Electrochemical Investigation of Iron(III) Complexes with Some Kojic Acid Derivatives

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The electrochemical reduction of $[Fe^{III}L_3]$ complexes, where L is anion of kojic acid, some kojic acid derivative, and maltol, has been investigated in methanol solution by cyclic voltammetry at a platinum electrode. The reduction of seven $[Fe^{III}L_3]$ complexes into $[Fe^{II}L_3]^-$ anions occurs at a potential from -0.66 V to -0.80 V *vs.* ferrocenium/ferrocene potential. The modification of the kojic acid with various substituents influences the redox properties of the studied complexes according to the ligand delocalization. The relative stability of the complexes $\beta(Fe^{II})/\beta(Fe^{III})$ was influenced by the degree of the ligand delocalization.

It is known that kojic acid forms with Fe(III) in solution a series of the coloured kinetically labile complexes. The formation of the complexes is immediate and they show stability for several hours. The formation of the complexes is also dependent on pH values and concentration of kojic acid in solution [1].

The absorption maximum measurements show that at pH 5.8 to 6.0 and the content of kojic acid $n(HL)$ $n(Fe(III)) = 8.3$ to 16.6, the maximum is not dependent on the concentration of kojic acid and small changes in pH values. Only one species is present – the yellow-orange complex $[Fe^{III}L_3]$ – at such condition in the solution, which is negligibly dissociated [2].

In this paper we describe the electrochemical investigation of the kinetically labile Fe^{III} complexes at the condition when only one six-coordinated iron(III) complex with the three uninegative bidentate ligands (Scheme 1) was in the solution.

EXPERIMENTAL

Kojic acid derivatives and maltol were synthesized, characterized by elemental analysis, NMR and IR spectra, and purified before use by recrystallization from methanol [3]. Methanol (Lachema, reagent grade) was distilled before use from $Mg(OCH_3)_2$. The other chemicals used were of reagent grade and used without further purification.

The iron complexes were synthesized directly in the electrolyzed cell to fulfil the condition of the presence only of one complex $[FeL_3]$ in the solution. To the methanol solution (1 mol dm^{-3} NaClO$_4$) one of the ligands ($c(HL) = 10^{-2}$ mol dm^{-3}) was added and then stepwise CH$_3$ONa so that the ratio of $n(HL)$ $n(CH_3ONa)$ was 1   1. At the end iron(III) nitrate
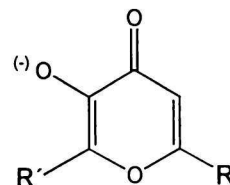
L	R'	R	
L1	CH₃	H	(anion of maltol)
L2	H	CH₂OH	
L3	H	CH₂(CH₂)₇CH₃	
L4	H	CH₂ScycloC₆H₁₁	*structure*
L5	H	CH₂N₃	
L6	H	CH₂SCNSC₆H₄	*structure*
L7	H	CH₂Cl	
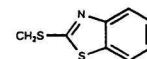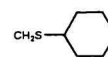
Scheme 1. The studied kojic acid derivatives and maltol anions.

methanol solution ($c = 10^{-1}$ mol dm^{-3}) was added. The concentration of Fe(III) was in the range from 6×10^{-4} to 9×10^{-4} mol dm^{-3} and the ratio of $n(HL)$ $n(Fe(III))$ was in the range from 10 to 14.

Cyclic voltammetry measurements were performed with a PA 3 polarographic analyzer (Laboratorní přístroje, Prague). The electrochemical cell employed the standard three-electrode configuration, a platinum-wire working electrode, a platinum-foil auxiliary electrode, and an aqueous saturated calomel reference

electrode (SCE). The SCE was separated from the test solution by a bridge filled with the solvent and supporting electrolyte.

All experiments were carried out under an argon atmosphere at ambient temperature with scan rate of 20, 50, 100, and 200 mV s^{-1}. At the end of the experiments, ferrocene was added to the test solution as an internal standard [4, 5], and all measured potentials were referenced to the formal potential of the ferrocenium/ferrocene (Fc$^+$/Fc) couple.

RESULTS AND DISCUSSION

Kojic acid derivatives and maltol were not electrochemically active in the investigated range of potentials. Anionic form of these derivatives behaves as bidentate ligand bonded to the central atom Fe(III) *via* the carbonyl and hydroxyl oxygen atoms [6]. This form exhibits totally irreversible L$^-$ → L$^·$ + e$^-$ oxidation at a potential around 0.6 V *vs.* SCE or 0.26 V *vs.* Fc$^+$/Fc, with no evidence for a well-defined cathodic peak (Fig. 1a). We are inclined to believe that the oxidized form is probably a radical. It is known that many hydroxylated derivatives of γ-pyrone such as kojic acid and maltol, may be oxidized by cerium(IV) in solutions to give radicals [7]. This electrochemical behaviour can be explained as due to either a poorer thermodynamic stability of the L radicals, or to the solvolysis reactions of the L$^·$ radicals being very fast.

At our experimental conditions, *i.e.* in the presence of strongly basic NaOCH$_3$ and at high ratios of c(HL) c(Fe(III)), the equilibrium between the kinetically labile complexes

$$Fe^{3+}(solv) \rightleftarrows [FeL]^{2+} \rightleftarrows [FeL_2]^+ \rightleftarrows [FeL_3]$$
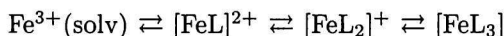
is almost completely shifted to the neutral high-spin complexes with the three uninegative bidentate ligands.

The formation of the iron(III) complexes was observed by diminishing of the anodic peak current of the ligand anion and the formation of a new wave in the cathodic region (Fig. 1b). Further investigation of cathodic wave was done at the condition that one six-coordinated complex [FeL$_3$] was present in the system and the reduction process had been attributed to the reduction of iron(III)

$$[Fe^{III}L_3] + e^- \rightleftarrows [Fe^{II}L_3]^-$$
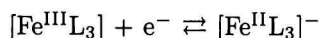
The complexes undergo a one-electron cathodic process at a platinum electrode which gives voltammetric responses consisting of a reduction peak on the forward scan and a corresponding oxidation one on the backward scan (Fig. 2). The number of electrons (n) involved in the redox process was determined using Malachesky equation [8] and was found to be 0.97 ± 0.04. The separation of the reduction and oxidation
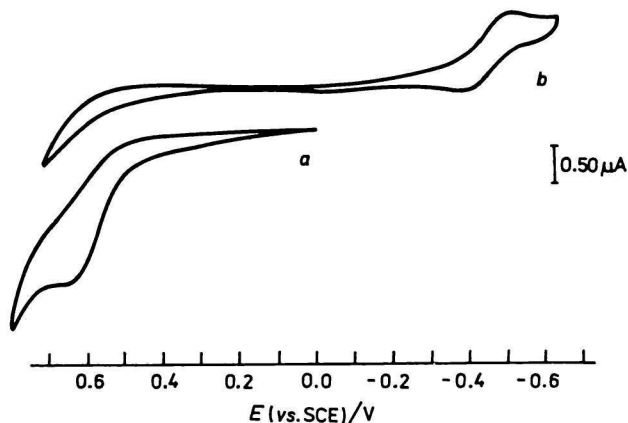

Fig. 1. Cyclic voltammograms of *a*) the ligand L2 and *b*) the complex [Fe(L2)$_3$] formed after adding Fe(NO$_3$)$_3$ to the solution – in methanol solution (1 mol dm^{-3} NaClO$_4$) at a scan rate of 20 mV s^{-1}.

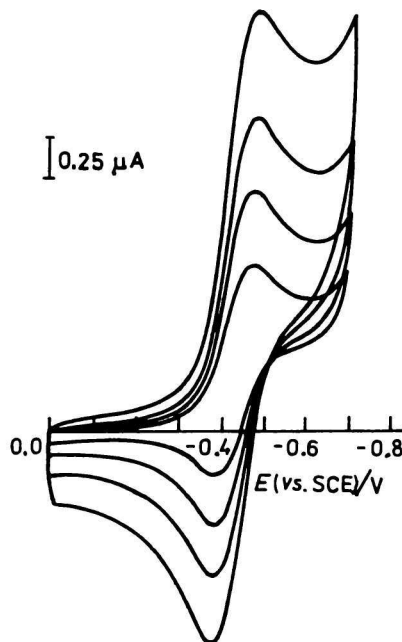**Fig. 2.** Cyclic voltammograms of the [Fe(L5)$_3$] complex in methanol solution (1 mol dm^{-3} NaClO$_4$) at scan rates of 20, 50, 100, and 200 mV s^{-1}.

peak potential, E_{pc} and E_{pa}, respectively, was in the range of 95—110 mV for the scan rate of 50 mV s^{-1}.

The data show the quasi-reversible behaviour for the complexes studied indicating that iron(II) complexes formed upon reduction are structurally not very similar to the initial iron(III) complexes. At our experimental conditions, the reversible couple ferrocenium/ferrocene has a ΔE_p value of 70 mV, which was used as the criterion for electrochemical reversibility. The formal potentials, E_f, were calculated as the average of the cathodic, E_{pc}, and anodic, E_{pa}, peak potentials. The E_f value of the complexes covered the range

Table 1. Electrochemical Properties of the [FeL$_3$] Complexes at the Scan Rate of 50 mV s^{-1}

Ligand(L)/Substituent(R)	E_f/V	ΔE_p/mV	i_{pa}/i_{pc}
Uncomplexed couple Fe^{2+}/Fe^{3+}	−0.83	140	0.64
L1/H	−0.80	95	0.87
L2/CH$_2$OH	−0.70	95	0.94
L3/CH$_2$(CH$_2$)$_7$CH$_3$	−0.70	120	1.00
L4/CH$_2$S$cyclo$C$_6$H$_{11}$	−0.70	100	0.90
L5/CH$_2$N$_3$	−0.69	95	0.90
L6/CH$_2$SCNSC$_6$H$_4$	−0.67	90	0.94
L7/CH$_2$Cl	−0.66	90	0.93

from −0.66 to −0.80 V *vs.* E_f of the redox system Fc$^+$/Fc.

The peak-current ratio, i_{pa}/i_{pc}, ranging from 0.87 to 1.00 at 50 mV s^{-1}, indicates that the iron(II) complexes have different stability in methanol solution, undergoing probably subsequent chemical reactions. In addition, plots of i_p *vs.* $v^{1/2}$ between 20 and 200 mV s^{-1} were linear indicating a diffusion-controlled process.

The E_f values, the peak potential separation, ΔE_p, and the peak-current ratios i_{pa}/i_{pc} obtained from the cyclic voltammograms at 50 mV s^{-1} for complexed and uncomplexed iron are summarized in Table 1.

In order to examine these processes more in detail, cyclic voltammograms were evaluated according to the theory of *Nicholson* and *Shain* [9]. Analysis of voltammograms shows that the studied complexes present a "kinetic case", *i.e.* a homogeneous chemical reaction is coupled to the electrode process. By using appropriate diagnostic criteria (E_{pc}, E_{pa} *vs.* v, i_{pa}/i_{pc} *vs.* v, $i_p/v^{1/2}$ *vs.* v, Table 2) it was qualitatively found that the one-electron reduction of the studied complexes (except [Fe(L3)$_3$]) was followed by a chemical reaction belonging to EC mechanism.

$$[\text{Fe}^{\text{III}}\text{L}_3] + e^- \underset{\text{E}}{\rightleftarrows} [\text{Fe}^{\text{II}}\text{L}_3]^- \underset{\text{C}}{\rightarrow} \text{X}$$
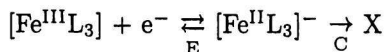
The electrochemical process is not limited to a one-electron transfer, since the reduction of [Fe$^{\text{III}}$L$_3$] yields more or less stable [Fe$^{\text{II}}$L$_3$]$^-$ Thus, the apparent reversibility depends on the stability of [Fe$^{\text{II}}$L$_3$]$^-$, if the potential sweep rate is increased, the decomposition

of [Fe$^{\text{II}}$L$_3$]$^-$ is limited and the peak ratio i_{pa}/i_{pc} increases according to the EC scheme. The electronic delocalization of the ligand increases the stability of [Fe$^{\text{II}}$L$_3$]$^-$ Furthermore, the delocalization of the ligand improves the electron transfer; the peak separation ΔE_p (Table 1) decreases with the delocalization of the ligand.

Quantitative evaluation of the ligand structure effect on the redox potential can be expressed by means of the general equation for the potential shifts with the complexation constants [10]

$$E_f^c = E_f^0 + RT/nF \ln \beta(\text{Fe}^{\text{II}})/\beta(\text{Fe}^{\text{III}})$$

where E_f^c is the observed formal potential, E_f^0 is the formal potential of Fe$^{\text{III}}$/Fe$^{\text{II}}$ [11] in methanol and β represents the complexation constant.

Electrochemical studies reveal a near-reversible, diffusion-controlled behaviour of the [Fe$^{\text{III}}$L$_3$]/[Fe$^{\text{II}}$L$_3$]$^-$ couple at potentials that are different from the uncomplexed Fe$^{\text{III}}$/Fe$^{\text{II}}$ couple in methanol (E_f = −0.83 V *vs.* Fc$^+$/Fc). In comparison with the frée Fe$^{\text{III}}$/Fe$^{\text{II}}$ redox couple the redox potentials of the complexes are more anodic: Fe$^{\text{II}}$ is more complexed than Fe$^{\text{III}}$; β(Fe$^{\text{II}}$) > β(Fe$^{\text{III}}$). When delocalization is introduced on the ligand [12], the anodic shift of the potential produces an increase in the complexation of Fe$^{\text{II}}$ *vs.* Fe$^{\text{III}}$. The potential shift is almost proportional to the ratio of the complexation constants of [Fe$^{\text{III}}$(L)$_3$] and [Fe$^{\text{II}}$(L)$_3$]$^-$ The ratio β(Fe$^{\text{II}}$)/β(Fe$^{\text{III}}$) increases when the delocalization increases, which means that the delocalized ligands are better stabilizers for Fe$^{\text{II}}$. It makes the electrochemical reduction of [Fe$^{\text{III}}$(L)$_3$] to [Fe$^{\text{II}}$(L)$_3$]$^-$ easier.

Besides the thermodynamic influence of the studied ligands, the ligand delocalization probably increases the kinetics of the electron transfer in some cases. The peak separation ΔE_p in cyclic voltammetry (Table 1) decreases from the free (uncomplexed) to the complexed couple Fe$^{\text{III}}$/Fe$^{\text{II}}$.

In summary, this paper deals with the electrochemical properties of six-coordinated iron(III) complexes with the three uninegative bidentate ligands. The ligand determines the relative stability β(Fe$^{\text{II}}$)/β(Fe$^{\text{III}}$) of the studied complexes, which depends on the position and the character of the substituents R and R′ The delocalization properties of the ligand are greater,

Table 2. Dependence of E_{pc}, E_{pa}, i_{pa}/i_{pc}, and $i_{pc}/v^{1/2}$ *vs.* v for the [Fe(L5)$_3$] Complex

v/(mV s^{-1})	E_{pc} /V^a	E_{pa} /V^a	i_{pa}/i_{pc}	$i_{pc}/v^{1/2}$/(μA/mV s^{-1})$^{1/2}$
20	−0.47^5	−0.39	0.85	2.18
50	−0.48	−0.38^5	0.94	2.02
100	−0.48^5	−0.38	1.01	1.85
200	−0.49	−0.37^5	1.08	1.75

a) *vs.* SCE.

when an electron-withdrawing substituent is on the phenoxyl ring, and smaller when the ring is modified with the electron-donating substituent. We can say that the ligand delocalization is obviously a complex function of many factors and in the studied case depends on the electronic properties of the substituents R and R' and their position on the ligand ring.

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