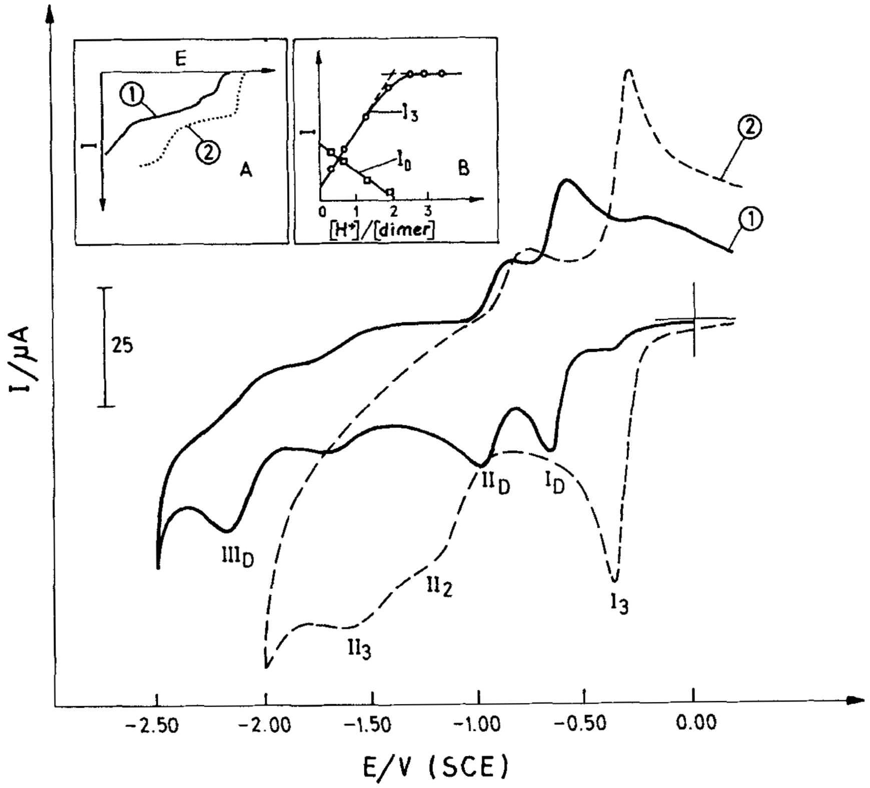

Figure 9 Cyclic voltammograms (0.20 V s^{-1}) for $[Fe(L)]_2O$ in 0.1 mol dm^{-3} TBAP + 0.05 mol dm^{-3} TEACl in the absence of H^+ added (1) and at $[H^+]$/[dimer] ratio 2.0 (2). Inset A: voltammograms at 600 r.p.m. Inset B: peak curent changes during protonation.

pairing with Li^+, resulting in stabilization of the negatively charged reaction products.

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