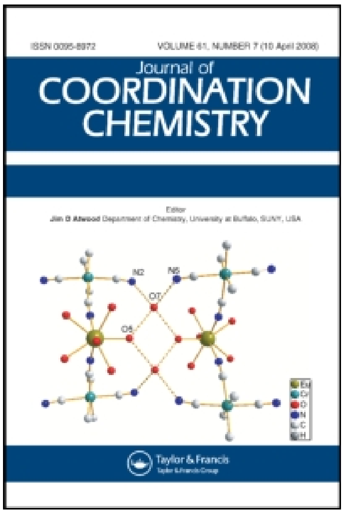

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ELECTROCHEMICAL BEHAVIOUR OF SOME NOVEL μ-OXO DIMERIC FE(III) COMPLEXES IN DMF

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Voltammetric behaviour of several μ-oxo dimers of Fe(III) of general formula $[FeL]_2O$ with ligands based on *S*-alkyl-1,4-*bis*(substituted salicylidene)isothiosemicarbazide was studied at a glassy carbon electrode in DMF solutions with different supporting electrolytes (tetrabutylammonium perchlorate, $LiClO_4$, LiCl). In perchlorate medium the investigated compounds are reduced in three, basic, one-electron steps accompanied by complex decomposition. Oxidation takes place in 2-3 multi-electron processes causing decomposition of the complex and the ligand. The primary dimer decomposition products, both of the reduction and oxidation, are corresponding monomeric species, undergoing further electrochemical reactions. The study encompassed the effects of Li^+ (formation of ion pairs with reduced dimer species), Cl^- and H^+ (phenol and $HClO_4$) on the behaviour of the dimers at the electrode and in the solution. It was found that differences in the behaviour of the complexes are determined by the nature of the substituent in the benzene ring. A general reaction scheme is proposed.

Keywords: Iron(III); monomer-dimer equilibria; substituent effect; voltammetry

INTRODUCTION

Oxo-bridged dimeric iron complexes constitute a group of compounds which are of considerable interest, primarily for their apparent similarity to some biologically important systems [1]. Besides, many of these dimers show unusual magnetic and spectroscopic properties, so that their physicochemical [1] and

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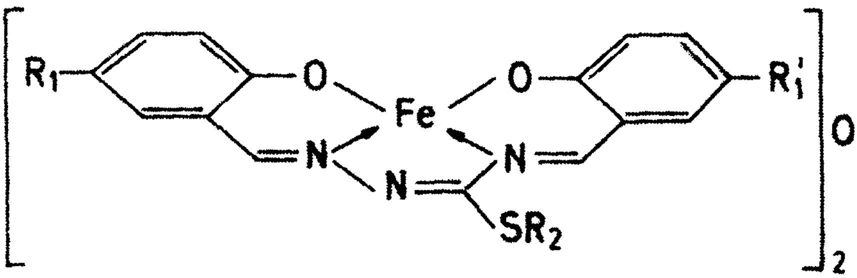

structural [2] studies can be of particular interest. It is known that monomer-dimer equilibria and stability of these dimers are strongly influenced by pH in solution. Therefore, the presence of water and of salts containing monodentate ligands (halide, pseudohalide, acetate, *etc.*) exerts a profound effect on the behaviour of these compounds in solution [1, 3].

The present work deals with the electrochemistry of a series of μ-oxo dimers of Fe(III) with potentially biologically active ligands based on *S*-alkyl-1,4-*bis*(substituted salicylidene)isothiosemicarbazide, $[FeL]_2O$, as follows.

$R_1 = R_1' = HR_2 = CH_3$ $H_2L^1R_1 = R_1' = CH_3$ $R_2 = CH_3H_2L^5$
$R_1 = R_1' = HR_2 = C_2H_5$ $H_2L^2R_1 = R_1' = OCH_3$ $R_2 = CH_3H_2L^6$
$R_1 = R_1' = HR_2 = n\text{-}C_3H_7$ $H_2L^3R_1 = H; R_1' = NO_2R_2 = CH_3H_2L^7$
$R_1 = R_1' = HR_2 = CH_2 = CH\text{-}CH_2$ $H_2L^4R_1 = R_1' = NO_2$ $R_2 = CH_3H_2L^8$

The syntheses of the complexes, their X-ray analyses and some physicochemical properties were described previously [4]. In addition, their acid-base behaviour and the possibility of titrimetric determination in DMF, using a three-electrode amperometric method were reported [5]. The same method was successfully developed for the determination of some other similar transition metal complexes [6, 7].

The electrochemistry of the "parent" monomeric complexes was previously reported [8]. This paper describes the complex voltammetric behaviour of the dimeric compounds, with a special reference to their monomerization.

EXPERIMENTAL

Complexes and Reagents

All investigated complexes were prepared in the Institute of Chemistry of the Moldavian Academy of Sciences, Kishinev, according to known procedures [4].

Their purity was checked by microanalysis. The salts $LiClO_4$, LiCl, and tetrabutylammonium perchlorate (TBAP) were recrystallized before use. DMF was dried over 4 A molecular sieves for two days and distilled twice under reduced pressure [9]. Only freshly distilled solvent was used. Phenol of analytical reagent grade and an aqueous solution of $HClO_4$ (6.4×10^{-2} mol dm^{-3}) prepared in triply distilled water were used for the investigation of acid-base properties. Nitrogen for deaeration was purged by passing over copper scrap heated to 450°C, and through two columns filled with 4A molecular sieves.

Electrodes

A glassy carbon disc (AMEL, Milan) was used as working electrode. To ensure its proper functioning, it was polished with a fine alumina suspension (Buehler Ltd., 0.5 μm and 0.05 μm). A glassy carbon plate (Sigri Elektrographit 2400, dimensions $1.6 \times 2.0 \times 0.2$ cm) served as working electrode in the controlled-potential electrolysis, and a Pt ring of sufficiently large surface area as counter electrode. An aqueous, saturated calomel electrode (SCE) with an asbestos tip (Ingold) connected to the solution *via* a double-junction salt bridge, served as 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 either on a Hewlett-Packard x-y recorder, or a Hewlett-Packard storage oscilloscope. Electronic spectra were recorded on a Cary spectrophotometer. Addition of $HClO_4$ solution was carried out by a Radiometer automatic piston burette.

Procedure

Solutions (1×10^{-3} mol dm^{-3}) of complexes in the presence of 0.1 mol dm^{-3} supporting electrolyte were prepared by weighing dried substances and dissolving them in purified and freshly distilled solvent. Purged and presaturated nitrogen was then bubbled through the solution (stirred with a magnetic stirrer) for 1 h; afterwards it was left to pass over the solution.

All experiments were performed at room temperature; solutions were thermostatted at 25.0 ± 0.2°C for kinetic measurements only. Peak potentials were determined with an accuracy of ±2 mV. All potentials are referenced to SCE.

RESULTS AND DISCUSSION

Complexes in TBAP Medium

The characteristic behaviour of the complexes is illustrated using the example of $[FeL^1]_2O$ as the simplest compound. As can be seen from Figure 1, the cyclic voltammogram for $[FeL^1]_2O$ is composed of five reduction peaks of different intensity (I_D-V_D, curve 1) and three oxidation peaks (curve 3). With the rotating electrode only three reduction waves of approximately same height, corresponding to peaks I_D, II_D, and V_D, are registered. The complex oxidation is represented by three peaks, the first of them, which is poorly defined, being present at about +0.76 V on all the voltammograms. The other, stronger, and apparently two-electron peak, observed in the range +1.1-1.3 V, preceeds multielectron oxidation of the coordinated ligand.

A more detailed insight into particular oxidation-reduction processes reveals all the complexity of the electron transfer processes in these compounds. With respect to their behaviour, they may be divided in two groups, involving the L^1-

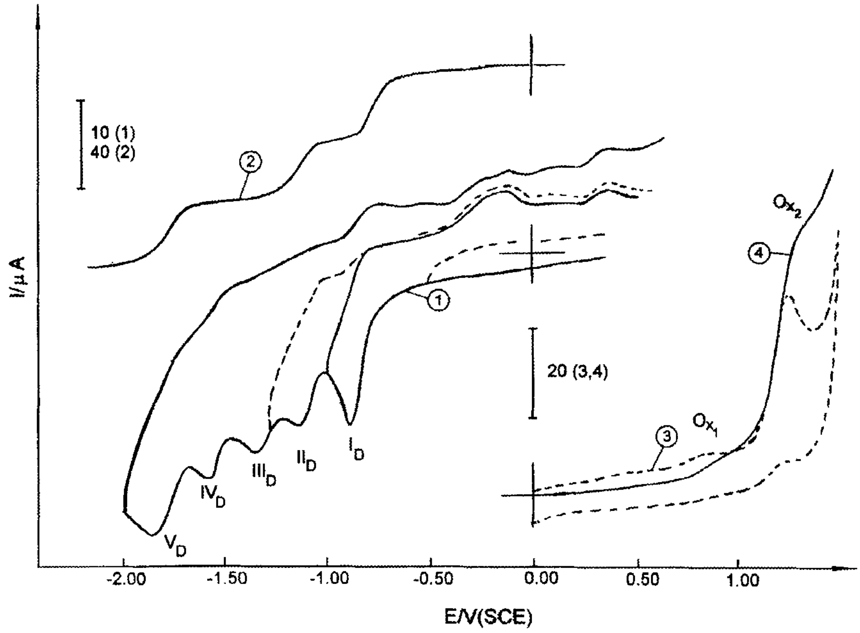

FIGURE 1 Voltammograms for $[FeL^1]_2O$ in the presence of 0.1 mol dm^{-3} TBAP; 0.20 V s^{-1} (1,3); 500 r.p.m. (2,4).

L^5 (L^6) and L^6-L^8 ligands, respectively. The difference in their behaviour stems from the nature of the substituents in the benzene ring; in the first group they exhibit a $+I$ and in the second a $-I$ effect.

Reduction

At moderate sweep rates the reduction of the L^1-L^5 complexes takes place in five successive peaks of different intensity (Figure 1, curve 1). In the same potential range the complexes L^6-L^8 give 6-8 rather poorly defined peaks which, when recorded with a rotating electrode, look like one or two slowly rising waves.

The effect of chemical reactions following each of the processes at peaks I_D, II_D and V_D, corresponding to the reduction of the original dimer, may be eliminated by increasing sweep rate, as can be seen in Figure 2, curve 2. At $\nu > 5$ V s^{-1} peaks III_D and IV_D disappear, and the remaining three peaks are approximately of the same height. In the reverse anodic scan at the same potential amplitude, in contrast to the reduction peaks, several poorly-defined oxidation peaks are registered. However, at a smaller amplitude (Figure 2, inset) and at increased ν the corresponding oxidation peak (I_D') emerges, whereas peak I_M' disappears, so that $i_p(I_D')/i_p(I_D) \sim 1$ at $\nu \geq 5$ Vs^{-1}. When the potential amplitude is extended beyond peak II_D, peak II_D' merges with peak I_D', and the peaks in the anodic scan are poorly defined.

On the other hand, at $\nu < 0.05$ V s^{-1} the apparently simple peaks II_D and V_D appear to be composed of two close peaks. Thus, the resulting cyclic voltammogram for the L^1-L^5 complexes at $\nu = 20$ mV s^{-1} exhibit even seven reduction peaks, of which only peak I_D is well defined and diffusion controlled. Consequently, the resulting anodic branch of the voltammogram is composed of several waves without any well defined peak except for the oxidation peak Ox_2.

If the electrode potential is held at -1.1 V (or, exhaustive electrolysis is carried out), the resulting voltammogram corresponds to that obtained at small ν, *i.e.*, to that having several successive residual peaks characterizing reduction of the dimer decomposition products. After consumption of 1.80 mol of electrons per mol of dimer, dimer reoxidation is not possible either electrochemically or chemically (O_2). The only oxidation peak is observed in the potential region of the Ox_2 peak, but the current decays rapidly as the electrode surface is blocked by adsorption of various oxidation products.

One of the possible products of dimer decomposition is the reduced "parent" monomer $[Fe^{II}L]^0$, whose electrochemistry has been described elsewhere [8]. The original complex species is reduced in two, one-electron processes, of which the first is *quasi*-reversible and, in the absence of Cl^-, chemically uncomplicated. The second peak is followed by irreversible chemical reactions. The potentials of these processes occur about −0.13 V and −1.35 V. Peak III_D on the cyclic voltammograms in Figure 1 and 2 corresponds to the second reduction peak of the monomer, and peak I_M' corresponds to the oxidation peak obtained after the first monomer reduction. This confirms that the primary product of the reduced dimer is the reduced monomer (see Figure 6, inset B). By analogy with the behaviour of the L^1-L^5 complexes, it can be supposed that the corresponding decomposition products are also involved (unfortunately, we had none of these monomers at our disposal to check this supposition). Peak IV_D corresponds, probably, to the reaction of the remaining fragment of the reduced dimer ($[FeL]O^-$), as discussed below. Some characteristics of the reduction processes for particular complexes are presented in Table I.

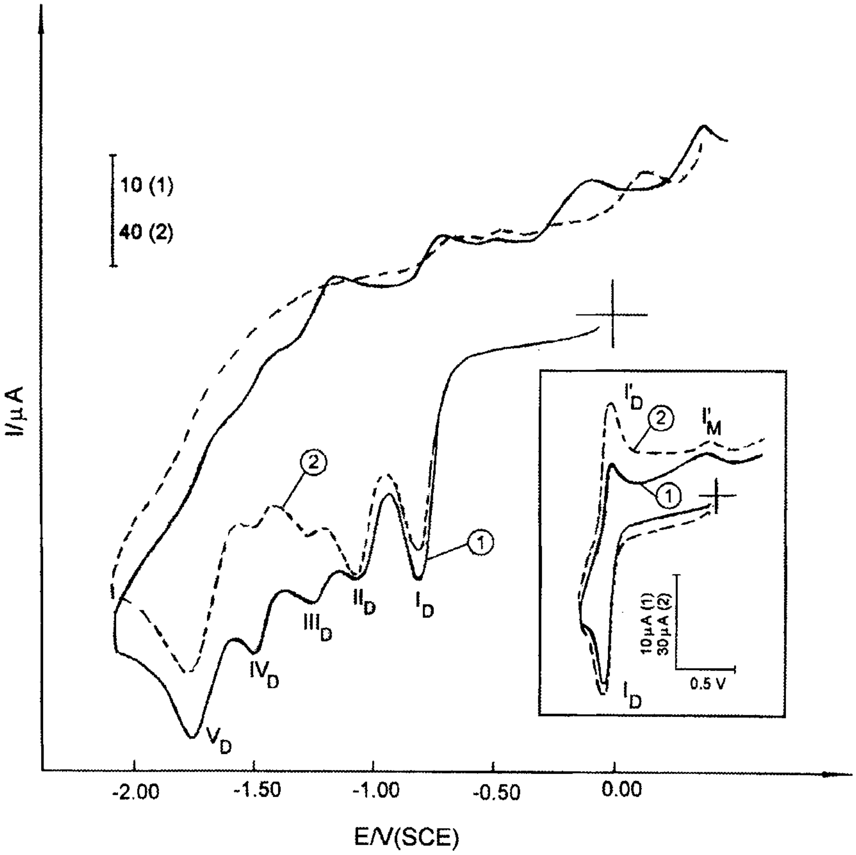

FIGURE 2 Cyclic voltammograms for reduction of $[FeL^1]_2O$ in the presence of 0.1 mol dm^{-3} TBAP; 0.20 V s^{-1} (1), 2.0 V s^{-1} (2); inset: 0.5 V s^{-1} (1), 5 V s^{-1} (2).

TABLE I Peak potentials (0.20 V s^{-1}) for the dimers in 0.1 mol dm^{-3} TBAP

Ligand	$E_p(I_D)$	$E_p(II_D)$	$E_p(III_D)$	$E_p(IV_D)$	$E_p(V_D)$	$E_p(Ox_2)$
L^1	−0.89	−1.14	−1.36	−1.57	−1.84	+1.23
L^4	−0.89	−1.15	−1.36	−1.58	−1.85	+1.23
L^5	−0.94	−1.17	−1.37	−1.61	−1.88	+1.17
L^6	−0.92	−1.14	−1.35	i.d.‡	−1.86	+0.97
L^7	−0.66 m.p.† −0.90	−1.14	i.d.	~1.6	−1.76	+1.28
L^8	~ −0.6 m.p. ~ −1.0	~ −1.1	i.d.	−1.65	−1.82	i.d.

M.p.—main peak i.d.—ill defined.

Oxidation

As already mentioned, the complexes are oxidized in three steps, the first being a one-electron poorly defined peak at E ~ +0.7 V, the second a two-electron peak at E ~ +1.1-1.3 V, and the multielectron peak at E > +1.5 V (Figure 1, curves 3 and 4). The effects of coupled chemical reactions are illustrated in Figure 3. After holding the electrode potential at a value more positive than peak Ox_2, the

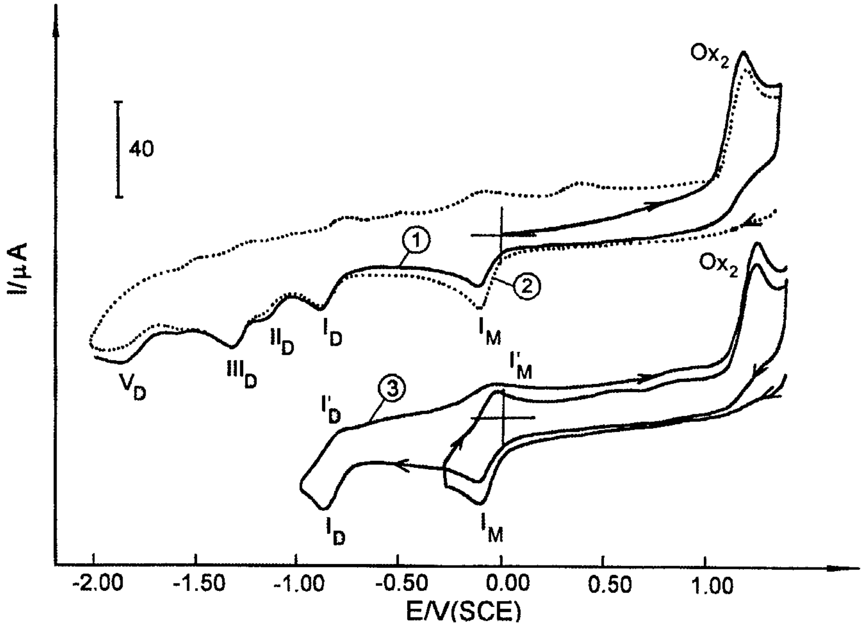

FIGURE 3 Cyclic voltammograms for oxidation of $[FeL^1]_2O$ in the presence of 0.1 mol dm^{-3} TBAP; 0.20 V s^{-1}.

resulting voltammogram, in addition to the above I_D-V_D peaks, contains a new reduction peak I_M. The height of this peak increases with time of potential dwell (the difference in heights of peak I_M in curves 1 and 2). On the other hand, if the potential reversal after the oxidation is set beyond peak I_M (curve 3), the height of the new oxidation peak I_M' is approximately equal to that of I_M. Potential cycling at this amplitude results in decrease of both I_M and I_M', and increase of Ox_2, which indicates involvement of the monomer-dimer equilibrium. The amplitude extension to peak I_D causes a certain decrease in peak I_M', which is also a consequence of the monomer conversion into dimer.

The course of electrolysis at +1.5 V (plateau of peak Ox_2) indicates the complexity of this process. In its first part, the electrolysis curve exhibits an abrupt decrease and then increases to a higher level, where it remains for hours. The colour of the solution changes from reddish to dark green. The resulting cyclic voltammogram does not contain the previous oxidation peaks, whereas some new ones appear instead, corresponding to the reaction of still unidentified decomposition products of the dimer. In view of the fact that the electrolysis potential is quite close to that for oxidation of the ligand itself, it is probable that the process involving the dimer is accompanied by oxidation of both coordinated and liberated ligand. This accounts for the obtained value of $n \gg 2$, expected also on the basis of the cyclic voltammogram. The potentials of Ox_2 peaks are also presented in Table I.

Effect of Li^+

As in the case of many Fe(III) complexes with thiosemicarbazides and semicarbazides [10, 11], cyclic voltammograms for the dimers in solution containing Li^+ undergo marked changes, as illustrated in Figure 4. Because of the formation of ion pairs between the reduction product obtained at peak V_D ($[FeL]_2O^{3-}$) with 2 Li^+, the potential of peak V_D shifts to more positive values with a slope $\Delta E/\Delta \log[Li^+] \sim 114$ mV dec^{-1}. Thus the potential of peak V_D reaches the range of potentials of peaks III_D and IV_D and overlaps with them. On the other hand, the shift of peak II_D to positive potentials by about 50 mV dec^{-1} indicates that $[Fel]_2O^{2-}$ reacts with one Li^+, forming the ion pair $[FeL]_2O^{2-}\ldots Li^+$.

On the basis of the above it can be supposed that the dimer (D) reduction product and Li^+ are involved in the following reactions1, where the constants K_1-K_4 represent the corresponding stability constants of the ion-pairs formed.

peak I_D $D + e^- \rightarrow D^-$
peak II_D $D^- + e^- \rightarrow D^{2-}$

$D^{2-} + Li^+ \rightarrow D^{2-}...Li^+ \quad (K_1)$

peak V_D $\quad D^{2-} + e^- \rightarrow D^{3-}$

$D^{2-}...Li^+ + e^- \rightarrow D^{3-}...Li^+$

$D^{3-} + Li^+ \rightarrow D^{3-}...Li^+ \quad (K_2)$

$D^{3-}...Li^+ + Li^+ \rightarrow D^{3-}...2Li^+ \quad (K_3)$

$D^{3-}...2Li^+ + Li^+ \rightarrow D^{3-}...3Li^+ \quad (K_4)$

Using the expression given by Peover *et al.* [12] where $\Delta E_{1/2}$ is the difference between half-wave potentials obtained for the system in the absence of Li^+ (TBAP) and in the presence of a certain Li^+ concentration ($[M^{z+}]$), and taking the obtained slope p = 0.85, we have $K_1 = (3.4 \pm 0.6) \times 10^2\ mol^{-1}\ dm^3$.

$$\Delta E_{1/2} = \frac{RT}{nF} \ln(1 + K_{as}[M^{z+}]^p)$$

However, the individual values of the other three constants could not be calculated from the available data. Taking into account the charges of interacting species and the observed potential shifts we can only suppose that $K_2 \gg K_3 > K_4$ and $K_2 \gg K_1$. As the presence of only a twofold excess of Li^+ per mol of dimer

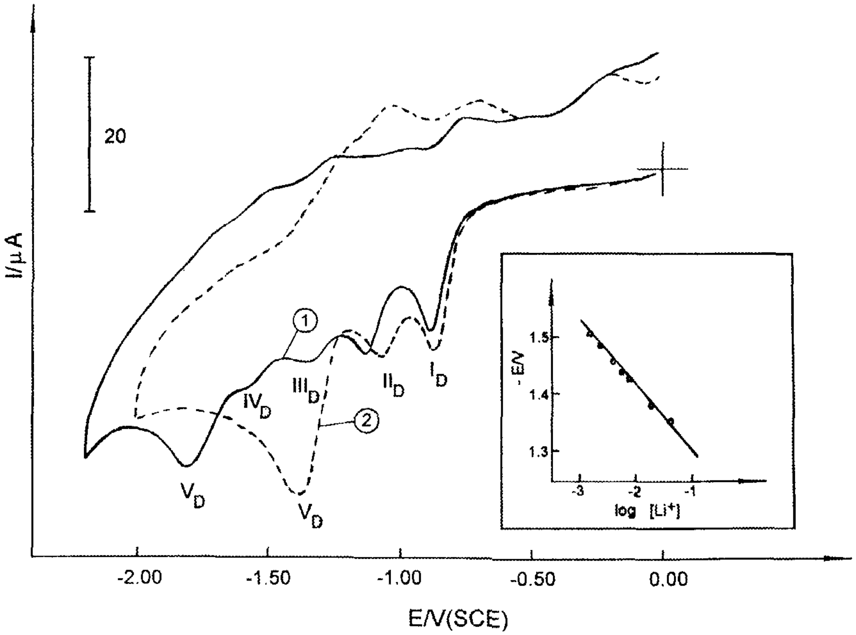

FIGURE 4 Cyclic voltammograms for $[FeL^1]_2O$ in the presence of 0.1 mol dm^{-3} TBAP before (1) and after (2) addition of 20 mmol dm^{-3} $LiClO_4$; 0.20 V s^{-1}; inset: $E_p(V_D)$ *vs* log $[Li^+]$.

caused a shift of the $E_{1/2}$ value for V_D of about 300 mV (compared to about 20 mV for the II_D process) and noting that p = 2, it can be assessed that $K_T = K_2K_3K_4 > 10^{10}$.

Similar behaviour was also observed for the L^1-L^6 complexes, the corresponding values of ion-pairing constants being of the same order of magnitude. However, because of ion-pairing with Li^+, the multielectron reduction of the L^7 and L^8 complexes is much easier, so that the corresponding peak overlaps with peaks III_D-V_D. Hence, the characterization of peak V_D for these complexes was not possible.

Effect of Cl^- (LiCl)

In view of the previous observation [8] that Fe(III) in the octahedral complexes of parent monomers in DMF exhibit significant affinity towards Cl^-, it was interesting to examine the effect of Cl^- on dimer behaviour. As expected, the addition of excess Cl^- caused partial monomerization of the dimer, especially in the case of the less stable (L^6-L^8) complexes. It can be assessed that a hundredfold excess of Cl^- causes monomerization of about 10% of the dimer. On the cyclic voltammograms are also evident the changes in potentials and the heights of the corresponding peaks of the dimer and monomer, caused by involvement of Cl^- in the reactions. The better defined peaks in the anodic branch are evidence for a higher stability of the monomeric reaction products. It should be mentioned that the presence of Cl^- caused a decrease in the available potential window by shifting its positive limit to +0.8 V, which hindered investigation of dimer oxidation.

Effect of H^+

The voltamograms recorded for the complexes in perchlorate medium in the presence of phenol (Figure 5) show that the reduced dimers are sensitive to the presence of weak acids. The addition of an equimolar amount of phenol caused an increase in the peak I_D current by 30%, disappearance of the oxidation peak of the complex, and the appearance of a new anodic peak at about −0.50 V (Figure 5, inset B). With a further phenol addition up to a five-fold excess, the peak I_D current was doubled on account of the decrease in the peak II_D current. Peak III_D, appearing on the resulting voltammogram (Figure 5, curve 2) represents the reduction of the monomer obtained by the decomposition of the dimer reduced at peak I_D. Judging from the slope $E_p(I_D) - c(ph)$ of +29 mV dec^{-1} (inset A) protonation takes place *via* a second order reaction and an ECEC mechanism, involving one proton per dimeric monoanion. In other words, although the dimer itself is a weak base, the monoanion obtained by the reduction is a sufficiently strong base to extract a proton from phenol. Most probably, the protonation takes place at the μ-oxo bridge.

It can be supposed that the following sequence is involved:

$[FeL]_2O + e^- \rightarrow [FeL]_2O^-$
$[FeL]_2O^- + HA \rightarrow [FeL]_2OH + A^-$
$[FeL]_2OH + e^- \rightarrow [FeL]_2OH^-$
$[FeL]_2OH^- \rightarrow [FeL]OH^- + [FeL] \rightarrow 2\,[FeL] + OH^-$

The obtained OH^- reacts with phenol (HA) giving H_2O.

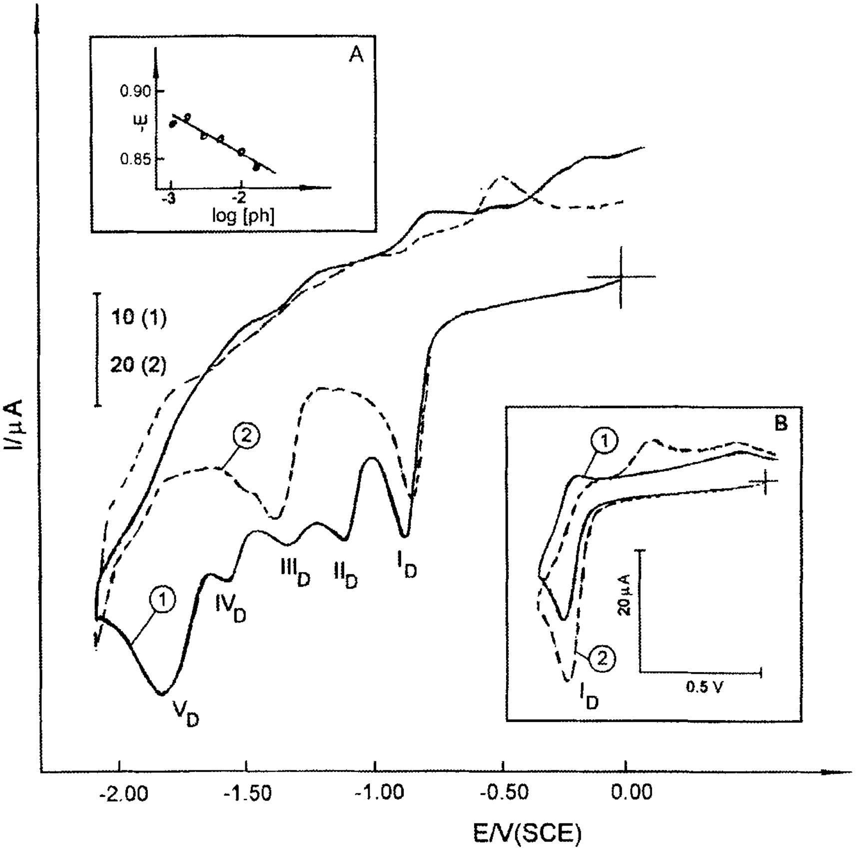

FIGURE 5 Cyclic voltammograms for $[FeL^1]_2O$ in the presence of 0.1 mol dm^{-3} TBAP before (1) and after (2) addition of 10 mmol dm^{-3} of phenol; 0.20 V s^{-1}; inset A: $E_p(I_D)$ *vs* log c(ph); inset B: peak I_D before (1) and after (2) addition of 1.04 mmol dm^{-3} of phenol.

When, however, a strong acid ($HClO_4$) is gradually added to the dimer solution, the dimer is protonated at the μ-oxo bridge, releasing the corresponding monomer (Figure 6, curve 2 and inset B). The reaction is fast and quantitative for the L^1-L^6 complexes, and its course can be monitored amperometrically at the I_M peak potential (about −0.4 V). The titration course and stoichiometry is evident from inset A of Figure 6. In previous work [5] we described the determination of these compounds by continuous three-electrode amperometric titration in the presence of $LiClO_4$. The introduction of an electrophylic substituent (ligands H_2L^6-H_2L^8) into the benzene ring induces a redistribution of electronic charge density over the molecule, due to which the bridge oxygen exhibits a decreased nucelophilicity, resulting in a less basic molecule as a whole. Because of this, the dimers containing an electrophylic substituent in each benzene ring behave as weak bases, so that the corresponding titration curves were practically unusable.

Effect of O_2

In the course of the experiments we noticed that solutions of the complexes are extremely sensitive to the presence of oxygen, which reacts either with the products of the electrochemical reduction, or with the original compound. The main changes observed on the voltammograms are in the range of potentials of the reduction peak I_D (Figure 7). For the L^1-L^5 complexes in insufficiently deaerated solution, a new reduction peak is observed about 100 mV more positive than peak I_D (curve 2); the peak disappears after prolonged bubbling of nitrogen. The reduction peak of free oxygen in TBAP is more negative than both these peaks, *i.e.*, its potential is about −1.05 V. On the basis of the experience gained in studying of some *S*-methylisothiosemicarbazone-based complexes (VO(II), Ni(II), Cu(II) [13], Fe(III) [8]), exhibiting similar behaviour, it can be supposed that in this case too we deal with an adduct of molecular oxygen with the dimer, which is reduced at the potentials 200 mV more positive than oxygen itself.

Reaction Scheme

As already mentioned, the complexes are reduced in five steps represented by peaks I_D-V_D, of which I_D, II_D and V_D are due to the reaction of the original complex species, whereas peaks III_D and IV_D can be ascribed to the reduction of dimer decomposition products. Peak III_D appears at the potential of peak II_M for the reduction of the corresponding original monomer. In the anodic scan at a narrower potential amplitude (to −1.30 V), a peak is observed corresponding to oxidation of the monomeric species that has accepted one electron (I_M'). Thus, one of the products of decomposition is the reduced monomer [$Fe^{II}L$] (or [$Fe^{II}L(DMF)_2$], as found for the original monomer [8]), which reacts further at peak III_D. As peaks III_D and IV_D behave in the same way (under the same conditions they appear and disappear to similar extent), it can be supposed that peak IV_D reflects the reaction of the other product of dimer decomposition.

Therefore, it can be postulated that the reduction of the dimer proceeds as follows.

The decomposition product [$Fe^{II}L$]O^{2-} behaves as a strong base capable of extracting proton from traces of water, which can again induce monomerization of the dimer (see the reaction with phenol).

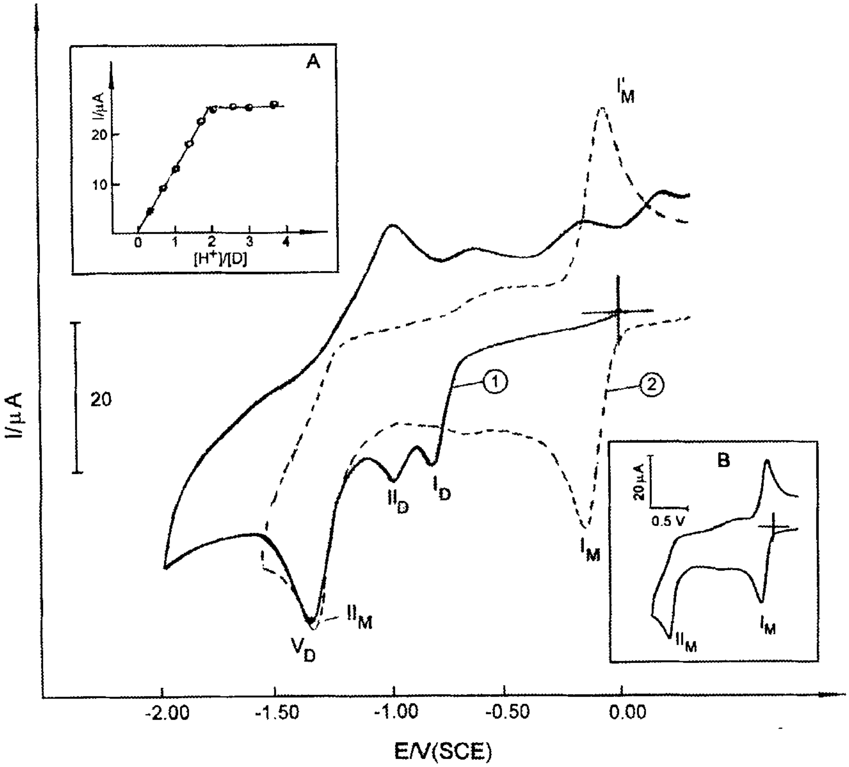

FIGURE 6 Cyclic voltammograms for [FeL^1]$_2$O in the presence of 0.1 mol dm^{-3} $LiClO_4$ before (1) and after (2) addition of 2.5 mole H^+/mole of dimer ($HClO_4$ aq. soln.); 0.20 V s^{-1}; inset A: $I_p(I_M)$ *vs* [H^+]; inset B: cyclic voltammogram for [FeL^1]Cl in TBAP.

Peak I_D $D + e^- \rightarrow D^-$

$D^- \xrightarrow{k_1} [Fe^{II}L] + [Fe^{III}L]O^-$

Peak II_D $D^- + e^- \rightarrow D^{2-}$

$D^{2-} \xrightarrow{k_2} [Fe^{II}L] + [Fe^{II}L]O^{2-}$

Peak III_D $[Fe^{II}L] + e^- \rightarrow [Fe^{I}L]^-$

Peak IV_D $[Fe^{III}L]O^- + e^- \rightarrow [Fe^{II}L]O^{2-}$

Peak V_D $D^{2-} + e^- \rightarrow D^{3-}$

$D^{3-} \xrightarrow{k_3} \text{products}$

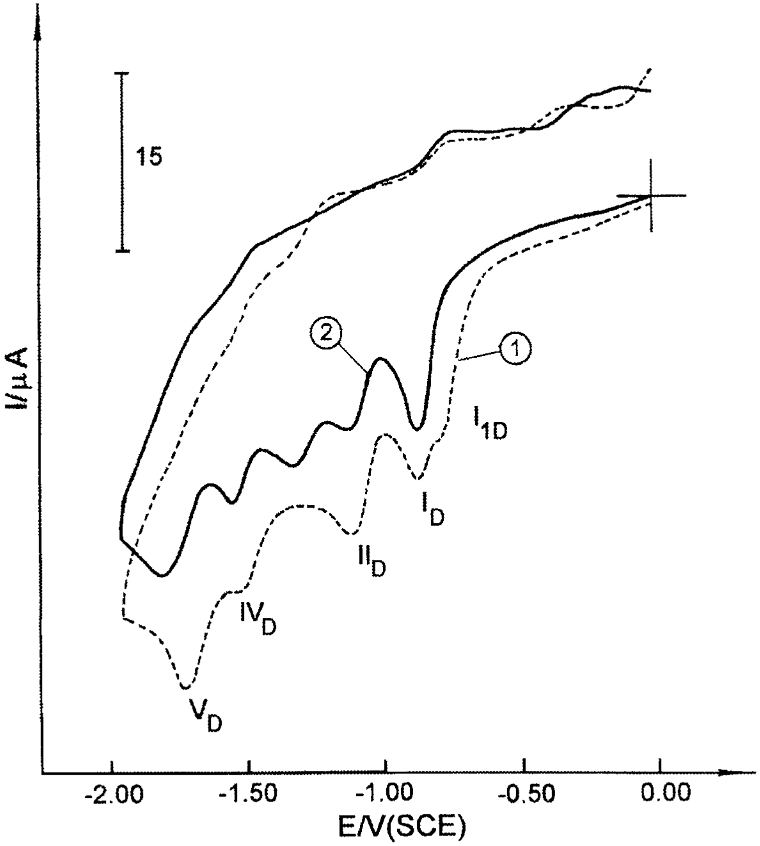

FIGURE 7 Effect of atmospheric oxygen on cyclic voltammograms for $[FeL^1]_2O$ in the presence of 0.1 mol dm^{-3} TBAP; 0.20 V s^{-1}; deaeration with N_2 for 10 min (1), and for 1 h (2).

Dimer oxidation at peak Ox_2 can be represented by the following reactions.

$D - 2e^- \rightarrow D^{2+}$
$D^{2+} \rightarrow [Fe^{III}L]^+ + [Fe^{III}L]O^+$

Decomposition of the oxidized dimer is relatively slow and stabilization of its products can be achieved by the addition of nucleophiles or anions such as Cl^-.

Acknowledgements

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