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Redox Behaviour of Divalent Metal Saccharinates

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Summary. The electrochemical behaviour of a series of divalent metal saccharinates of stoichiometry $[M^{II}(sac)_2(H_2O)_4]\cdot 2H_2O$ was studied by cyclic voltammetry in *DMF* solutions using a glassy carbon electrode. The oxidation and the reduction of the metallic centers Fe(II) and Cu(II), respectively, is shown to occur in one electron-steps and to be quasireversible. The second electron transfer for the copper saccharinate is followed by decomposition of the complex associated with loss of the ligand and copper electrodeposition. Reduction of the ligand was observed for Ni(II), Fe(II), and Co(II) saccharinates at highly negative potential. On the contrary, oxidation or reduction peaks were not observed with sodium saccharinate. The uncoordinated ligand was inactive in the analyzed potential range.

Keywords. Cyclic voltammetry; Metal saccharinates; Redox behaviour.

Elektrochemisches Verhalten zweiwertiger Metallsaccharinate

Zusammenfassung. Das elektrochemische Verhalten einer Reihe zweiwertiger Metallsaccharinate der Stöchiometrie $[M^{II}(sac)_2(H_2O)_4]\cdot 2H_2O$ wurde in *DMF* mit Hilfe cyclischer Voltammetrie an Glaskohlenstoff-Elektroden untersucht. Die Oxidation bzw. Reduktion von Fe(II) und Cu(II) erfolgt durch einen Einelektronenprozeß und erwies sich als quasi-reversibel. Die zweite Elektronenübertragung wird im Falle des Kupfersaccharinats von einer Zersetzung des Komplexes begleitet, welche unter Ligandenverlust zur Abscheidung von Kupfer auf der Elektrode führt. Im Falle der Ni(II)-, Fe(II)- und Co(II)-Komplexe wurde eine Reduktion des Liganden bei sehr negativen Potentialen beobachtet. Dagegen wurden für Natriumsaccharinat keine Oxidations- oder Reduktionspeaks beobachtet; der unkomplexierte Ligand erwies sich im untersuchten Potentialbereich als inaktiv.

Introduction

Renewed interest in the chemistry of saccharin (*p*-sulfobenzimide) and its metal complexes has developed in the last few years, probably due to its suspected carcinogenic nature [1–4]. Notwithstanding, systematic studies on general physico-chemical properties of saccharinate complexes of biologically relevant transition metals are very scanty.

Structural data for different metal complexes of general stoichiometry $[M^{II}(sac)_2(H_2O)_4]\cdot 2H_2O$ (M^{II} = Fe, Co, Ni, Cu [5, 6]; Mn [7]; Cr, Zn [8, 9]; V [10]) are known. Recently, we have investigaged the ^{57}Fe *Mössbauer* spectrum [11] and the *Raman* and resonance *Raman* spectra [12] of the Fe(II) complex as well as the magnetic behaviour and electronic spectra of some other divalent metal saccharinates [13]. On the other hand, we have also shown that some of the $[M^{II}(sac)_2(H_2O)_4]\cdot 2H_2O$ complexes exhibit superoxide-dismutase-like (SOD) activity [14]. This finding prompted us to investigate the electrochemical behaviour of these systems in detail. In this paper we report a cyclic voltammetric study of the saccharinates of Fe(II), Cu(II), Zn(II), Ni(II), and Co(II) in aprotic media.

Results and Discussion

The cyclic voltammogram (CV) of Fe(II) saccharinate at 0.1 V/s in the potential range +1.3 to −1.75 V is shown in Fig. 1. The first scan exhibits a quasi-reversible electron transfer process (A/A'), an irreversible reduction peak (B) at −1.57 V, and an oxidation peak (C) at −0.23 V.

We have investigated the behaviour of the couple A/A′ in the −0.2 V to +0.7 V potential range at scan rates from 0.005 V/s to 0.8 V/s. At rates between 0.005 V/s and 0.05 V/s, the charge transfer is reversible as the difference in peak potential values is constant and equal to 0.065 V. The ratio of the peak currents due to cathodic and anodic sweeps is close to unity (1.00 ± 0.03), the current function $i_p/v^{1/2}$ is constant, and the difference between $E_{p/2}$ and E_p is approximately 0.06 V. Since a difference of 0.057 V/n between $E_{p/2}$ and E_p is predicted for systems which are both electrochemically and chemically reversible, the electron transfer for the couple A/A' must be rapid. At these low sweep rates we have estimated the formal redox potential $E_{1/2}$ as +0.31 V *vs.* NHE; this oxidation process represents the transfer of a single electron [18–20].

At increasing sweep rates ($v > 0.05$ V/s), the oxidation and reduction peak potentials E_p^A and $E_p^{A'}$ are shifted to more positive and negative values, respectively. The peak potential difference increases ($\Delta E_p = 0.085$ V at 0.06 V/s and $\Delta E_p = 0.18$ V at 0.8 V/s), indicating a kinetic inhibition of the electron transfer process (quasi-reversible behaviour). The ratio of the peak currents remains close to unity, independent of the sweep rate used. That means that the charge transfer coefficient α is 0.5 [19].

Thus, this wave can be ascribed to a one electron-oxidation of the metal centre:

$$[Fe(sac)_2(H_2O)_4]\cdot 2H_2O \underset{A'}{\overset{A}{\rightleftharpoons}} [Fe(sac)_2(H_2O)_4]^+\cdot 2H_2O + e^-$$

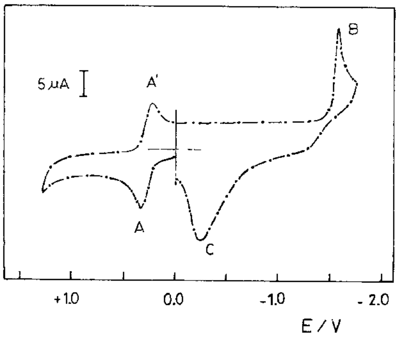

Fig. 1. Cyclic voltammogram of $[Fe(sac)_2(H_2O)_4]\cdot 2H_2O$ at $v = 0.1$ V/s in the potential range from +1.3 V to −1.75 V *vs.* NHE

Current peak B indicates the irreversible reduction of the ligand accompanied by an adsorption process at the electrode. The adsorbed species is electrodesorbed in the reverse scan and creates current peak C. This adsorption process has been confirmed by holding the potential at −1.8 V for a certain time τ. When the potential sweep was continued in a positive direction, a higher contribution of the current peak C was observed.

From the current ratio between the reduction peak A′ and B at the different sweep rates employed it is possible to infer cautiously that reduction process B involves the transfer of two electrons.

We have also investigated the redox behaviour of Zn(II), Ni(II), Co(II), and Cu(II) saccharinates. The Zn(II) saccharinate was inactive in the potential range analyzed (+1.3 V to −1.9 V).

The CV obtained for the Co saccharinate at $v = 0.1$ V/s is shown in Fig. 2. We have observed only an irreversible reduction peak B and an electrodesorption peak C for both the Ni and Co saccharinate. Oxidation or reduction of the metallic centre was not accessible under experimental conditions in the analyzed potential range.

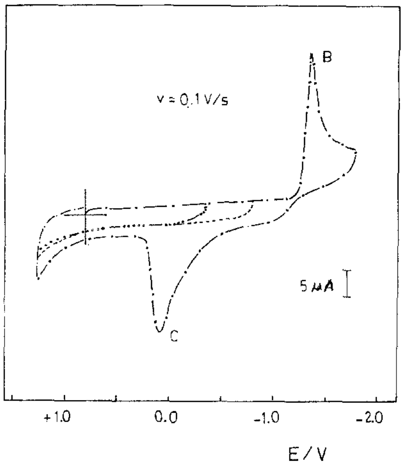

Fig. 2. Cyclic voltammogram of $[Co(sac)_2(H_2O)_4]\cdot 2H_2O$ at $v = 0.1$ V/s in the potential range from +1.3 V to −1.8 V *vs.* NHE; the CV shows the dependence of the electrodesorption peak C on peak B

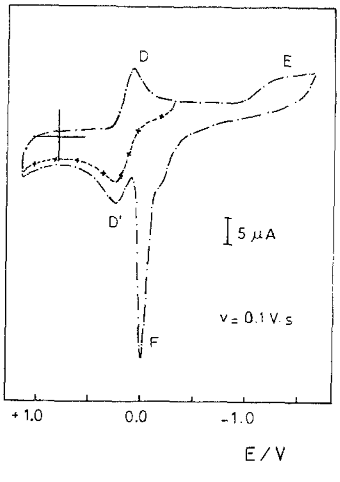

Fig. 3. Cyclic voltammogram of $[Cu(sac)_2(H_2O)_4]\cdot 2H_2O$ obtained at $v = 0.1$ V/s in the potential ranges a) +1.1 V to −0.15 V (——— × ———); b) +1.1 V to −1.6 V (————————·) *vs.* NHE

The cyclic voltammetric behaviour of Cu(II) saccharinate is shown in Fig. 3. The complete scan (+1.1 V to −1.6 V) reveals two reduction peaks (D and E), a large anodic peak F at 0.0 V preceded by a small shoulder, and another oxidation peak D′ at +0.25 V.

The oxidation peak D′ is smoother than the reduction peak D, and its current peak is lower. The ratio $i_p^{D'}/i_p^D$ is constant and equal to 0.87 ± 0.02 in all sweep ranges analyzed. This constant value indicates the absence of a perturbing chemical reaction after the first reduction process. Following the *Nicholson* criteria [21], the symmetry of the curves is affected in this way when $\alpha > 0.5$. Thus, from the dependence of the couple D/D′ on the sweep rate (0.004 V/s to 0.8 V/s), we can conclude that the criteria for a equal-reversible one electron transfer process are met [19, 20]. From the lowest scan rate a formal redox potential of about +0.17 V *vs.* NHE can be estimated.

The cyclic voltammetric behaviour of $Cu(ClO_4)_2$ in *DMF* exhibits general features resembling those of copper saccharinate, but some differences are detected. At $v > 0.2$ V/s, the CV consists of one reduction and one oxidation peak. The redox process corresponds to the one electron quasi-reversible reduction of Cu(II) to Cu(I). At $v < 0.2$ V/s, the reduction process is followed by a disproportionation:

$$\mathrm{Cu(II)} + \mathrm{e}^- \rightleftharpoons \mathrm{Cu(I)}$$

$$2\mathrm{Cu(I)} \rightleftharpoons \mathrm{Cu(II)} + \mathrm{Cu}^0$$

Metallic copper is adsorbed at the glassy carbon electrode and is stripped from the surface in the reverse scan. The sharp current peak obtained is characteristic of this type of processes (Fig. 4).

For copper saccharinate, it must be noted that the general behaviour delineated above does not change with the sweep rate. The measurements performed at sweep rates between 0.004 V/s and 0.2 V/s showed no sign of disproportionation. The CV obtained at 0.1 V/s for copper saccharinate and perclorate can be observed in Fig. 4 for comparison.

On the other hand, the second reduction wave depicted in Fig. 3 (E) apppears at a more negative potential than the wave for $\mathrm{Cu(I)} + \mathrm{e}^- \rightarrow \mathrm{Cu}^0$ ($E_p = -0.55$ V) obtained in our experiments with $Cu(ClO_4)_2$. This shift to a more negative potential indicates that the coordination with the saccharinate ligand results in the stabilization of the lower valence states of copper. However, after the acquisition of

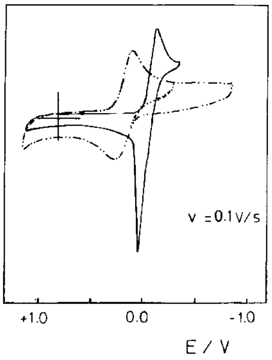

Fig. 4. Cyclic voltammogram of $[Cu(\mathit{sac})_2(H_2O)_4]$ in the potential ranges a) +1.15 V to −0.28 V (···· × × × ····) and b) +1.15 V to −0.9 V (····——····) $i = 5\,\mu A/cm$, and $Cu(ClO)_2$ in the potential range from +1.15 V to −0.33 V (————); $i = 10\,\mu A/cm$, $C = 10^{-3}\,M$, and $v = 0.1$ V/s

the second electron, the reduced species dissociates and affords metallic copper adsorbed at the surface of the electrode. This is supported by the fact that when the potential was held at -1.75 V for a few seconds, enabling more product to be formed, the anodic process was enhanced and the peak was narrower and more symmetrical showing the typical shape of stripping peaks.

Thus, the electrochemical behaviour for this complex can be summarized as follows:

$$[\mathrm{Cu}(sac)_2(\mathrm{H_2O})_4]\cdot 2\mathrm{H_2O} + e^- \underset{D'}{\overset{D}{\rightleftharpoons}} [\mathrm{Cu}(sac)_2(\mathrm{H_2O})_4]^-\cdot 2\mathrm{H_2O}$$

$$[\mathrm{Cu}(sac)_2(\mathrm{H_2O})_4]^-\cdot 2\mathrm{H_2O} + e^- \xrightarrow{E} [\mathrm{Cu}(sac)_2(\mathrm{H_2O})_4]^{2-}\cdot 2\mathrm{H_2O}$$

$$[\mathrm{Cu}(sac)_2(\mathrm{H_2O})_4]^{2-}\cdot 2\mathrm{H_2O} \rightarrow \mathrm{Cu}^0_{(\mathrm{ads})} + 2sac^- + 6\mathrm{H_2O}$$

$$\mathrm{Cu}^0_{(\mathrm{ads})} \xrightarrow{F} \mathrm{Cu(II)} + 2e^-$$

The two electron transfer of the electrodissolution process was verified by an additional experiment (Fig. 5). The voltammetric sweep was started at $+0.8$ V in the negative direction in order to observe the two electroreduction peaks described above. The sweep rate was reversed at -1.75 V; immediately after the detection of peak F, connected with metallic copper, the sweep direction was again reversed. Two additional waves related to the reduction of free Cu(II) to Cu(I) and then to Cu^0 were observed.

In the potential range analyzed, for Cu(II) saccharinate no reduction of the ligand was observed. This system exhibits a different behaviour compared with the other ones investigated. The species $[\mathrm{Cu}(sac)_2(\mathrm{H_2O})_4]^{2-}\cdot 2\mathrm{H_2O}$ is unstable, and loss of the ligand, accompanied by copper deposition on the electrode, is observed.

The free saccharinate ligand is inactive in the potential range analyzed ($+1.1$ V to -1.9 V). That was confirmed by an additional measurement of a 10^{-3} *M* sodium saccharinate solution in *DMF* $+0.1$ *M* $[(TBA)\mathrm{PF_6}]$.

As is well known, the two half reactions $\mathrm{O_2} + e^- \rightarrow \mathrm{O_2^-}$ and $\mathrm{O_2^-} + 2\mathrm{H^+} + e^- \rightarrow \mathrm{H_2O_2}$ have potentials of $E^0 = -0.45$ V and $E^0 = +0.98$ V *vs.* NHE, respectively. Therefore, any redox pair with a potential intermediate between the above two values can act as a catalyst for the SOD reaction [22, 23]. The investigated Fe(II)

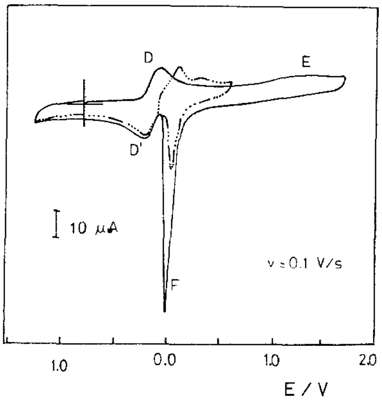

Fig. 5. Cyclic voltammogram of $[\mathrm{Cu}(sac)_2(\mathrm{H_2O})_4]\cdot 2\mathrm{H_2O}$ at $v = 0.1$ V/s in the potential range from $+1.3$ V to -1.75 V (see text)

and Cu(II) complexes clearly fulfil this requirement and, in particular, the Cu(II) complex presents the highest SOD activity of all divalent metal saccharinates [14].

Conclusions

The electrochemical behaviour of a series of divalent metal saccharinates of stoichiometry $[M^{II}(sac)_2(H_2O)_4]\cdot 2H_2O$ was studied by cyclic voltammetry in *DMF* solutions at a glassy carbon electrode. The oxidation and the reduction of the metallic centres Fe(II) and Cu(II), respectively is shown to occur in a one electron step and to be quasi-reversible. The second electron transfer for the copper saccharinate is followed by decomposition of the complex accompanied by loss of the ligand and copper electrodeposition. Reduction of the ligand at very negative potentials was observed with Ni(II), Fe(II), and Co(II) saccharinates. On the contrary, oxidation or reduction waves were not observed in sodium saccharinate solution. The uncoordinated ligand was inactive in the analyzed potential range.

Experimental

Cyclic voltammetric experiments were performed on a Bioanalytical Systems Inc. CV-1B assembly using a three electrode cell; working electrode: glassy carbon disk, counter electrode: platinum wire, reference: Ag/0,01 *M* $AgNO_3$ in CH_3CN. The system was calibrated against the $[Fe(C_5H_5)_2]^+$/ $[Fe(C_5H_5)_2]$ redox couple for which a redox potential of 0.4 V *vs.* the normal hydrogen electrode (NHE) was assumed [15, 16]. Potentials are given *vs.* NHE in volts.

The supporting electrolyte, tetrabutylammonium hexafluorophosphate ($[(TBA)PF_6]$, electrochemical grade) was purchased from Fluka. Reagent grade dimethylformamide (*DMF*; from Carlo Erba) was dried over molecular sieve and repurified by distillation at reduced pressure [17]. The solutions were 0.1 *M* in $[(TBA)PF_6]$; the concentration of the divalent metal saccharinates was 10^{-3} *M*. Oxygen was removed by purging the solutions with pure nitrogen, and a continuous stream of nitrogen was passed over the solutions while the measurements were being performed. The response for all scan rate experiments (0.004–0.8 V/s) was recorded on a Houston Instrument Omnigraphic 2000 XY recorder.

The investigated complexes were prepared according to published procedures [13].

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