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A Voltammetric Identification of Complex Species in *DMF* Solutions of Iron(III) Complexes with Salicylaldehyde *S*-Methylthiosemicarbazone

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The complex species existing under voltammetric conditions (0.1 mol dm^{-3} LiCl) in *DMF* solutions of several iron(III) complexes with salicylaldehyde *S*-methylthiosemicarbazone (H_2L) have been identified by adding $[FeCl_4]^-$ and H^+ and recording voltammograms at a glassy carbon electrode, both in stationary and rotating mode. By the action of Cl^-, a ligand release occurs, and the bis(ligand) cation $[Fe(HL)_2]^+$ is transformed into $[Fe(HL)Cl_3]^-$. The same species is obtained in the reaction of $[FeL_2]^-$ with $[FeCl_4]^-$. Besides, the possibility has been demonstrated to obtain some complexes (and finally $[FeCl_4]^-$) starting from a more basic type, by a careful addition of H^+ generated *in situ* from a Pd/H electrode. A practical application of the latter procedure could be the determination of the iron(III) content in such and similar compounds.

[Keywords: Iron(III) complexes; Salicylaldehyde S-methylthiosemicarbazone; Voltammetric identification]

Die voltammetrische Identifizierung der Komplex-Spezies in DMF Lösungen von Eisen(III) Komplexen mit Salicylaldehyd-S-methylthiosemicarbazon

Die Spezies, die unter voltammetrischen Bedingungen (0.1 mol dm^{-3} LiCl) in *DMF* Lösungen einiger Eisen(III)-Komplexe mit Salizylaldehyd-*S*-methylthiosemicarbazon (H_2L) vorhanden sind, wurden durch Zusatz von $[FeCl_4]^-$ und H^+ und Aufnahme von Voltammogrammen an der stationären und rotierenden Glaskohlenstoffelektrode identifiziert. Unter der Wirkung von Cl^--Ionen kommt es zu einem Ligandenaustausch, wobei das bis(Ligand)-Kation $[Fe(HL)_2]^+$ in $[Fe(HL)Cl_3]^-$ übergeht. Die gleiche Substanz erhält man bei der Reaktion von $[FeL_2]^-$ mit $[FeCl_4]^-$. Ferner wird die Möglichkeit der Gewinnung einiger Komplexe (schließlich von $[FeCl_4]^-$) ausgehend von der basischen Form durch stufenweise Zugabe von H^+-Ionen, die *in situ* mit Hilfe einer Pd/H-Elektrode gebildet werden, beschrieben. Eine praktische Anwendung des letztgenannten Prozesses wäre die Bestimmung des Gehalts von Fe(III) in Lösungen der genannten und ähnlichen Komplexverbindungen.

Introduction

Salicylaldehyde *S*-methylthiosemicarbazone (H_2L) can take part in the coordination with Fe(III) either as a monoanion HL^- (formed by deprotonation of the phenolic OH group of salicylaldehyde) or di-anion L^{2-} (the second deprotonation occuring at the coordinated NH_2 group). Consequently, it was possible to synthesize one mono(ligand) and three bis(ligand) complexes: $Fe(HL)Cl_2$, $[Fe(HL)_2]Cl$, $Fe(HL)L$ and $Li[FeL_2] \cdot 2\,H_2O$[1,2]. Their preparation was accomplished by a careful adjustment of *pH* of the warm alcoholic solutions of the reactants.

The objective of the present work has been a study of the complex equilibria occuring in the solutions of the above complexes in *N,N'*-dimethylformamide (*DMF*) under voltammetric conditions, *i.e.,* in the presence of an excess of salt, serving as supporting electrolyte. Our approach was to identify the species existing in the solution by monitoring changes in voltammograms occuring after a consecutive addition of the mono(ligand) complex to the solution containing a bis(ligand) species. In a similar way we followed changes in the solution of each complex after a discontinuous addition of H^+ ions (generated at a constant current from a Pd/H electrode). Apart from voltammetry, the changes occuring in the solution were also monitored by recording the corresponding electronic spectra.

Experimental

Chemicals

The studied complexes were synthesized in our laboratory[2] and their purity was checked by elemental analysis. *DMF* was either spectroscopic grade (Merck) or freshly twice distilled solvent of different manufacturers. The salts serving as supporting electrolytes were recrystallized before use.

Apparatus

Voltammetric experiments were carried out with AMEL electrochemistry equipment coupled to a Hewlett-Packard 7044A *x-y* recorder, or a Hewlett-Packard 1741 storage oscilloscope. A glassy carbon disc (surface area: 7 mm^2) served as a working electrode with the possibility to work either in the stationary or rotating mode. The counter electrode was a Pt ring, while an aqueous saturated calomel electrode (Ingold) served as the reference.

A conventional constant-current coulometry set-up, consisting of a power supply and a precise mA-meter, served for the generation of H^+ ions from a Pd/H electrode. This electrode was a Pd bar (99.98%; dimensions 1.2 × 0.5 × 0.3 cm) embeded in a glass tube by means of the Araldite epoxy resin. The charging[3], washing and storing procedures were essential for its proper functioning.

Electronic spectra were recorded on a Cary 219 spectrophotometer, using 1 and 2 mm cuvettes. In order to correlate the results to those of voltammetric studies, the same complex solutions (containing supporting electrolyte, too) were employed.

Procedure

The *DMF* solution of Li[FeL_2], or Fe(HL)L, of an approximative concentration $1 \cdot 10^{-3}$ mol dm^{-3}, containing 0.1 mol dm^{-3} LiCl, was thoroughly deaerated by nitrogen and the voltammograms were run at both stationary and rotating glassy carbon electrodes. Then, a small portion of the mono(ligand) complex Fe(HL)Cl_2 (which in the solution behaves as a dimer [Fe(HL)$_2$] [$FeCl_4$]) was added to the solution, followed again by deaeration and recording of the voltammograms. The procedure was repeated each time a new portion of the complex was added.

A constant current of 3.00 mA was employed for a discontinuous addition of H^+ ions to the solutions of the complexes. After each interruption of the titration, the voltammetric curves were recorded as in the preceding procedures.

In both cases, at the most important stages of the titration, the solution samples were taken (by applying nitrogen pressure, in order to minimize possible interactions with atmospheric oxygen) for recording of electronic spectra.

Results and Discussion

Three reduction peaks are noticeable on a cyclic voltammogram for [Fe(HL)$_2$]Cl obtained in LiCl as supporting electrolyte (Fig. 1). From a

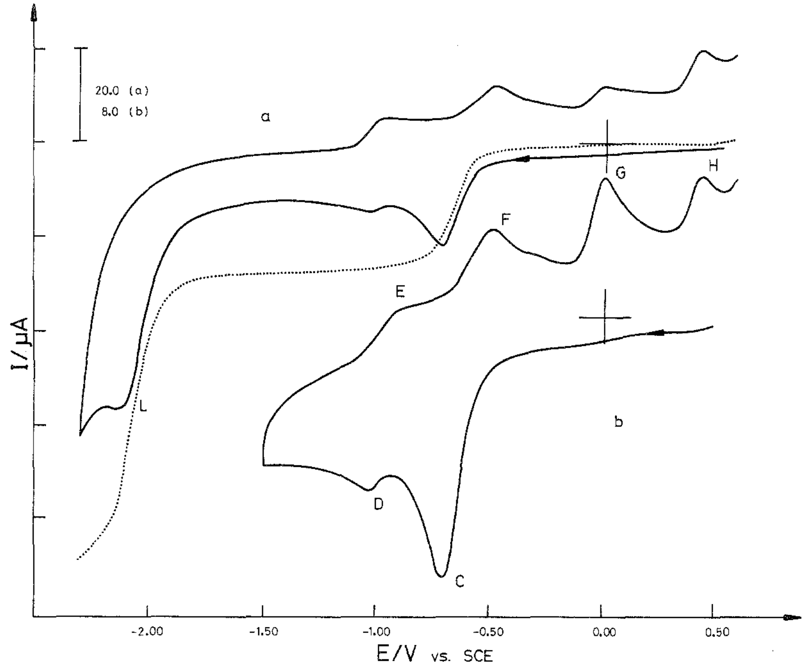

Fig. 1. Voltammograms for [Fe(HL)$_2$]Cl in 0.1 mol dm^{-3} LiCl obtained at stationary (———, 0.200 V s^{-1}) and rotating (· · · ·, 500 r.p.m.) glassy carbon electrode

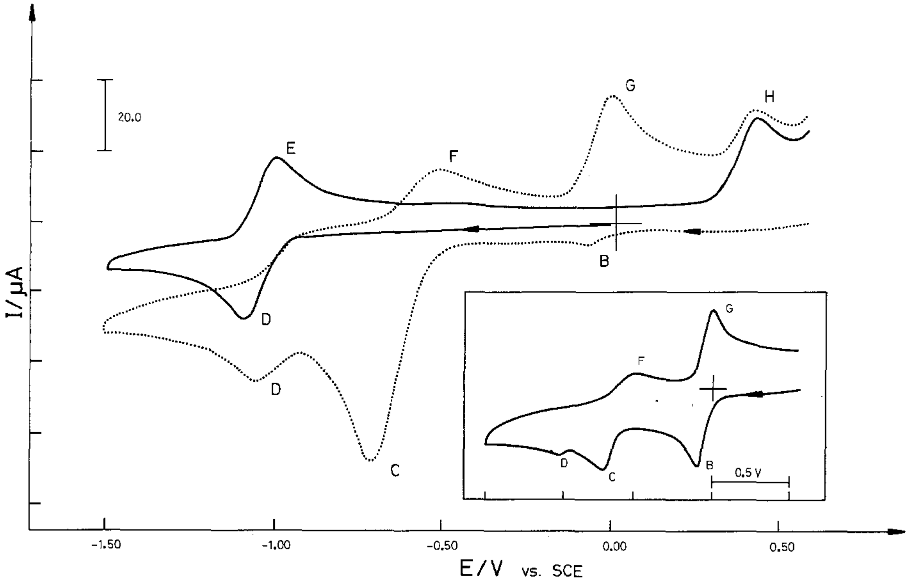

Fig. 2. Cyclic voltammograms for Li[FeL_2] (———); [Fe(HL)$_2$] [FeCl$_4$] : Li[FeL_2], mole ratio 1.20 : 1.19 (····) and [Fe(HL)$_2$] [FeCl$_4$] (inset). Glassy carbon electrode, 0.200 V s^{-1}, 0.1 mol dm^{-3} LiCl

comparison of this curve with that recorded at the rotating electrode it can be concluded that only peak C (oxidation counterpart: F) and peak L can be attributed to the species present in the bulk; peak D being a consequence of a chemical reaction, taking place after reduction at C. Since peak L is characteristic for a free ligand, the question of its origin arises. On the other hand, the peak L is not observable on the voltammograms for Li[FeL_2] (see Fig. 2). Therefore, it is plausible to suppose that in *DMF* solution in the presence of a hundredfold higher concentration of LiCl, a ligand release process occurs, so that the species reacting at peak C is not a bis(ligand) cation [Fe(HL)$_2$]$^+$, but a mono (ligand) entity [Fe(HL)Cl$_x$]$^{2-x}$, where x is most probably equal to 3. It should be mentioned that, to some extent, another ligand cleavage process takes place after reduction at peak C, resulting in [FeL_2]$^-$ (reacting at peak D) and FeCl$_2$ (oxidation peak: G)*.

In order to check the above supposition we designed an experiment enabling a ligand redistribution between the bis(ligand) species [FeL_2]$^-$

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* A detailed electrochemistry of the cited complexes (including also those with similar ligands), giving all possible reaction pathways, will be described elsewhere.

and "free" Fe^{3+} ions. Since it is rather difficult to have an anhydrous and acid-free Fe(III) salt, we employed the mono(ligand) complex $Fe(HL)Cl_2$, instead. In view of our earlier findings[2], this complex behaves in *DMF* as a dimer $[Fe(HL)_2][FeCl_4]$, so that the actual "titrant" was $[FeCl_4]^-$ ion. (It should be noted that the constituent cation $[Fe(HL)_2]^+$ also undergoes the above ligand release process.) This is also evident from the corresponding cyclic voltammogram shown in Fig. 2 (inset). In the same figure there have been presented the cyclic voltammograms for both the original bis (ligand) complex $Li[FeL_2]$ (full line) and after an addition of the equimolar amount of $[Fe(HL)_2][FeCl_4]$ (dotted line). The only explanation for such changes would be the reaction:

$$[FeL_2]^- + [FeCl_4]^- + 2\,HS^+ + 2\,Cl^- \rightarrow 2\,[Fe(HL)Cl_3]^- + 2\,S \qquad (1)$$

The possible source of proton could be the residual traces of water, or some other impurity present in the solution. On the other hand, it might be speculated that the role of H^+ could be played by Li^+. This question remains still open.

Changes in the wave currents for all species during the entire course of "titration" have been presented in Fig. 3. It is evident that the wave currents for D and H (corresponding to reduction/oxidation of $[FeL_2]^-$) decrease to zero at the equivalence point, after which the wave B (reduction of $[FeCl_4]^-$) appears and shows an increase in height with further addition of $[Fe(HL)_2][FeCl_4]$. Until the equivalence point is reached, for each $[Fe(HL)_2][FeCl_4]$ entity added to the solution, three $[Fe(HL)Cl_3]^-$ species appear (two of them being formed in reaction (1); the third one being obtained in the reaction of $[Fe(HL)_2]^+$ with chloride of the supporting electrolyte). Afterwards, wave C shows a threefold slower increase. This can be concluded on the basis of the ratio of the slopes (3 : 1) of the corresponding straight lines before and after the equivalence point. On the other hand, the current for ligand (L) shows a linear increase, and it is approximately doubled when the 1 : 1 mole ratio is reached. This means that the ligand release process takes place all the time, and no reaction between $[FeCl_4]^-$ and the apparently free ligand occurs, at all.

The analogous diagrams have been also obtained from the voltammograms recorded at a stationary electrode, differing only in species reacting at D, whose concentration is influenced by chemical reaction coupled to the electrode process at C.

The same conclusion can be also drawn from the experiments in which $Fe(HL)L$ (*i.e.*, $[Fe(HL)_2][FeL_2]$[2]) has been taken instead of $Li[FeL_2]$.

By adding H^+ ions to the solution of each of the studied complexes (in the presence of LiCl as supporting electrolyte) it is possible to transform it,

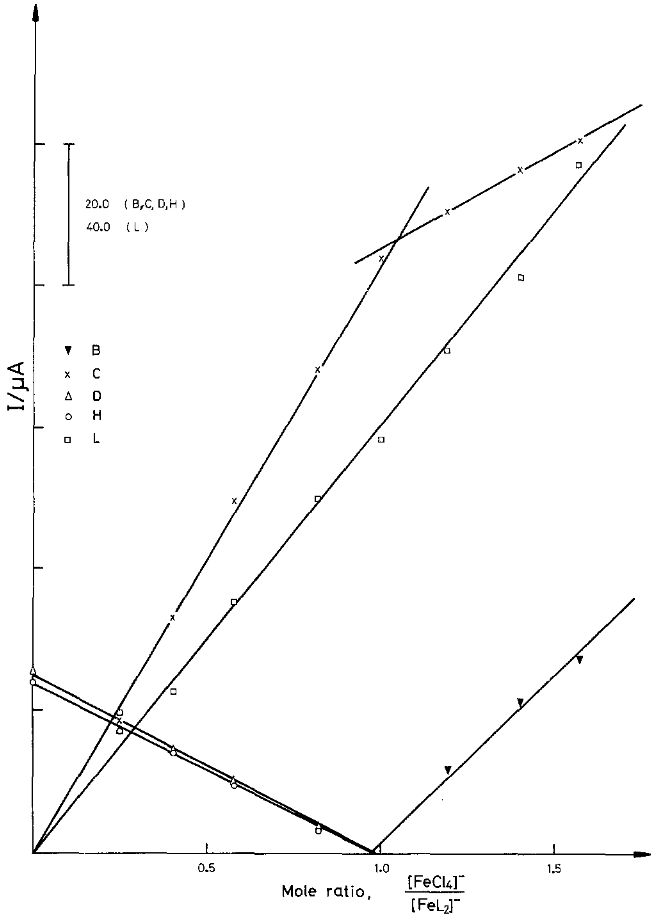

Fig. 3. Current changes at particular waves during addition of $[Fe(HL)_2][FeCl_4]$ to $Li[FeL_2]$

due to protonation of the ligand, into a more acidic form, and finally, to attain its complete decomposition, resulting in $[FeCl_4]^-$. In this way it is possible to identify the particular electrochemical reactants, and to prepare a species in the solution starting from a more basic one. Due to the colour change from dark-brown to yellow, the titration end point can be readily observed.

Fig. 4 contains cyclic voltammograms of the most basic complex, $Li[FeL_2]$ and after addition of H^+ to its solution to molar ratios 1 and 4.

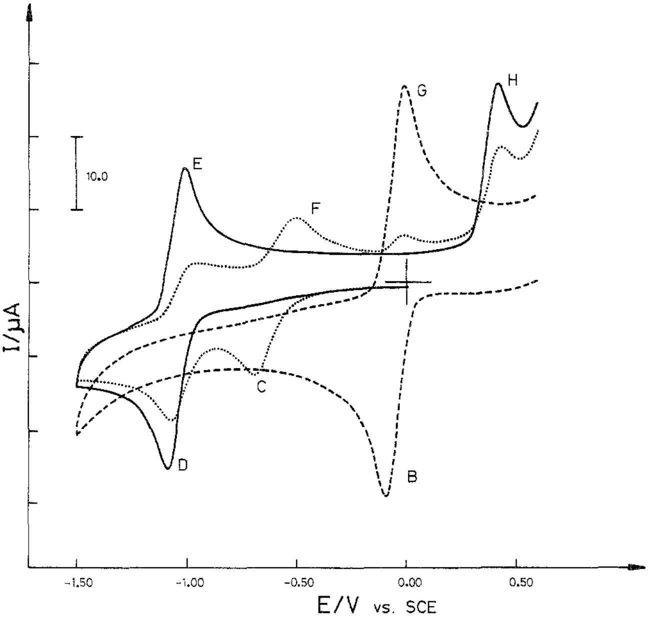

Fig. 4. Cyclic voltammograms for Li[FeL_2] obtained at different $H^+/[FeL_2]^-$ mole ratios: 0 (———); 1 (·····) and 4 (— — —). Glassy carbon electrode, 0.200 V s^{-1}, 0.1 mol dm^{-3} LiCl

The corresponding reactions can be written as:

$$[FeL_2]^- + H^+ \rightarrow [Fe(HL)L] \tag{2}$$

$$2\,[Fe(HL)L] + 3\,Cl^- \rightarrow [Fe(HL)Cl_3]^- + [FeL_2]^- + HL^- \tag{3}$$

and,

$$[FeL_2]^- + 4\,H^+ \rightarrow [FeCl_4]^- + 2\,H_2L \tag{4}$$

The entire course of the titration as monitored *via* decrease/increase in the particular wave currents after each addition of H^+ ion, has been depicted in Fig. 5. Similar graphs have been also obtained if the voltammograms were recorded at a stationary electrode; the straight lines being somewhat obscured (depending on the potential sweep rate), due to chemical reactions coupled to the electron transfer.

The voltammograms recorded at the $H^+/[FeL_2]^-$ mole ratios equal to 1, 2, 3, and 4 are identical to those obtained under the same conditions for the original complexes: $[Fe(HL)_2][FeL_2]$, $[Fe(HL)_2]Cl$, $[Fe(HL)_2][FeCl_4]$ and $[FeCl_4]^-$; the points in between represent the corresponding mixtures. Further, if one of the mentioned complexes is titrated, the graph follows exactly the same pattern from the

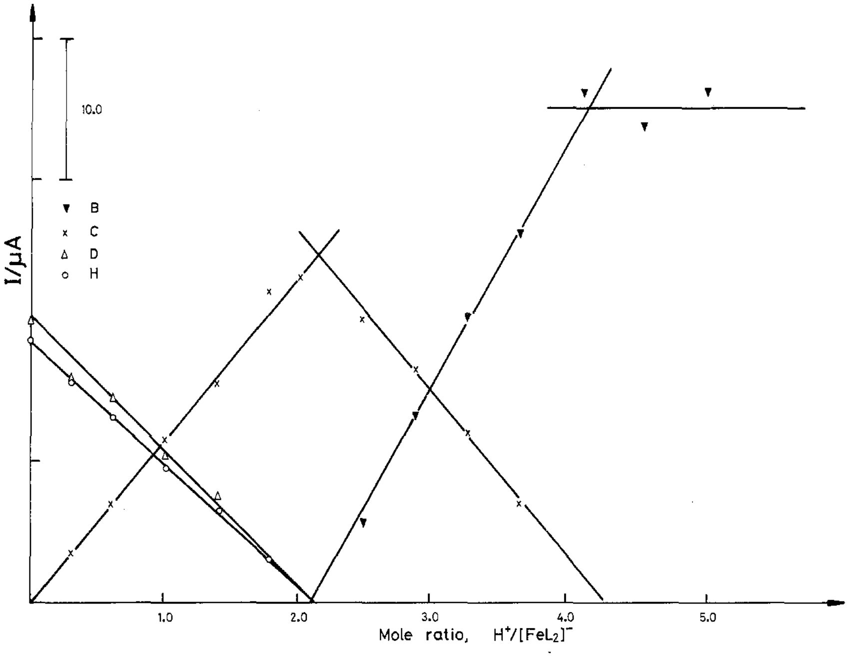

Fig. 5. Current changes of the particular waves during titration of Li[FeL_2] with H^+

corresponding point onwards. In this way, all the species reacting at the electrode in the solution of a particular complex can be identified.

The same conclusion can be drawn from the electronic spectra recorded for solutions of the complexes parallel to their voltammograms.

In contrast to the above, titration of the complexes cannot be successfully performed in perchlorate media ($LiClO_4$, tetrabutylammonium perchlorate). In *DMF*, which has a high donor number, the cationic species are more or less strongly solvated; some particular species can have different solvation numbers in such solutions. Thus, instead of $[FeCl_4]^-$ arising at the equivalence point in LiCl, in perchlorate medium (since ClO_4^- is much less attractive ligand to Fe^{3+}, if compared to Cl^-), two species belonging to differently solvated Fe^{3+} appear. In addition, a portion of the cationic complex remains apparently unchanged. The solution has a brownish-green colour which changes immediately to yellow if LiCl is added to a concentration exceeding $1 \cdot 10^{-2}\,mol\,dm^{-3}$. At the same time, a cyclic voltammogram gives evidence of the presence of solely $[FeCl_4]^-$ and H_2L. This is another support to the notion of ligand release effect of chloride in the solutions.

Finally, apart from being useful in identification of the reacting species in the solution containing LiCl, the described procedure has been successfully employed for determination of the iron content in several newly synthesized complexes of iron(III) with different *S*-alkyl derivatives of the title ligand, as well as their approximate molar masses. The method consisted in comparing the peak/wave currents for $[FeCl_4]^-$ obtained from a standard compound with those of the investigated one. Besides, a possibility appears to follow the above coulometric titrations continuously (*e.g.*, by an amperometric or photometric method) with the aim of determining the purity of the studied (and similar) preparations.

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References

[1] *Gerbeleu N. V., Turte K. E., Canić V. D., Leovac V. M., Arion V. B.,* Koordinatsionnaya khimiya **6**, 446 (1980).
[2] *Leovac V. M., Bjelica L., Jovanović Lj.,* Polyhedron (in press).
[3] *Kaufman S.,* Anal. Chem. **47**, 494 (1975).