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Electrochemical Characterization of Iron(III)–Glycine–Nitrilotriacetate Mixed Ligand Complexes and Their Stability in Aqueous Solutions*

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Electrochemical characterization of iron(III)–glycine–nitrilotriacetate (iron(III)-Gly-NTA) mixed ligand complexes and determination of their stability constants and retention time in aqueous solutions (I = 0.1 mol dm^{-3} in $NaClO_4$, pH = 8.0±0.1 at 25±1 °C), using differential pulse cathodic voltammetry (DPCV), cyclic voltammetry (CV) and direct current (d.c.) polarography with a static mercury drop electrode (SMDE), were performed. Iron(III) concentrations were varied from 5×10^{-6} to 6×10^{-4} mol dm^{-3}, NTA total concentrations varied from 2×10^{-5} to 1×10^{-3} mol dm^{-3} and glycine total concentrations were 0.2, 0.02 and 0.002 mol dm^{-3}. Iron(III) redox reaction in the mixed ligand system (by the techniques employed) was found to be a one-electron reversible process. At total concentration ratios of 1 : 800 : 2 for iron(III), glycine and NTA, respectively, the iron(III)-Gly-NTA mixed ligand complexes were dissolved and stable (>18 hours) in the aqueous solution. The complexes were formed either by the addition of NTA into the iron(III) and glycine aqueous solution or by the addition of iron(III) to the mixture of glycine and NTA. Under these conditions, iron(III) hydrolysis was highly suppressed. By fitting of experimental data, the following stability constants for mixed ligand complexes, not found in the literature so far, in 0.1 mol dm^{-3} $NaClO_4$ aqueous solution were calculated: for iron(III) log $\beta_1([FeGlyNTA]^{-})$ = 27.23±0.69, log $\beta_2([Fe(Gly)_2NTA]^{2-})$ = 30.29±0.77; for iron(II) log $\beta_1([FeGlyNTA]^{2-})$ = 14.13±0.43 and log $\beta_2([Fe(Gly)_2NTA]^{3-})$ = 18.51±0.51.

Keywords
iron(III)
mixed ligand complexes
nitrilotriacetate (NTA)
glycine
stability constants
voltammetry
aqueous solution

INTRODUCTION

Iron is an essential element, whose key chemical and biological functions involve oxidation/reduction processes and interactions with oxygen[1] of great biogeochemical importance in natural aquatic systems.[2,3] Also, it is one of the most abundant metals in the Earth's crust.[4] However, very low concentrations (< 10^{-9} mol dm^{-3}) of dissolved, mostly iron(III) organic complexes are present in natural waters due to the low solubility of its thermodynamically stable 3+ ionic form.[5,6] Low concentrations of dissolved iron(III) are the reason why the input rate of bioavailable iron must exert a strong influence on oceanic productivity.[7,8] It is therefore very important to determine its chemical speciation as well as concentrations. In the oceanic water column, dissolved iron is mostly complexed with organic matter (>90 %), suggesting that biological processes are limited also by insufficient amounts of available iron.[9,10] Ionic iron should be dissolved during a sufficiently long period of time in

* Dedicated to the memory of the late Professor Marko Branica.

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order to be available for biological growth of various organisms[11–13] (bacteria, phytoplankton, algae, *etc.*).

One of the most utilized and studied iron(III) chelating agents is nitrilotriacetic acid (NTA) and/or its salts.[14–18] Since NTA is a biodegradable molecule (aerobic as well as anaerobic), it is used instead of phosphate as a detergent builder with nontoxic glycine as an intermediary. It is well known from the literature that NTA produces dissolved complexes with transition metals, such as iron(III).[19] There are only a few papers describing the characteristics of the iron(III)-NTA system by using sensitive electrochemical techniques, such as differential pulse cathodic voltammetry (DPCV),[20–22] while potentiometry and cyclic voltammetry have been used in a larger number of papers.[16–18,23–25]

It is known that some naturally occurring substances, *e.g.*, α-amino acids, form complexes with trace metal ions.[26] Thus, it seems desirable to quantitatively estimate the avidity of biologically significant trace metal ions such as iron(III) for complex-forming agents such as glycine.[26–28] Only a few reports deal with the voltammetric analysis of the iron(III)-glycine system in aqueous solutions with a mercury electrode.[21,29] The main reason for the lack of voltammetric experiments is the strong iron(III) hydrolysis capacity, presuming the use of a large excess of glycine in order to enable formation of iron(III) glycine complexes and to obtain voltammetric signals.[21,29]

In natural water systems containing various ligands, mixed ligand complexes are more likely to occur than simple metal-ligand ones.[30] Their quantitative characterization is not an easy task and is not often described in the literature.[31–34] The iron(III)-EDTA-NTA mixed ligand complex was characterized by titration with sodium hydroxide.[31] Mixed ligand complexes were also studied to improve the sensitivity of voltammetric techniques by multiple enhancement of mixed ligands complexes adsorption onto the mercury drop electrode surface, known as synergetic adsorption.[35–37]

In this work, formation of stable iron(III)-Gly-NTA mixed ligand complexes enabled us to control the retention time of dissolved iron(III) by selecting appropriate experimental conditions and to characterize them by means of electrochemical measurements.

EXPERIMENTAL

Equipment

Experiments were performed using a μ-AUTOLAB multimode potentiostat controlled by GPES 4.5, and a General Purpose Electrochemical System software package through a personal computer with a data acquisition routine (ECO Chemie, Utrecht, The Netherlands).

The pH of the solutions was measured with a glass electrode connected to an ATI Orion PerpHecT Meter, model 320 (Cambridge, MA, USA).

Measurements were performed in a 50-cm^3 electroanalytical quartz cell at 25±1 °C. The working electrode was a 303A static mercury drop electrode (SMDE) (EG&G Princeton Applied Research, Princeton, USA) with a modified holder of electrode components.[38] The mercury drop was of medium size, with an area of 1.55 mm^2. An Ag/AgCl electrode with saturated NaCl and a platinum wire were used as reference and counter electrodes, respectively.

Electrochemical techniques applied were differential pulse cathodic voltammetry (DPCV) with the pulse amplitude, a = 25 mV; potential step increment, E_{inc} = 2 mV; time between pulses, t_{int} = 0.2 s; pulse duration, t_p = 0.05 s; cyclic voltammetry (CV) with E_{inc} = 2 mV; scan rate, ν = 0.1 V s^{-1} and direct current polarography (d.c.) with the drop time, t_d = 0.5 s and E_{inc} = 2 mV.

Chemicals and Solutions

Stock solutions of 10^{-2} mol dm^{-3} of $Fe(NO_3)_3 \cdot 9H_20$ (*p.a.*, Kemika, Zagreb, Croatia), 10^{-1} and 10^{-2} mol dm^{-3} of glycine (H_2NCH_2COOH) (Merck, Darmstadt, Germany), 10^{-2} mol dm^{-3} of disodium nitrilotriacetate (Na_2NTA) (Sigma-Aldrich Chemie, Germany), and 7.13 mol dm^{-3} of $NaClO_4$ (*p.a.*, Fluka Chemie, Buchs, Switzerland) were prepared. All chemicals were prepared using Milli-Q water.

Concentrations of dissolved trace metal impurities in the supporting electrolyte ($NaClO_4$), which could be the source of errors, were lowered by potentiostatic electrolysis (reduction) using an EG&G potentiostat model PAR 273. Electrolysis was carried out at the potential of –1.25 V for at least 4 h under an N_2 atmosphere.

By adding diluted *s.p.* HClO4 or *p.a.* NaOH (Merck, Darmstadt, Germany), the pH of solutions was maintained at 8.0±0.1.

RESULTS AND DISCUSSION

Characterization of Iron(III)–Glycine–Nitrilotriacetate Mixed Ligand System

Electrochemical measurements of the dissolved iron(III)-Gly-NTA mixed ligand system in the 0.1 mol dm^{-3} $NaClO_4$ aqueous solution were performed at pH = 8.0±0.1 and 25±1 °C, using DPCV, CV and d.c. polarography. Iron(III) concentrations were varied from 2.5×10^{-5} to 6×10^{-4} mol dm^{-3}, NTA total concentrations varied from 2×10^{-5} to 1×10^{-3} mol dm^{-3} and glycine total concentrations were 0.2, 0.02 and 0.002 mol dm^{-3}.

Figure 1 shows differential pulse voltamograms of iron(III) in a mixture of glycine (0.2 mol dm^{-3}) and NTA (5×10^{-4} mol dm^{-3}). Mixed ligand complex reduction peak currents dependence on iron(III) concentrations are shown in Figure 1 (inset). Basic line (voltamogram 1) represents the solution with both ligands present, without iron(III). It does not contain any reduction peak which implies electrochemical inactivity of these two ligands under the experimental conditions applied. When iron(III) was ad-

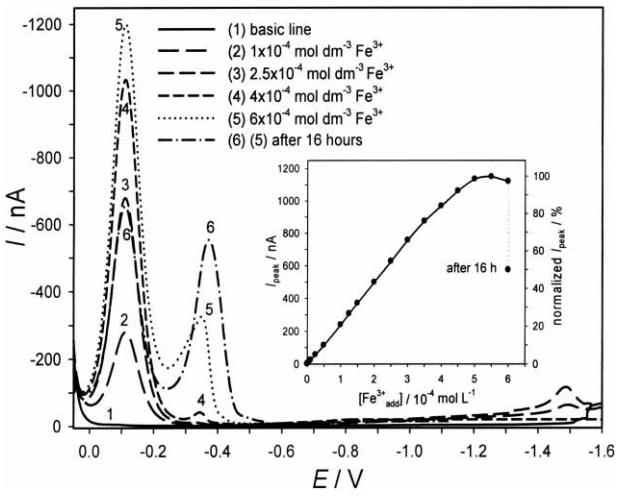

Figure 1. DPC voltamograms; Inset – dependence of iron(III)-Gly-NTA peak currents on added iron(III). 0.2 mol dm^{-3} glycine, 5×10^{-4} mol dm^{-3} NTA, 0.1 mol dm^{-3} $NaClO_4$; pH = 8.0±0.1, E_{inc} = 2 mV, a = 25 mV, t_p = 0.05 s, t_{int} = 0.2 s.

ded, the reduction peak potentials remained constant at –0.112 V, indicating stability of the formed species. These peaks were the response to iron(III) reduction in mixed ligand complexes. Peaks are symmetrical, with identical half-peak widths. On differential pulse voltamograms, measurement of the half-peak width and comparison of its value with the theory is probably the simplest way of assessing the reversibility of the electrode process. Half-peak width values ($w_{1/2}$) of iron(III)-Gly-NTA reduction peaks at –0.112 V in Figure 1 are ≈90 mV, which is, according to the differential pulse voltammetric theory,[39] characteristic of the one-electron reversible reduction process at the mercury drop electrode. Applying small pulse amplitudes (a < 100 mV), the $w_{1/2}$ amount to 3.52 RT/nF (at 25 °C: $w_{1/2}$ = 90.4/n mV, n = number of electrons exchanged). Half-peak widths larger than 90.4/n mV indicate quasi-reversible or irreversible electrode processes. The mixed ligand complexes reduction peak currents dependence on iron(III) concentration is linear until the iron(III) concentration reaches 3×10^{-4} mol dm^{-3} (Figure 1, inset). Above this iron(III) concentration, the slope decreases until it reaches a plateau at the iron(III) concentration of 5×10^{-4} mol dm^{-3}. It can be assumed that below 3×10^{-4} mol dm^{-3} of iron(III), free species concentrations of both ligands are sufficient to bind dissolved iron(III) to the stable, electrochemically reversible mixed ligand complexes. Above 3×10^{-4} mol dm^{-3} of added iron(III), the free ligand concentration is insufficient for complete binding of iron(III), resulting in a slope decrease. Appearance of reduction peaks at ≈ –0.38 V, which can be attributed to the reduction electrode process of iron(III)-hydroxide complexes (Figure 1, voltamograms 4–6). When the iron(III) concentration exceeds free ligand concentrations, the hydrolysis process starts. After 16 hours (Figure 1, voltamogram 6) from the last iron(III) addition

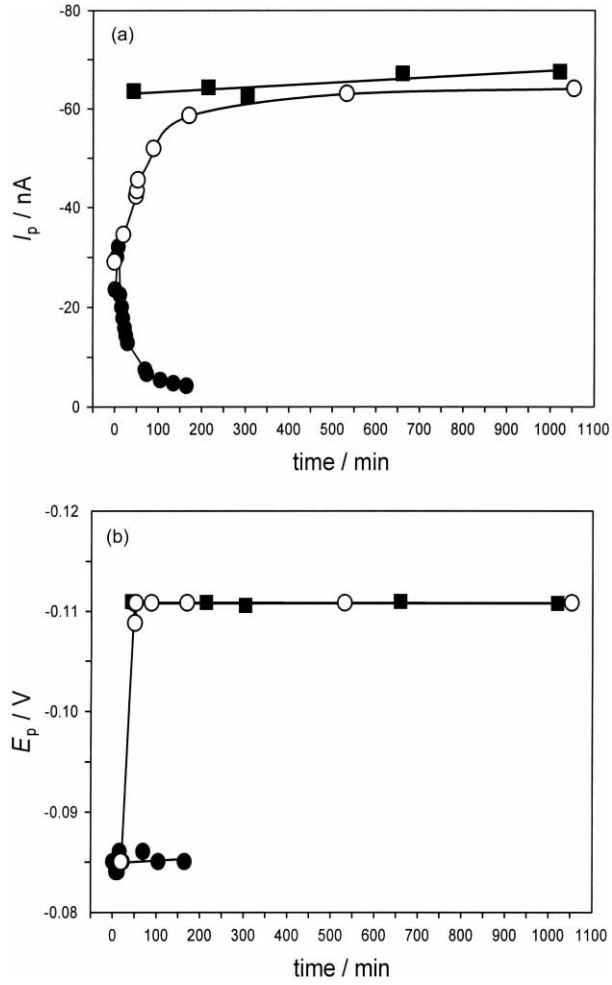

Figure 2. Dependences of reduction peak currents (a) and reduction peak potentials (b) on the time of experiment. Filled circles: iron(III) + glycine; empty circles: iron(III) + glycine, NTA added after 40 min; squares: iron(III) + glycine + NTA; c(Fe^{3+}) = 2.5×10^{-5} mol dm^{-3}; c(Gly) = 0.2 mol dm^{-3}; c(NTA) = 5×10^{-4} mol dm^{-3}; c($NaClO_4$) = 0.1 mol dm^{-3}; pH = 8.0±0.1; technique DPCV; E_{inc} = 2 mV; a = 25 mV; t_p = 0.05 s; t_{int} = 0.2 s.

(6×10^{-4} mol dm^{-3}), the mixed ligand complex reduction current dropped almost to half its value from voltamogram 5, while the iron(III) hydroxide reduction current increased to 512 nA. By summing up the iron(III) mixed ligand complex (590 nA) and iron(III) hydroxide (512 nA) current values (Figure 1, voltamogram 6), one obtains approximately 1100 nA, practically matching the current value of the mixed ligand complex immediately after the last iron(III) addition (Figure 1, voltamogram 5). Peaks at around –1.5 V in Figure 1 are a result of the two-electron reduction process of iron(II) at the mercury drop electrode. Iron(II) was formed in the bulk of solution from iron(III) one-electron reduction, and will be the subject of further studies.

Figure 2 shows experiments in three different perchlorate-water solutions: only glycine and iron (filled circles), glycine, NTA and iron (squares) and NTA added after 40 min into the glycine-iron mixture (empty cir-

cles). Figure 2a represents the iron(III) mixed ligand complex reduction current dependences on the experimental time. Iron(III) concentration was 2.5×10^{-5} mol dm^{-3}, NTA 5×10^{-4} mol dm^{-3} with 0.2 mol dm^{-3} of glycine in 0.1 mol dm^{-3} $NaClO_4$ at pH = 8.0±0.1. Filled circles in Figure 2a show reduction currents of the Fe^{III} glycine complex. Only a few minutes after iron(III) addition, hydrolysis progressed. Iron(III) showed a strong tendency towards hydrolysis[21,29] at glycine concentrations ≤ 0.2 mol dm^{-3}. Approximately 3 hours after adding iron(III) into the glycine solution, reduction signals disappeared due to complete iron(III) hydrolysis. In Figure 2a, empty circles show Fe^{III} reduction current values in the experiment when NTA was added about 40 minutes after equilibration of the iron(III) and glycine mixture. Before addition of NTA, the Fe^{III}-glycine complex was formed and after NTA addition, successive formation of mixed iron(III)-glycine-NTA complexes took place. After approximately 8 hours, the mixed ligand complexes current reaches the maximum value. It is clear that the presence of both ligands, glycine and NTA, stabilizes dissolved iron(III) in the solution, maintaining the peak current (Figure 2a, empty circles) constant for more than 18 hours. When NTA was added into the glycine aqueous solution prior to addition of iron(III) ions, the Fe^{III} mixed ligand complex was formed instantaneously (Figure 2a, squares). The presence of both ligands in the aqueous solution results in formation of the highly stable iron(III)-Gly-NTA complex that keeps iron(III) in the solution.

Figure 2b shows the iron(III) reduction peak potential dependences on the time of experiment from Figure 2a. Full circles in Figure 2b show the iron(III) reduction peak potentials in the glycine complex. Constant reduction potentials throughout the experiment at –0.085 V indicate that the system does not change. In another experiment, after about 40 minutes NTA was added into the iron(III) glycine solution (Figure 2b, empty circles) and the reduction peak potential shifted by 27 mV in the negative direction. This indicates the formation of stable iron(III)-Gly-NTA mixed ligand complexes. These peak potentials were constant at –0.112 V after the NTA addition. The iron(III) glycine complex tendency towards hydrolysis was suppressed by the NTA addition (Figure 2b, empty circles). Simultaneous addition of both ligands, glycine and NTA, into the electroanalytical cell prior to iron(III) ions results in reduction peak potentials at about –0.112 V (squares, Figure 2b), which did not change during the experiment. It is presumed that the mixed ligand system was formed immediately after the iron(III) ions addition.

Characterization of the iron(III) redox mechanism at the mercury drop electrode was carried out using cyclic voltammetry. Iron(III) concentrations were 2.5×10^{-5} and 5×10^{-5} mol dm^{-3}, glycine 0.2 mol dm^{-3} and NTA 5×10^{-4} and 1×10^{-3} mol dm^{-3} in 0.1 mol dm^{-3} $NaClO_4$ at pH = 8.0±0.1. On cyclic voltamograms of iron(III) in the glycine solution, a difference of about 60 mV between the reduction (negative) and the oxidation (positive) peak currents[39,40] was recorded. This indicates the reversible nature of the iron(III) one-electron redox process in iron(III)-glycine complexes[21,29] (Figure 3, voltamogram 1). The same happens in the experiment with the mixed ligand system[21] iron(III)-Gly-NTA (Figure 3, voltamogram 2). Voltamograms 1 and 2 show two signals on the negative (reduction) side and only one signal on the positive (oxidation) side. The reduction signal in voltamogram 1 at –0.125 V is the response to the iron(III) one-electron reduction in the glycine complex. Its corresponding positive (oxidation) peak lies at –0.065 V, with a difference of 60 mV between them, indicating the reversible nature of iron(III) glycine reduction. The reduction peak at –0.38 V (voltamogram 1) corresponds to the iron(III) one-electron reduction of hydroxide complexes, implying the strong tendency of iron(III) to hydrolyze. No oxidation peak is registered on the positive side of the voltamogram due to the formation of poorly soluble iron(III) oxyhydroxides[5,8,41] and their irreversible electrode reduction, described earlier.[21,22] In voltamogram 2 (one-electron process of iron(III) in the mixed ligand complex), the reduction peak at –0.156 V has the corresponding oxidation signal at –0.097 V with almost 60 mV difference between them. This also shows the reversible character of iron(III) mixed ligand complexes. The peak at about –0.40 V corresponds to the one-electron reduction of the iron(III) hydroxide and this process did not have an oxidation signal, indicating its irreversible character. The iron(III)-NTA system (Figure 3, voltamogram 3) showed the quasi-reversible reduction nature. Quasi-reversibility of the iron(III)-NTA reduction was also pointed out earlier.[16,18,21,22,25] The difference between reduction and oxidation peaks in voltamogram 3 was about 90 mV (–0.25 V for reduction and –0.16 V for oxidation peak), confirming the quasi-reversible reduction character.[39,40] The iron(III)-NTA reduction peak has an asymmetrical shape. This is caused by the unstable nature of the iron(III)-NTA system with several species involved, such as iron(III)-$(NTA)_x$-$(OH)_y$ mixed ligand system, iron(III)-$(NTA)_x$ complexes and binuclear iron(III)-NTA, described earlier.[16,18,22] Voltamogram 3 in Figure 3 did not reveal the iron(III) hydroxide reduction peak, which was overlapped by the asymmetrical and wide (iron(III)-NTA) reduction signal.

Figure 4 shows the normalized d.c. polarogram of the iron(III)-Gly-NTA reduction and the logarithmic dependence of reduction currents on the potential (inset). The Fe^{III} concentration was 2×10^{-4} mol dm^{-3}, NTA 5×10^{-4} mol dm^{-3} with 2×10^{-2} mol dm^{-3} glycine in 0.1 mol dm^{-3} $NaClO_4$ at pH = 8.0±0.1. Circles represent original polarographic data while the full line shows a simulated polarogram[42,43] for the reversible one-electron iron(III)

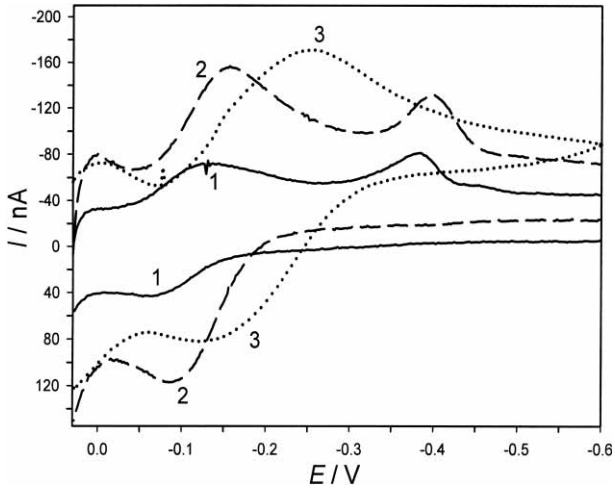

Figure 3. Cyclic voltamograms in 0.1 mol dm^{-3} $NaClO_4$; pH = 8.0±0.1; E_{inc} = 2 mV; scan rate, v = 0.1 V s^{-1}: (1) 2.5×10^{-5} Fe^{3+} + 0.2 mol dm^{-3} glycine; (2) 5×10^{-5} mol dm^{-3} Fe^{3+} + 0.2 mol dm^{-3} glycine + 1×10^{-3} mol dm^{-3} NTA; (3) 5×10^{-5} mol dm^{-3} Fe^{3+} + 5×10^{-4} mol dm^{-3} NTA.

reaction. Excellent matching of the theoretical model (line) and the measured polarogram (circles) confirms the reversible character of iron(III) reduction in the mixed ligand complex with glycine and NTA, as confirmed by cyclic voltammetry measurements (Figure 3). Logarithmic analysis of the polarogram is suitable for testing the system reversibility[39,40,42,43] as well as for determining the number of electrons involved in an electrode reaction. Logarithmic analysis of the polarogram gives us the slope value of 58.8±0.1 mV. Dependence of the number of electrons on the slope for the reversible electrode reaction can be expressed as follows: slope = (0.059 V) / n, where n is the number of electrons involved in an electrode half-reaction (in this case n = 1). It clearly shows that the oxidation/reduction reaction of the iron(III)-Gly-NTA mixed ligand complexes is a one-electron, reversible electrode reaction.

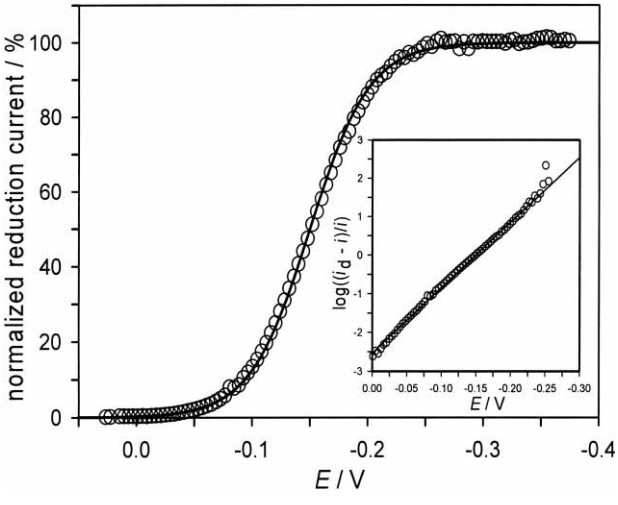

Figure 4. Normalized d.c. reduction polarogram of Fe^{3+}-Gly-NTA system; Circles – experimental polarogram, solid line – simulated model for reversible electrode reaction, inset – dependence of the current logarithm on potential; c(Fe^{3+}) = 2×10^{-4} mol dm^{-3}; 2×10^{-2} mol dm^{-3} glycine; 5×10^{-4} mol dm^{-3} NTA; 0.1 mol dm^{-3} $NaClO_4$; pH = 8.0±0.1; t_d = 0.5 s; E_{inc} = 2 mV.

Determination of Stability Constants for the Iron(III)–Glycine–Nitrilotriacetate Mixed Ligand System

As the reduction reaction of iron(III) in a mixed ligand solution is proven to be reversible and it is assumed that iron(III) in that solution forms mixed ligand complexes, the procedure for their stability constants determination was carried out. Experiments with 5×10^{-5} mol dm^{-3} of iron(III) and total ligand concentration combinations ($[NTA]_{tot}$ of 0–5×10^{-4} mol dm^{-3}, $[Gly]_{tot}$ 0.002, 0.02 and 0.2 mol dm^{-3} at pH = 8.0±0.1 in 0.1 mol dm^{-3} $NaClO_4$) resulted in the peak potential shifts as given in Table I.

TABLE I. DPCV peak potentials (E_p/V) of iron(III) (5×10^{-5} mol dm^{-3}) reduction in 0.1 mol dm^{-3} $NaClO_4$ solution at pH = 8.0±0.1 with various glycine and NTA concentrations

$[Gly]_{tot}$ / mol dm^{-3}:	0.002	0.02	0.2
10^4 · $[NTA]_{tot}$ / mol dm^{-3}		E_p / V	
0.0	–	–	–0.085
0.2	–0.152	–0.129	–0.103
0.5	–0.164	–0.131	–0.113
0.8	–0.168	–0.131	–0.115
1.2	–0.167	–0.131	–0.117
2.0	–0.166	–	–0.117
5.0	–0.154	–0.135	–0.116

The potential of the iron(III) one-electron reversible redox system is given by the expression:[44]

$$E_{1/2} = E^\circ - \frac{RT}{(3-2)F} \ln \frac{[Fe^{2+}]}{[Fe^{3+}]} \qquad (1)$$

where $E_{½}$ is the half-wave reversible potential, which is calculated from the equation:[39] $E_{½} = E_p + a/2$ (E_p is taken from Table I, a is the pulse amplitude); E° (0.77 V) is the standard potential for the one-electron reduction of the free, non-complexed Fe^{3+} ions *vs.* hydrogen electrode.[45] It was recalculated to the Ag/AgCl saturated reference electrode (used in the experiment), and reads 0.573 V; R = 8.314 J K^{-1} mol^{-1}; F = 96 484.6 C mol^{-1} and T = 298.15 K. The shift of the free Fe^{3+} ions standard potential due to the ionic strength effect (standard potential is given for the ionic strength 0) was estimated to fall within the uncertainty of the peak potential determination and was not calculated as another term in the error propagation formula.

Experimental data points were fitted to various potentially possible models:

$$E_{1/2} = E^\circ - \frac{RT}{F} \ln \frac{1+\sum_{i=1}^{n} \beta_{i,\mathrm{III}} [\mathrm{Gly}]^i [\mathrm{NTA}]}{1+\sum_{j=1}^{n} \beta_{j,\mathrm{II}} [\mathrm{Gly}]^j [\mathrm{NTA}]} = E^\circ - \frac{RT}{F} \ln \frac{F_{0,3}}{F_{0,2}} \quad (2)$$

where $\beta_{i,\mathrm{III}}$ (i = 1, 2,..) and $\beta_{j,\mathrm{II}}$ (j = 1, 2,…) are cumulative stability constants for iron(III)-Gly-NTA complexes and iron(II)-Gly-NTA complexes, respectively. The following constants were used:[46,47] for glycine log K(HL) = log ([HL]/[L^-][H^+]) = 9.54 where HL is $C_2H_5NO_2$, log K(H_2L^+) = log ([H_2L^-]/[HL][H^+]) = 2.39; for NTA: log K_1 = 9.84, log K_2 = 2.52, log K_3 = 1.81 and log K_4 = 1. Since, the condition of excess ligand is not fulfilled for NTA, prior to fitting, the free ligand concentration was calculated from the mass balance equations, taking into account all the known stability constants of iron with glycine,[21,29] NTA[21,22] and hydroxides,[46] and with the stability constants estimations for mixed ligand complexes.

The fitting program was designed in Microsoft® Excel 2002 for fitting in three dimensions with two independent variables ($\mathrm{Gly_{free}}$ and $\mathrm{NTA_{free}}$) *vs*. ΔE. The results of fitting to the model with two iron(III) complexes and two iron(II) complexes were found to be the best. Fitting models presented in two dimensions by solid lines and experimental points presented by symbols (triangles –0.2, circles –0.02 and filled circles –0.002 mol dm^{-3} of glycine) are shown in Figure 5, proposing the following stability constants:

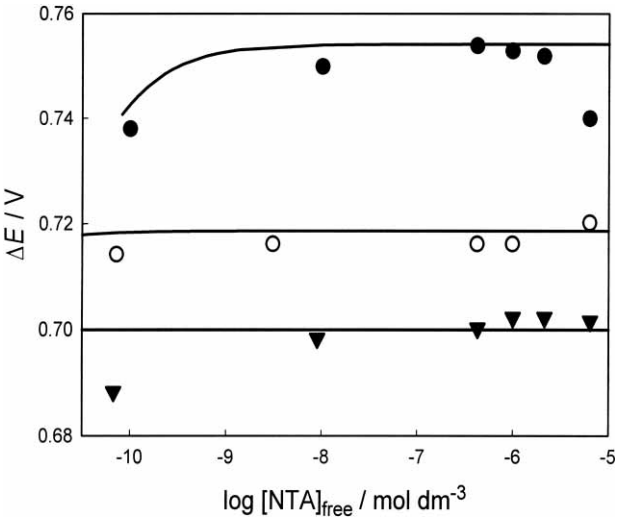

Figure 5. Dependences of ΔE on log $[\mathrm{NTA}]_{\mathrm{free}}$ for the calculated stability constants obtained by a single three dimensional fitting – solid lines; experimental points for total glycine concentrations in mol dm^{-3}: 0.2 – triangles, 0.02 – circles, 0.002 – filled circles.

For iron(III) complexes:

$$\log \beta_1 = \frac{[\mathrm{FeGlyNTA}^-]}{[\mathrm{Fe}^{3+}][\mathrm{Gly}^-][\mathrm{NTA}^{3-}]} = 27.23 \pm 0.69 \quad (3)$$

$$\log \beta_2 = \frac{[\mathrm{Fe(Gly)_2NTA}^{2-}]}{[\mathrm{Fe}^{3+}]([\mathrm{Gly}^-])^2[\mathrm{NTA}^{3-}]} = 30.29 \pm 0.77 \quad (4)$$

and for iron(II) complexes:

$$\log \beta_1 = \frac{[\mathrm{FeGlyNTA}^{2-}]}{[\mathrm{Fe}^{2+}][\mathrm{Gly}^-][\mathrm{NTA}^{3-}]} = 14.13 \pm 0.43 \quad (5)$$

$$\log \beta_2 = \frac{[\mathrm{Fe(Gly)_2NTA}^{3-}]}{[\mathrm{Fe}^{2+}]([\mathrm{Gly}^-])^2[\mathrm{NTA}^{3-}]} = 18.51 \pm 0.51 \quad (6)$$

where ± values are the standard errors obtained by taking into account the propagation of errors due to the peak potential read out and fitting uncertainties of each parameter. The obtained high values of the stability constants are in accordance with the disappearance of the iron(III)-NTA reduction peak, whose stability constant is three orders of magnitude lower, and also with successful competition with iron(III) hydroxo complexes that without the presence of the mixed ligand complexes rapidly precipitate and eliminate iron from the solution.

CONCLUSIONS

The iron(III)-Gly-NTA mixed ligand complexes in a 0.1 mol dm^{-3} $NaClO_4$ aqueous solution at pH = 8.0±0.1 and 25±1 °C using differential pulse cathodic voltammetry (DPCV), cyclic voltammetry (CV) and direct current (d.c.) polarography, have been characterized. Iron(III) concentrations were varied from 5×10^{-6} to 6×10^{-4} mol dm^{-3}, NTA total concentrations varied from 2×10^{-5} to 1×10^{-3} mol dm^{-3} and glycine total concentrations were 0.2, 0.02 and 0.002 mol dm^{-3}.

In the above mentioned concentration ranges, new dissolved mixed ligand complexes were formed either by addition of NTA into the solution with iron(III) and glycine or by the addition of iron(III) into the glycine and NTA mixture. They express fast equilibration, stability and retention in the soluble phase during the experiment (>18 hours for total iron(III), glycine and NTA concentration ratios of 1 : 800 : 2, respectively).

Reduction of iron(III) in mixed ligand complexes shows the one-electron reversible character, like the iron(III) reduction in glycine complexes, while the iron(III) reduction in complexes with NTA only exhibits the quasi-reversible one-electron electrode reaction.

By fitting of experimental data, the following stability constants for iron(III) mixed ligand complexes, not reported in the literature so far, in 0.1 mol dm^{-3} $NaClO_4$ aqueous

solution, were calculated: for iron(III) log $\beta_1([FeGlyNTA]^-)$ = 27.23±0.69, log $\beta_2([Fe(Gly)_2NTA]^{2-})$ = 30.29±0.77; for iron(II) log $\beta_1([FeGlyNTA]^{2-})$ = 14.13±0.43 and log $\beta_2([Fe(Gly)_2NTA]^{3-})$ = 18.51±0.51.

Further experiments are foreseen to examine the bioavailability of these and analogous systems in model and natural aquatic systems.

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SAŽETAK

Elektrokemijska karakterizacija miješanih kompleksa željeza(III) s glicinom i nitrilotriacetatom i njihova stabilnost u vodenim otopinama

Vlado Cuculić i Ivanka Pižeta

Elektrokemijski su karakterizirani miješani kompleksi željeza(III) s glicinom i nitrilotriacetatom (Fe^{III}GlyNTA), te su određene njihove konstante stabilnosti i vrijeme zadržavanja u vodenim otopinama (I = 0,1 mol dm^{-3} u $NaClO_4$, pH = 8,0±0,1 pri 25±1 °C) diferencijalnom pulsnom katodnom voltametrijom (DPKV), cikličkom voltametrijom (CV), te polarografijom s izravnim uzorkovanjem struje na elektrodi s visećom živinom kapi. Koncentracije željeza(III) mijenjane su od 5×10^{-6} do 6×10^{-4} mol dm^{-3}, ukupne koncentracije NTA od 2×10^{-5} do 1×10^{-3} mol dm^{-3}, dok su ukupne koncentracije glicina bile 0,2, 0,02 i 0,002 mol dm^{-3}. Redoks reakcija željeza(III) u sustavu miješanih liganada (uporabljenim tehnikama) bila je jednoelektronski reverzibilni proces. Pri omjeru totalnih koncentracija 1 : 800 : 2 (željezo : glicin : NTA), Fe^{III}GlyNTA kompleksi su otopljeni i stabilni (>18 sati) u vodenoj otopini. Kompleksi su formirani kako dodatkom NTA u vodenu otopinu željeza(III) i glicina tako i dodatkom željeza(III) u smjesu glicina i NTA. Pod ovim uvjetima hidroliza željeza(III) je u većoj mjeri spriječena. Primjenom eksperimentalnih podataka izračunate su konstante stabilnosti kompleksa miješanih liganada u 0,1 mol dm^{-3} $NaClO_4$, koje do sada nisu opisane u literaturi: za željezo(III) log β_1([FeGlyNTA]$^-$) = 27,23±0,69 i log β_2([Fe(Gly)$_2$NTA]$^{2-}$) = 30,29±0,77; za željezo(II) log β_1([FeGlyNTA]$^{2-}$) = 14,13±0,43 i log β_2([Fe(Gly)$_2$NTA]$^{3-}$) = 18,51±0,51.