

Voltammetric and Titrimetric Study of Acid-Base Properties of Some μ -oxo Dimeric Iron(III) Complexes in *DMF*

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Summary. The acid-base properties of the μ -oxo bridged dimeric iron complexes $[\text{FeL}]_2\text{O}$ with the ligands based on S-alkyl-1,4-bis(substituted salicylidene)isothiosemicarbazide and a tetramer with S-methyl-1,4-bis(salicylidene)isothiosemicarbazide, $\{[\text{FeL}]_2\text{O}\}_2\text{I}_3\cdot\text{I}_2$, were investigated by cyclic voltammetry at glassy carbon electrode in *DMF*. Studies were carried out in the presence of either a weak (phenol) or a strong (HClO_4 aq.) acid. The stoichiometry of the reaction, changes in the general voltammetric pattern and the electrode reaction mechanism were discussed. These studies served as the basis for three-electrode amperometric titrations to determine the content of several of these complexes.

Keywords. Iron complexes; Acid-base properties; Cyclic voltammetry; Titrimetric determination; Three-electrode amperometry.

Voltammetrische und titrimetrische Untersuchung der Säure-Base-Eigenschaften einiger μ -oxo dimerer Eisen(III)-Komplexe in *DMF*-Lösungen

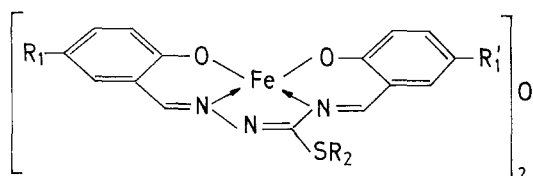
Zusammenfassung. Die Säure-Base-Eigenschaften einiger dimerer μ -oxo-Eisen(III)-Komplexe $[\text{FeL}]_2\text{O}$ mit Liganden auf Basis von 1,4-bis(substituierten Salicyliden)S-(alkyl)isothiosemicarbaziden sowie eines tetrameren Komplexes mit 1,4-Bis(salicyliden)S-methylisothiosemicarbazid, $\{[\text{FeL}]_2\text{O}\}_2\text{I}_3\cdot\text{I}_2$, wurden mittels zyklischer Voltammetrie an der Glaskohlenstoffelektrode in *DMF*-Lösungen untersucht. Die Messungen wurden in Gegenwart entweder einer schwachen (Phenol) oder einer starken (HClO_4 aq.) Säure ausgeführt. Die Stöchiometrie der Reaktion, die Änderungen der voltammetrischen Kurven und der Elektroden-Reaktionsmechanismus wurden diskutiert. Diese Untersuchungen stellten eine Basis für Drei-Elektroden amperometrische Titrations dar, die für die Bestimmung des Gehalts einiger dieser Komplexe angewendet wurden.

Introduction

The 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 structural [2] studies can be of particular interest. Because the monomer-dimer equilibria

and stability of these dimers are strongly affected by the *pH* of the solution, the presence of water and of salts containing monodentate ligands (halide, pseudo-halide, acetate, etc.) exert a profound effect on the behaviour of these compounds in their solutions [1, 3].

A series of μ -oxo dimers of Fe(III) with some potentially biologically active ligands based on S-alkyl-1,4-bis(substituted salicylidene)isothiosemicarbazide $[\text{FeL}]_2\text{O}$ where



$R_1 = R'_1 = \text{H}$	$R_2 = \text{CH}_3$	H_2L^1
$R_1 = R'_1 = \text{H}$	$R_2 = \text{C}_2\text{H}_5$	H_2L^2
$R_1 = R'_1 = \text{H}$	$R_2 = n\text{-C}_3\text{H}_7$	H_2L^3
$R_1 = R'_1 = \text{H}$	$R_2 = \text{CH}_2 = \text{CH-CH}_2$	H_2L^4
$R_1 = R'_1 = \text{CH}_3$	$R_2 = \text{CH}_3$	H_2L^5
$R_1 = \text{H}, R'_1 = \text{NO}_2$	$R_2 = \text{CH}_3$	H_2L^6
$R_1 = R'_1 = \text{NO}_2$	$R_2 = \text{CH}_3$	H_2L^7
$R_1 = R'_1 = \text{OCH}_3$	$R_2 = \text{CH}_3$	H_2L^8

have been synthesized and their x-ray analysis, together with some physico-chemical properties, were described [4]. A detailed report on an electrochemical study of the dimers in *DMF*, with relevance to the "parent" monomers [5], is in preparation.

The present work deals with the investigation of acid-base properties of several of these dimers sufficiently soluble in *DMF*, including the possibility of their titrimetric determination by a three-electrode amperometric method, developed earlier for determination of some other transition metal complexes [6, 7]. Finally, the stability of the tetramer $\{[\text{FeL}^1]_2\text{O}\}_2\text{I}_3\cdot\text{I}_2$, where H_2L^1 is the same ligand as above, with a Fe(III) : Fe(IV) ratio 3 : 1 [8], was tested with special reference to monomer-dimer equilibria in solution.

Experimental Part

All investigated complexes were prepared in the Institute of Chemistry of Moldavian Academy of Sciences, Kishinev (USSR), according to known procedures [4, 8]. Their purity was checked by microanalysis. The salts serving as supporting electrolytes (LiClO_4 , LiCl) and phenol were of analytical reagent grade, while tetrabutylammonium perchlorate was prepared in the laboratory and recrystallized twice before use [9]. Solutions made in freshly-distilled *DMF* served to run the cyclic voltammograms, whereas continuous volumetric titrations were carried out in commercial (analytical reagent) *DMF*. A solution of HClO_4 ($0.06436 \text{ mol dm}^{-3}$) was prepared in triply-distilled water.

Voltammetric experiments were performed on a conventional AMEL set-up. The working electrode was a glassy carbon (GC) disc (7 mm^2), the counter electrode was a Pt ring, and an aqueous saturated calomel electrode (SCE) served as reference. Continuous volumetric titrations were carried out using a Radiometer ABU 12 piston burette and the titration curves were registered on a Servogor *x-t* recorder.

Solutions of the investigated complexes were prepared by dissolving 14–19 mg of the compounds in 25 cm^3 of *DMF* ($8 \times 10^{-4} \text{ mol dm}^{-3}$). In addition, the solutions contained 0.1 mol dm^{-3} of the

supporting electrolyte. The solutions were stirred on a magnetic stirrer and purged with prepurified nitrogen for 30 min. The course of the titration was followed by continuous recording the wave current (GC electrode) at -0.40 V. The results were corrected for a blank titration.

Results and Discussion

Acid-base properties of metal complexes, as well as of the products of their chemical and electrochemical reduction in solution, can be effectively studied by recording their cyclic voltammograms under the conditions of varying acidity of the solution. However, in order to elucidate all the findings, one has to run the electrochemical experiments in the absence of a proton donor and in the presence of an inert electrolyte. Since all the complexes with the exception of H_2L^6 and H_2L^7 have similar general voltammetric appearance, their behaviour will be illustrated on the example of the "parent" dimer, $[FeL^1]_2O$. In addition to two one-electron reduction peaks, the complexes of the nitro-derivatives, H_2L^6 and H_2L^7 , exhibit a third multi-electron peak at $E < -1.1$ V ($LiClO_4$). Due to a fast decomposition of the reduction products of the latter complexes and partial blocking of the electrode surface, their cyclic voltammograms exhibited no defined peaks in the reversal scan. Thus, cyclic voltammetry was not suitable for characterization of acid-base properties of these dimers.

As can be seen from Fig. 1, the "parent" dimer in 0.1 mol dm^{-3} TBAP is reduced in two one-electron processes (peaks I_D and II_D , the direct exhaustive electrolysis at the potential of peak II_D giving two moles of electrons per mole of the dimer), each of them resulting in monomeric units which are further reduced at the potentials

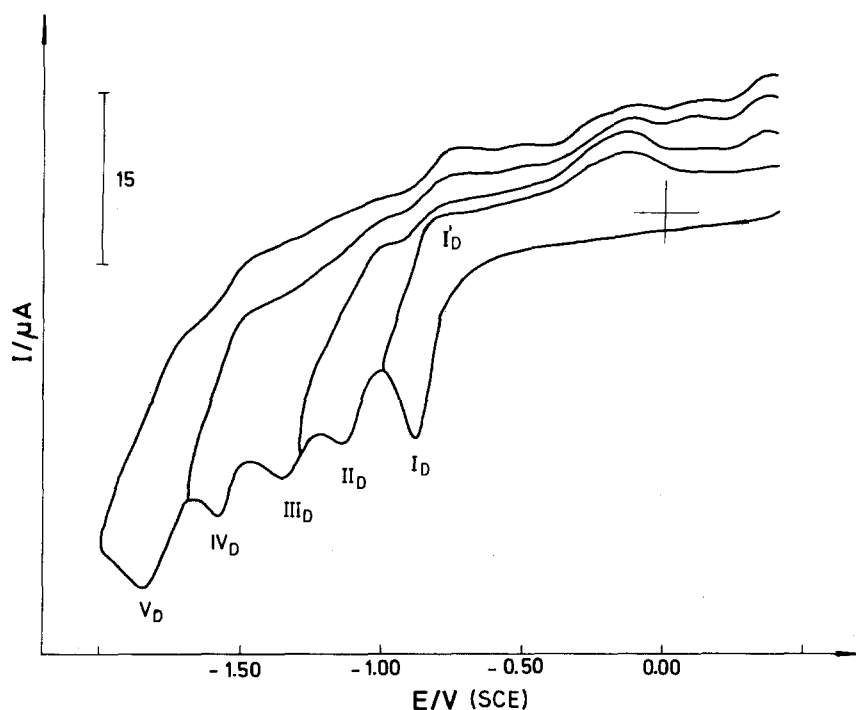


Fig. 1. Cyclic voltammograms for the reduction of $[FeL^1]_2O$ in 0.1 mol dm^{-3} TBAP. GC electrode, 0.20 V s^{-1}

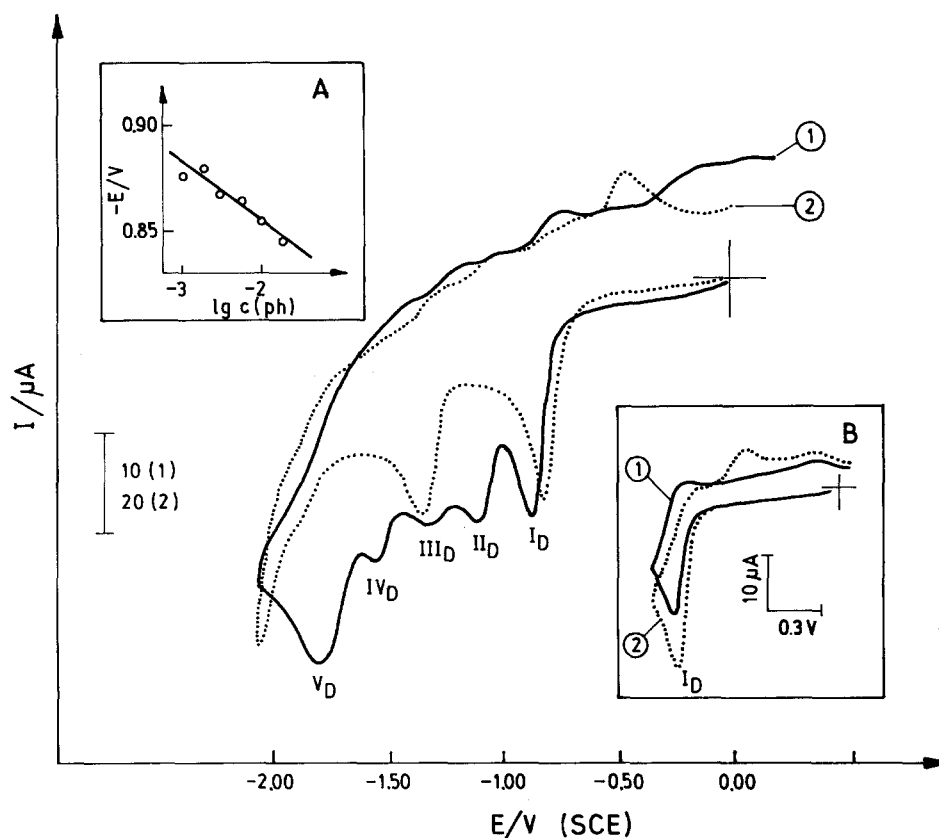
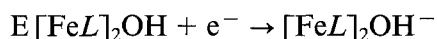
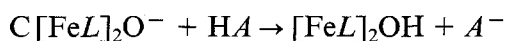
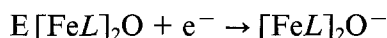


Fig. 2. Cyclic voltammograms for $[\text{FeL}^1]_2\text{O}$ (0.90 mol dm^{-3}) in 0.1 mol dm^{-3} TBAP prior to (1) and after (2) addition of 10.4 mol dm^{-3} phenol. Inset A: Dependence of $E_p(I_D)$ on $\lg c(\text{ph})$. Inset B: cyclic voltammograms of peak I_D before (1) and after (2) addition of phenol ($c = 1.04 \text{ mol dm}^{-3}$). GC electrode, 0.20 V s^{-1}

of peaks III_D and IV_D . The remaining portion of the dimer undergoes a new reduction at peak V_D , and the resulting product decomposes into several species of different composition. The oxidation peaks of the dimers appear at potentials more positive than $+1.0 \text{ V}$ and are followed by peaks of further ligand oxidation. However, because of the accompanying fast decomposition reaction, these processes were not suitable for acid-base characterization of the complexes.

When a weak acid, such as phenol, is added to the solution of a dimeric complex, significant changes in the corresponding cyclic voltammograms are observed (Fig. 2). The addition of an equimolar amount of phenol causes an increase in the current of peak I_D by 30%, disappearance of the oxidation peak of the complex, and the appearance of a new anodic peak at $E \sim -0.50 \text{ V}$ (inset). With a further addition of phenol (to a 5-fold excess) the height of peak I_D is approximately doubled on the account of a decrease of peak II_D , and the cyclic voltammogram becomes quite similar to the curve 2 in Fig. 2. The peak at $E \sim -1.40 \text{ V}$ represents a further reduction of the monomeric species formed by decomposition of the dimer after its reduction at the potential of peak I_D . The slope of the function $E_p(I_D) - c(\text{phenol})$ of $+29 \text{ mV dec}^{-1}$ (inset) suggests the presence of a second order reaction

according to an ECEC mechanism involving the addition of one proton per dimeric monoanion. It is clear that the μ -oxo dimer itself is a too weak base to extract a proton from the phenol molecule, whereas the monoanion obtained by reduction of the complex is a sufficiently strong nucleophile to bind a proton, most probably, at the oxygen atom of the μ -oxo bridge. Thus, the reaction sequence can be written as:



The hydroxyl ion formed reacts probably with phenol (HA) giving H_2O .

On the other hand, in the presence of a strong acid (HClO_4 aq.) the dimeric complexes are transformed into an equivalent amount of the corresponding monomers. In contrast to those obtained in *TBAP* solutions (Figs. 1 and 2), the cyclic voltammograms of $[\text{FeL}^1]_2\text{O}$ recorded in the presence of LiClO_4 (Fig. 3, curve 1) contain a new reduction peak at -1.35 V. This composite peak is a result of superimposition of peaks III_D and IV_D with peak V_D whose potential is positively shifted for about 500 mV due to a fast ion-pairing reaction of the reduced dimer

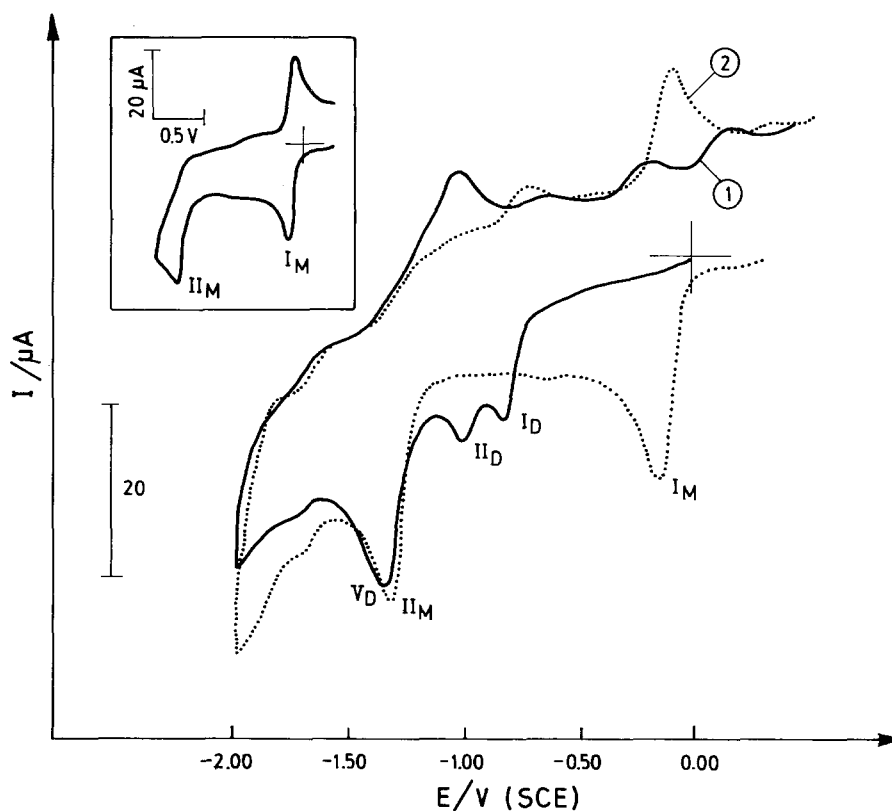


Fig. 3. Cyclic voltammogram for $[\text{FeL}^1]_2\text{O}$ before (1) and after (2) addition of 2 equivalents of H^+ (HClO_4). Inset: voltammogram of the solution after (2), smaller amplitude. GC electrode, $0.1 \text{ mol dm}^{-3} \text{ LiClO}_4$, 0.20 V s^{-1}

with 2Li^+ ($[\text{FeL}]_2\text{O}^{3-} + 2\text{Li}^+ \rightarrow [\text{FeL}]_2\text{O}^{3-} \dots 2\text{Li}^+$). Similar observations on ion-pairing interactions of polyvalent anions with alkali metal ions of the supporting electrolyte are well known in the literature [10–13] and quite common with thiosemicarbazone-based anionic complexes [14, 15]. Successive addition of HClO_4 in LiClO_4 to the dimer solution caused a decrease in the heights of peaks I_D and II_D and an increase in peak I_M at -0.16V ; the cyclic voltammogram for $n(\text{H}^+)/n(\text{dimer})=2$ is of the shape as in Fig. 3, curve 2. As can be seen, the pattern is quite similar to that obtained for the corresponding monomer, $[\text{FeL}^1(\text{DMF})_2]^+$ (see inset in Fig. 3), whose voltammetric and spectral characteristics have already been described [5]. A linear increase in the I_M peak current and relatively fast protonation reaction, as well as the sufficient stability of the resulting monomer in the presence of an excess of proton, enabled us to perform continuous volumetric titrations of these complexes (Fig. 4) by monitoring the current of the first reduction wave of the monomer ($E = -0.40\text{V}$). The method has been developed for the determination of Fe(III) complexes with the isothiosemicarbazide-based tridentate ligands [6] and some similar complexes of Co(III), Cr(III) and V(V) [7].

As can be seen from Fig. 4, the increase in the current before the equivalence point is linear. The corresponding slope and, consequently, the possibility of such determination, depended on the nature of the coordinated ligand in the dimeric complex. The introduction of an electrophilic substituent ($-\text{OCH}_3$, $-\text{NO}_2$) into the benzene ring induced a redistribution of the electronic charge density over the molecule, due to which the bridge-oxygen exhibited a decreased nucleophilicity, resulting in a less basic molecule as a whole. Because of that, the dimers containing an electrophilic substituent in each benzene ring (H_2L^7 and H_2L^8) behaved as weak bases, so that the corresponding titration curves were practically unusable. These complexes, however, could be determined only discontinuously by plotting the I_M peak currents determined from the cyclic voltammograms recorded after addition of each increment of HClO_4 . It should be pointed out that all dimeric complexes react with H^+ in a ratio 1:2.

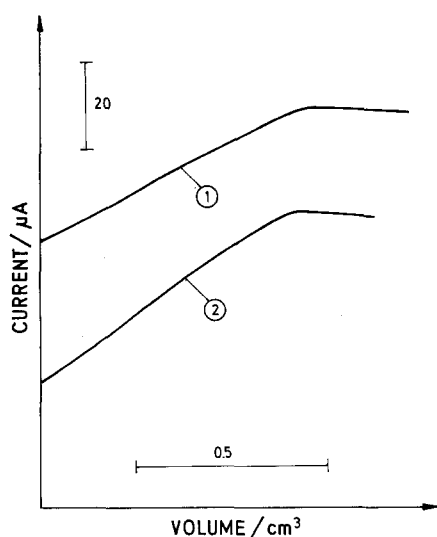


Fig. 4. Three-electrode amperometric titration curves for $[\text{FeL}^1]_2\text{O}$ (1) and $[\text{FeL}^3]_2\text{O}$ (2) with $0.06436\text{ mol dm}^{-3}\text{ HClO}_4$

Table 1. Results of three-electrode amperometric titrations of Fe(III) dimers with $0.06436 \text{ mol dm}^{-3}$ HClO_4 (average of six determinations)^a

Complex	Recovery (%)	Average deviation (%)
$[\text{FeL}^1]_2\text{O}$	101.2	0.8
$[\text{FeL}^2]_2\text{O}$	100.6	0.6
$[\text{FeL}^3]_2\text{O}$	103.7	1.8
$[\text{FeL}^4]_2\text{O}$	100.3	1.6
$[\text{FeL}^6]_2\text{O}$	100.6	1.5

^a Amounts from 14–19 mg of dimers per 25 cm^3 of DMF in the presence of 0.1 mol dm^{-3} LiClO_4

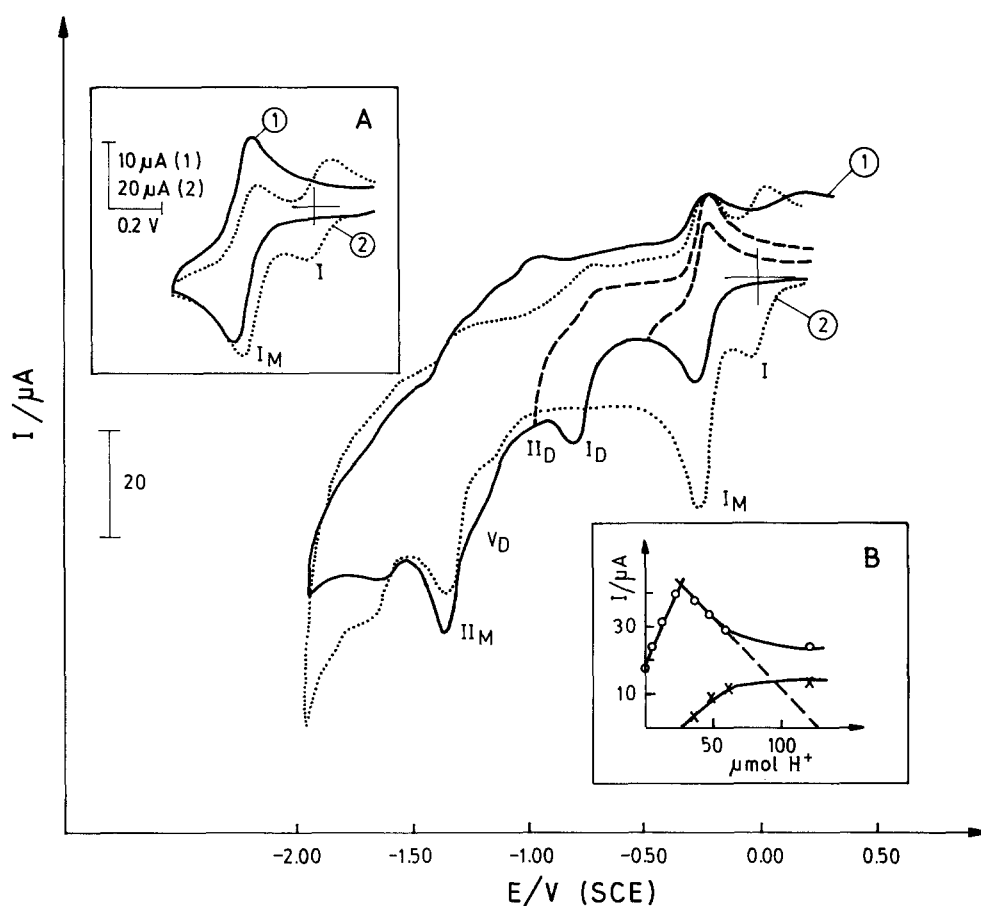


Fig. 5. Cyclic voltammograms for $10 \mu\text{mol } \{[\text{FeL}^1]_2\text{O}\}_2\text{I}_3\text{I}_2$ in the presence of 0.1 mol dm^{-3} LiCl before (1) and after (2) addition of $60 \mu\text{mol H}^+$ (HClO_4). Inset A: voltammogram of the solution after (2), smaller amplitude. Inset B: changes in peak currents for $I_M(o)$ and $I(x)$ during titration

The results of these simple volumetric titrations of several dimeric complexes are shown in Table 1. For the amounts of 14–19 mg of the dimers (ca. 2×10^{-5} mol) the results corrected for the blank titration (basic impurities present in non-distilled

DMF) gave a recovery close to 100% with a satisfactory average deviation. Therefore, the method is sufficiently accurate and can be used for analytical determination of this kind of compounds.

Special attention has been paid to the study of acid-base properties and the possibility of determination of the tetramer $\{[\text{FeL}^1]_2\text{O}\}_2\text{I}_3\cdot\text{I}_2$. The cyclic voltammogram of this compound recorded in the presence of *TBAP* exhibits a number of poorly-shaped reduction peaks which are complicated by chemical reactions involving iodide and, especially, iodine. The addition of LiCl to the tetramer solution resulted in a cyclic voltammogram having several well-defined reduction peaks (Fig. 5, curve 1). They can be identified as the reduction peaks of the monomer (I_M and II_M) and of the dimer (I_D , II_D , and V_D). Therefore, the decomposition of the tetramer complex results in app. 50% of the dimer and the corresponding amount of the monomer which is in the presence of an excess of Cl stabilized in the form of $[\text{FeL}^1\text{Cl}_2]^-$ [5]. In the presence of proton, the dimer is transformed into the monomer and in an excess of H^+ the latter is partly converted into $[\text{FeCl}_4]^-$ and H_2L^1 (Fig. 5, curve 2). By recording the cyclic voltammograms during the successive protonation of the complex we were able to obtain valuable information on both the distribution of particular complex species and their stability. The course of such a discontinuous titration (HClO_4 aq.) was followed by measuring the I_M peak current, showing that the increase in the current in the ascending portion of the curve (slope $\sim 1.0 \mu\text{A}/\mu\text{mol H}^+$) was approximately twice the one observed for its descending part ($0.4 \mu\text{A}/\mu\text{mol H}^+$). Taking into account that the dimer reacts with H^+ in a mole ratio 1:2 (see above), the two-fold higher increase can be explained by decomposition of the dimeric complex in two species reacting at the potential of peak I_M . On the other hand, a molecule of the monomer also reacts with two H^+ , which can be concluded on the basis of the extrapolated part of the curve (Fig. 5, inset B). On the basis of the amount of H^+ consumed before the maximum of the I_M peak is reached it can be concluded that the monomer and dimer in the initial solution are present in an approximate ratio 60:40. The monomeric complex is relatively stable in the presence of H^+ , which is evident from the fact that about 55% of the monomer remains unprotonated even if a 20% excess of H^+ is present. Because of that a continuous titration of the tetramer solution is of no practical importance.

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