VOLTAMMETRY OF DISSOLVED IRON(III) - NITRILOTRIACETATE - HYDROXIDE SYSTEM IN WATER SOLUTION

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ABSTRACT

The investigation of the dissolved iron(III) - nitrilotriacetate - hydroxide system in the water solution (I = 0.1 mol L^{-1} in $NaClO_4$; pH = 8.0±0.1) using differential pulse cathodic votammetry, cyclic voltammetry, and sampled direct current (d.c.) polarography, was carried out on a static mercury drop electrode (SMDE). The dissolved iron(III) ion concentrations varied from 2.68×10^{-6} to 6×10^{-4} mol L^{-1} and nitrilotriacetate concentrations were 1×10^{-4} and 5×10^{-4} mol L^{-1}. By deconvoluting of the overlapped reduction voltammetric peaks using Fourier transformation, four relatively stable, dissolved iron(III) complex species were characterized, as follows: $[Fe(NTA)_2]^{3-}$, mixed ligand complexes $[FeOHNTA]^-$ and $[Fe(OH)_2NTA]^{2-}$, showing a one-electron quasireversible reduction, and binuclear diiron(III) complex $[NTAFeOFeNTA]^{2-}$, detected above 4×10^{-4} mol L^{-1} of the added iron(III) ions, showing a one-electron irreversible reduction character. The calculations with the constants from the literature were done and compared with the potential shifts of the voltammetric peaks. Fitting was obtained by changing the following literature constants: log $\beta_2([Fe(NTA)_2]^{3-})$ from 24 to 27.2, log $\beta_1([FeNTA]^-)$ from 8.9 to 9.2, log $\beta_2([Fe(NTA)_2]^{4-})$ from 11.89 to 15.7 and log $\beta_2([Fe(OH)_2NTA]^{3-})$ from 15.63 to 19. The determination of the electrochemical parameters of the mixed ligand complex $[FeOHNTA]^-$, such as: transfer coefficient (α), rate constant (k_s) and formal potential ($E^{0\prime}$) was done using a sampled d.c. polarography, and found to be 0.46±0.05, 1.0±0.3 $\times10^{-3}$ cm s^{-1}, and -0.154±0.010 V, respectively. Although known previously in the literature, these four species have now for the first time been recorded simultaneously, i.e. proved to exist simultaneously under the given conditions.

Keywords: iron(III), nitrilotriacetate, hydroxide, speciation, voltammetry, water solution.

INTRODUCTION

Iron is one of the most abundant elements in the earth's crust. However, very low concentrations ($< 10^{-9}$ mol L^{-1}) of a dissolved iron(III) organic complexes are present in natural waters because of a low solubility of its thermodynamicaly stable +3 oxidation state [1-3]. A dissolved iron(III) as an organic complex, is very important for a large variety of the biological and chemical processes in natural waters [4,5]. One of the most utilized and studied iron(III) chelating agents is a nitrilotriacetic acid and/or its salts [6-10]. A relatively high level of NTA concentration in the environment is a result of the industrial and agricultural activites. Since NTA is a biodegradable molecule (aerobic as well as anaerobic), it is used instead of phosphate as a detergent builder [11,12] with an untoxic glycine as an intermediary. It is well known from the literature that NTA produces the dissolved, stable complexes with the transition metals, hence iron(III) [13,14]. The application of the iron(III) - NTA complexes in medicine has been investigated, particularly for in vitro biophysical studies utilizing Fe(III) as donors or buffers in order to prevent hydrolysis and precipitation of the iron hydroxides and oxides at a physiological pH [15,16]. An aqueous solution of the Fe(III) chelated with particular aminopolycarboxilic acids, such as a nitrilotriacetic acid (NTA), an ethylenediaminetetraacetic acid (EDTA) and a diethylenetriaminepentaacetic acid (DETPA), efficiently oxidizes the hydrosulfide ion into the elemental sulfur in the desulfurization of fuel gases at pH 8.0 to 8.5 [17]. The stability of the Fe^{3+} - NTA complexes has been employed in the investigations of a catalytic systems in the trace metal analysis [14]. Furthermore, an alkaline range (pH = 8 - 9) with a relatively high iron(III) - NTA concentrations (above 10^{-4}

mol L^{-1}), allows a formation of an oxo-bridged dinuclear iron(III) complexes which are very important in the chemistry of the dioxygen activations [1,8,9,18-20]. The hydrolysis of iron(III) is also very extensive at these pH values [1,3].

A large majority of the investigations were carried out using the spectroscopic methods [8,10], while a cyclic voltammety and potentiometry were the most used electrochemical methods [8,9,17,19,20]. Very few papers published elsewhere, describe the investigations of the iron(III) - NTA system using other, more sensitive electrochemical methods, such as DPCV, which could offer a help in characterizing the system [14].

The definition of the iron(III) chelate system with the NTA and hydroxide has a problem because doubts are raised about the iron(III) complex species present in equilibrium under various experimental conditions, especially at the physiological and seawater pH of around 7.2 and 8.1, respectively. In order to shed some light on the speciation of the iron(III) - NTA - OH system in model water solution, we applied various voltammetric methods and the results of the appropriate electrochemical experiments were compared.

EXPERIMENTAL

Equipment

The experiments were performed using an µAUTOLAB multimode polarograph controlled by GPES 4.5, General Purpose Electrochemical System software package through a IBM compatible personal computer with a data acquisition routine (ECO Chemie, Utrecht, The Netherlands). The software package GPES 4.5 runs with the Microsoft Windows operating system.

The pH of the solutions was measured with the glass electrode connected to an Orion Research pH meter (Cambridge, MA, USA).

The measurements were performed in an electroanalytical quartz cell. The working electrode was a 303A static mercury drop electrode (SMDE) (EG&G Princeton Applied Research, Princeton, USA) with the modified holder of the electrode components [21]. The size of the mercury drop was medium, with area of 1.55 mm^2. An Ag/AgCl electrode with a saturated NaCl, and a platinum wire, were used as reference and counter electrodes, respectively. Prior to electrochemical measurements, the solutions were deaerated by bubbling with an extra pure nitrogen for about 15 minutes.

The electrochemical techniques used were a differential pulse cathodic voltammetry (DPCV), a cyclic voltammetry (CV), and a direct current polarography (d.c.), applied under the selected conditions of an initial potential (E_i), a final potential (E_f), a pulse amplitude (A), a potential step increment (E_{inc}), a time between pulses (t_{int}), a pulse duration (t_p), a drop time (t_d) and a scan rate (v).

Chemicals and solutions

The stock solutions of a 10^{-2} mol L^{-1} of $Fe(NO_3)_3 \times 9H_20$ (p.a., Kemika, Zagreb, Croatia), a 10^{-1} and a 10^{-2} mol L^{-1} of disodium nitrilotriacetate (Na_2NTA) (Sigma-Aldrich

Chemie, Steinheim, Germany) and a 7.13 mol L^{-1} of the $NaClO_4$ (p.a., Fluka Chemie, Buchs, Switzerland) were prepared. All the chemicals used were prepared with a bidistilled, Milli-Q water.

The solution of a 7.13 mol L^{-1} $NaClO_4$ was purified for about 5 hours on a mercury pool electrode at the constant reduction potential of -1.3 V vs. Ag/AgCl under the nitrogen atmosphere. Prior to electrolysis, the solution (7.13 mol L^{-1}) was pretreated overnight with an active carbon and filtered through a 0.22 Millipore filters (Millipore corp., Bedford, USA).

The pH of the solutions was maintained by the addition of a dilluted s.p. $HClO_4$ or a p.a. NaOH (Merck, Darmstadt, Germany).

RESULTS AND DISCUSSION

The electrochemical measurements of the redox system Fe(III)-NTA-OH were performed in a model solution of a 0.1 mol L^{-1} $NaClO_4$ (I = 0.1 mol L^{-1}) at pH = 8.0±0.1. Various electrochemical techniques were used, such as: a differential pulse cathoding voltammetry (DPCV), a cyclic voltammetry (CV) and a sampled d.c. polarography. The dissolved Fe(III) ion concentrations varied from 2.68×10^{-6} to 6×10^{-4} mol L^{-1} and the nitrilotriacetate concentrations were 1×10^{-4} and 5×10^{-4} mol L^{-1}.

DPC voltammetry

Fig. 1 illustrates the DPC voltammograms of a model solution with nitrilotriacetate (5×10^{-4} mol L^{-1}) titrated with the iron(III) solution. Until the concentration level of iron(III) reaches 5×10^{-5} mol L^{-1}, the reduction peaks of the Fe(III)-NTA redox system are regular in shape at the potential of about -0.16 V vs. Ag/AgCl electrode. Subsequent additions of iron(III) to the NTA solution result in the appearance of a "shoulder" on the positive side of the peak. The "shoulder" maintains its reduction potential at about -0.1 V during the whole titration time, and takes shape of a regular voltammetric peak as the iron(III) concentration increases. The higher peak shifts towards the negative reduction potentials reaching the final position at about -0.34 V with a 4.5×10^{-4} mol L^{-1} of the added iron(III). This reduction peak also increases during the titration becoming constant at a 5×10^{-4} mol L^{-1} of the added Fe(III). At the 4×10^{-4} mol L^{-1} (voltammogram 8) of the added Fe(III), a new peak appears at the reduction potential of about -0.56 V reaching the maximum value at 5.5×10^{-4} mol L^{-1} (voltammogram 11) of the metal added. Since the two more positive reduction peaks overlapped (Fig. 1), they were separated by a deconvolution [22,23] in order to distinguish between their reduction potentials and the reduction current values, using the Fourier transform with the following parameters: n = 0.9; Boxcar filter with $\omega_o = 20/T_o$, (T_o = 1.024 V), where n represents the width of the deconvolution function.

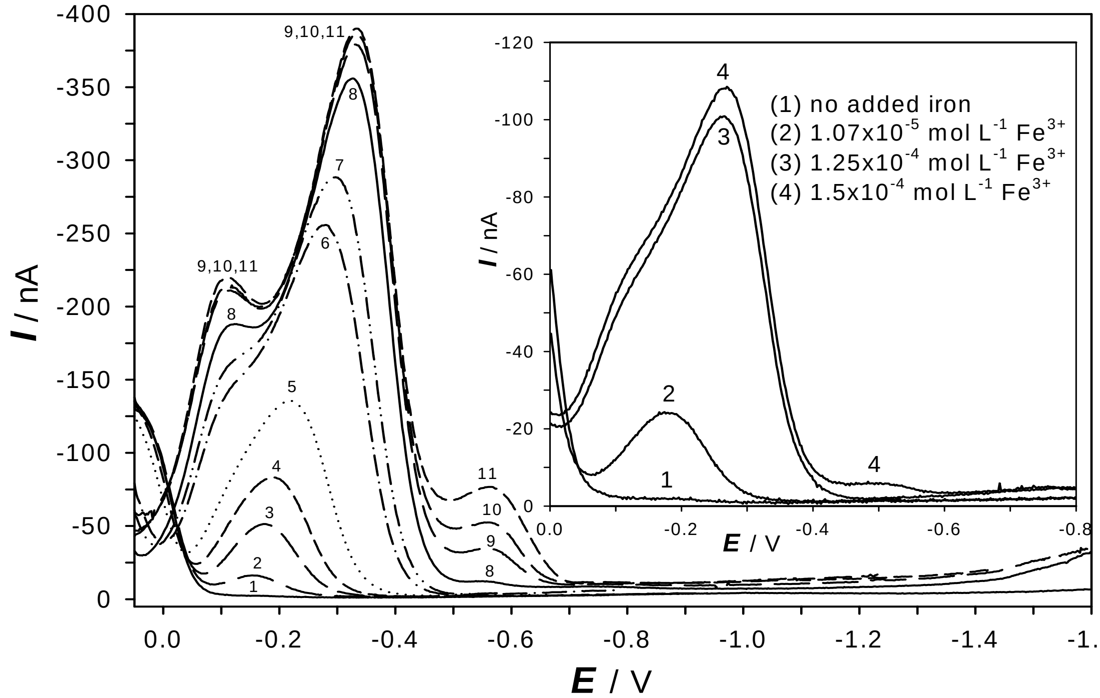

Fig. 1 DPC voltammograms of Fe^{3+} - NTA system: NTA titrated with Fe^{3+}. 5×10^{-4} mol L^{-1} NTA; 0.1 mol L^{-1} $NaClO_4$; pH = 8.0±0.1; ΔE = 2 mV; a = 25 mV; t_{puls} = 0.05 s; Δt_{puls} = 0.2 s. $c(Fe^{3+}$ /mol $L^{-1})$ = (1) 0; (2) 5.4×10^{-6}; (3) 2.5×10^{-5}; (4) 5×10^{-5}; (5) 1×10^{-4}; (6) 2.5×10^{-4}; (7) 3×10^{-4}; (8) 4×10^{-4}; (9) 4.5×10^{-4}; (10) 5×10^{-4}; (11) 5.5×10^{-4}. **Inset**: DPC voltammograms of Fe^{3+} - NTA system: NTA titrated with Fe^{3+}. 1×10^{-4} mol L^{-1} NTA; 0.1 mol L^{-1} $NaClO_4$; pH = 8.0±0.1; ΔE = 2 mV; a = 25 mV; t_{puls} = 0.05 s; Δt_{puls} = 0.2 s.

The deconvoluted peaks and their reduction potentials as well as the reduction current values presented in the arbitrary units [22,23], are shown in Fig. 2, A and B, respectively. One can easily observe the constant reduction potentials of a more positive peak at about -0.09 V. This peak is probably a result of the one-electron reduction of the complex $[Fe(NTA)_2]^{3-}$. This complex represents about 20% of the total iron in the solution at the beginning of the titration under the conditions described [8,9]. When the NTA concentrations are the same or in excess of the Fe(III) concentrations, iron is completely complexed and Fe(III) hydrolysis is well suppressed. At a pH = 8, the reduction peaks are wider (100 - 200 mV), suggesting the presence of the mixture of several species with similar reduction potentials. When NTA is in excess, the chemical distribution [8,9,24] of Fe(III) in the NTA at pH = 8.0 suggests the three main Fe(III) - NTA species in the solution: $[Fe(NTA)_2]^{3-}$ (20% of $Fe(III)_{TOT}$), $[FeOHNTA]^-$ (20% of $Fe(III)_{TOT}$) and $[Fe(OH)_2NTA]^{2-}$ (60% of $Fe(III)_{TOT}$).

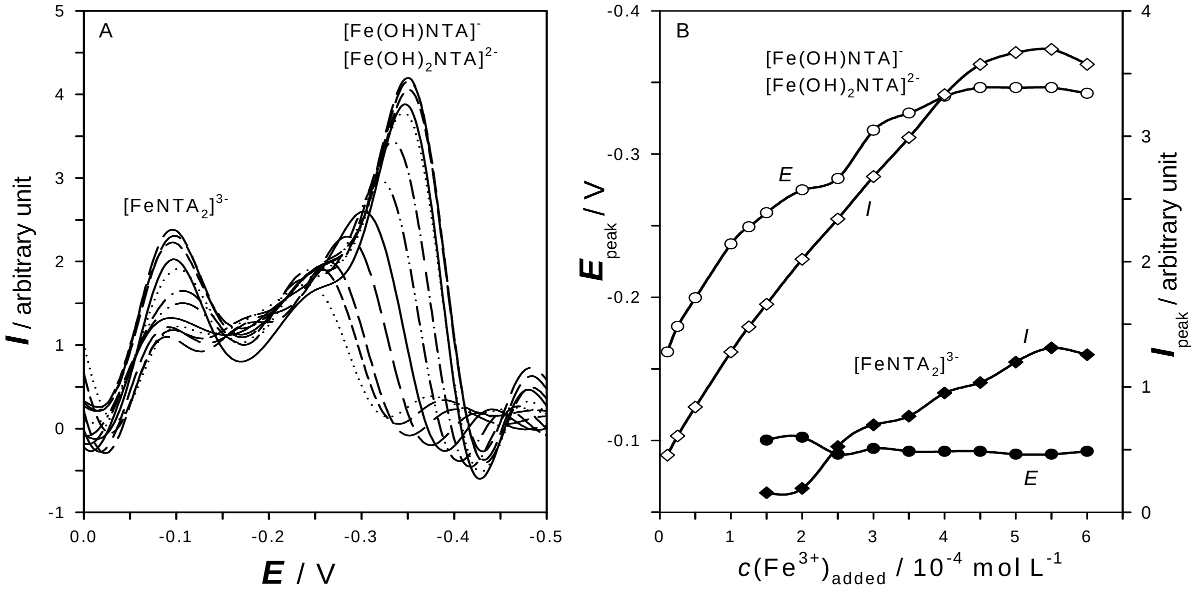

Fig. 2 Deconvoluted voltammetric peaks (A) from fig. 1 and their reduction potentials as well as reduction current values (B) presented in arbitrary units. Deconvolution parameters: n = 0.9; Boxcar filter with $\omega_o = 20/T_o$, (T_o = 1.024 V).

This represents the most probable composition of the solution at the beginning of the titration experiment (ligand is in excess) when only one wide peak is observed (voltammograms 2, 3, 4 and 5 in Fig. 1). At the 5×10^{-4} mol L^{-1} of the added Fe(III) (ratio metal - ligand is 1 : 1), current values of both peaks ("shoulder" which represents the one-electron reduction signal of $[Fe(NTA)_2]^{3-}$ and the higher peak which is probably the result of the one-electron reduction of the mixed ligand complexes $[FeOHNTA]^-$, and $[Fe(OH)_2NTA]^{2-}$) remain constant because there is no enough ligand for further formation of complexes (Figs. 1 and 2). In the reports published elsewhere [8,9], at the 1 : 1 metal to ligand ratio and relatively high total concentrations at pH about 8, the portion of $[Fe(NTA)_2]^{3-}$ complex decreases significantly, and the iron(III) is mostly complexed as $[FeOHNTA]^-$ and $[Fe(OH)_2NTA]^{2-}$, while the formation of the diiron(III) complex $[NTAFeOFeNTA]^{2-}$ is well enhanced. The ligand to metal ratio of 1:1 as well as the higher total concentrations of both, are favourable for the formation of the binuclear iron(III) complex [1,8,9,18-20]. The results presented in the inset in Fig. 1, is similar to those in Figs. 1 and 2. showing the DPC voltammograms of a five-times lower concentration (1×10^{-4} mol L^{-1}) of a nitrilotriacetate titrated with the iron(III) solution and recorded at the same pH of 8.0±0.1. The Fe(III)-NTA-OH system reduction peaks are regular in shape at the beginning of the titration, and a "shoulder" appears with the addition of iron(III) of 1×10^{-5} mol L^{-1}. The "shoulder" appears at a five-times lower iron(III) ion concentration than in the experiment in which a 5×10^{-4} mol L^{-1} nitrilotriacetate is added. The "shoulder" which represents the one-electron reduction of $[Fe(NTA)_2]^{3-}$, appears at both nitrilotriacetate concentration levels (1×10^{-4} and 5×10^{-4} mol L^{-1}), when metal to ligand ratio is about 1:10. The 1-electron reduction of the binuclear diiron(III) complex $[NTAFeOFeNTA]^{2-}$ at both nitrilotriacetate concentration levels, also shows consistent pattern of behaviour. The binuclear reduction signal appears at -0.55 V when the metal to ligand ratio is 1 : 1. This confirms numerous reports on the binuclear diiron(III) - NTA formation in the electrolyte solutions [1,8,9,18-20].

Table 1 Literature stability constants [9] for specified chemical reactions and in this work experimentally determined reduction peak potentials from Figs. 1 and 2.

Reaction	log *β* [9]	*E* (V)
$Fe^{3+} + 2NTA^{3-} \leftrightarrow [Fe(NTA)_2]^{3-}$	24	-0,093
$Fe^{3+} + NTA^{3-} + OH^{-} \leftrightarrow$ $[FeOHNTA]^{-}$	24,9	mixture: from -0,16
$Fe^{3+} + NTA^{3-} + 2OH^{-} \leftrightarrow$ $[Fe(OH)_2NTA]^{2-}$	31,1	to -0,34
$2Fe^{3+} + 2NTA^{3-} + 2OH^{-} \leftrightarrow$ $[NTAFeOFeNTA]^{2-} + H_2O$	51,72	-0,55

For better illustration, we give Table 1 which presents both the literature values of the cumulative stability constants [9,24], and the respective experimentally determined reduction peak potentials of the ferric - NTA complexes obtained in this work. As one can see, with increasing stability constants, respective peak potentials also increase from -0.093 V (log β = 24 for the reduction of $[Fe(NTA)_2]^{3-}$) to -0.55 V (log β = 51.72 for the reduction of binuclear ferric complex $[NTAFeOFeNTA]^{2-}$). This apparent binuclear reduction potential (-0.55 V) is in a very good agreement with the behaviour of the binuclear complex at -0.525 V vs. the SCE electrode at pH = 6 previously described [9].

In order to quantify presented results, the calculations with the constants from the literature were done and compared with the potential shifts of the peaks. For the range of interest (1×10^{-6} to 6×10^{-4} mol L^{-1} of added Fe(III), 5×10^{-4} mol L^{-1} NTA and given pH = 8.1, using the dissociation constants of NTA (log k_1 = 9.84, log k_2 = 2.52, log k_3 = 1.81, log k_4 = 1), stability constants of Fe(III)-NTA complexes (log β_1 = 15.9, log β_2 = 24), Fe(II)-NTA complexes (log β_1 = 8.9, log β_2 = 11.89), Fe(III)-hydroxide complexes (log β_1 = 11.27, log β_2 = 21.8, log β_3 = 28.4, log β_4 = 34.4), Fe(II)-hydroxide complexes (log β_1= 4.2, log β_2 = 7.5, log β_3 = 13), Fe(III)-hydroxide-NTA mixed complexes (log β_1 = 24.9, log β_2 = 31.1), Fe(II)-hydroxide-NTA mixed complexes (log β_1 = 11.7, log β_2 = 15.63) for redox reactions Fe(III)-NTA ↔ Fe(II)-NTA and Fe(III)-OH-NTA ↔ Fe(II)-OH-NTA, calculation of theoretical reduction potential shift was provided using the Nernst equation [25]:

$$E_{1/2c} = E_{1/2f} - RT/nF \ln(F_0),$$

where $E_{1/2f}$ = 0.573 V vs. Ag/AgCl (redox potential of free couple Fe(III)/Fe(II)), F_0 for the first peak is

$$F_0 = \frac{1+\beta_1(FeNTA)\times[NTA]^{3-}+\beta_2([Fe(NTA)_2]^{3-})\times([NTA]^{3-})^2}{1+\beta_1([FeNTA]^{-})\times[NTA]^{3-}+\beta_2([Fe(NTA)_2]^{4-})\times([NTA]^{3-})^2},$$

F_0 for the second peak is

$$F_0 = \frac{1+\beta_1([FeOHNTA]^{-})\times([OH]^{-}[NTA]^{3-})+\beta_2([Fe(OH)_2NTA]^{2-})\times(([OH]^{-})^2[NTA]^{3-})+\beta_1([FeOH]^{2+})}{1+\beta_1([FeOHNTA]^{2-})\times([OH]^{-}[NTA]^{3-})+\beta_2([Fe(OH)_2NTA]^{3-})\times(([OH]^{-})^2[NTA]^{3-})+}$$

$$\ldots\frac{\times[OH]^{-}+\beta_2([Fe(OH)_2]^{+})\times([OH]^{-})^2+\beta_3(Fe(OH)_3)\times([OH]^{-})^3+\beta_4([Fe(OH)_4]^{-})\times([OH]^{-})^4}{+\beta_1([FeOH]^{+})\times[OH]^{-}+\beta_2(Fe(OH)_2)\times([OH]^{-})^2+\beta_3([Fe(OH)_3]^{-})\times([OH]^{-})^3}$$

and other symbols have their usual meaning.

Experimentally obtained peak shifts P1 and P2, and calculated from the literature [24,26] L1 and L2 are shown in Figure 3, respectively.

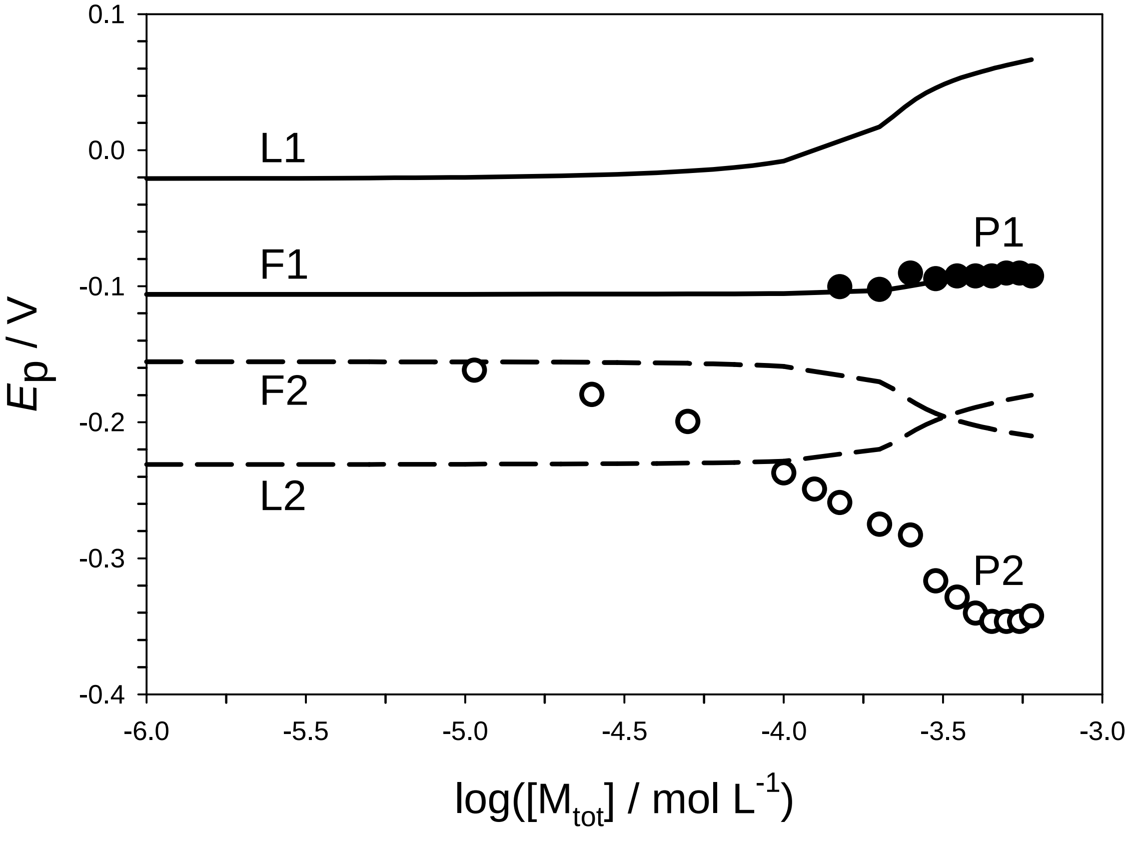

Fig. 3 Experimentally obtained (dots) and literature [24,26] peak shifts P1 and P2, and L1 and L2, respectively. F1 and F2 - fitted curves obtained by changing literature constants [24,26].

As the redox reactions are quasi-reversible, the actual peak positions should be corrected for the reversible part, which is a constant shift in positive direction under presumption of not changing reversibility during the experiment performance conditions. As the distance of the curves are more pronounced than expected, and the shapes are not matching neither, a fitting approach was applied in order to best approach to the measuring points. The result is shown by the curves F1 and F2 in Fig. 3. Fitting was obtained by changing the following literature constants [24,26]: log $\beta_2([Fe(NTA)_2]^{3-})$ from 24 to 27.2, log $\beta_1([FeNTA]^{-})$ from 8.9 to 9.2, log $\beta_2([Fe(NTA)_2]^{4-})$ from 11.89 to 15.7 and log $\beta_2([Fe(OH)_2NTA]^{3-})$ from 15.63 to 19. It should be stressed that such calculation is only an orientation and is a motive for reconsidering the stability constants values, while in any case it should be corrected for the reversibility part, which was not done at this stage. Also, for the second peak, shape matching was not obtained, which indicates for not well defined model of the calculation.

Cyclic voltammetry

The characterization of the iron(III)-NTA-OH redox mechanism at the mercury electrode under the given experimental conditions using cyclic voltammetry, was carried out. Figure 4 shows the cyclic voltammograms recorded in 0.1 mol L^{-1} $NaClO_4$ with a 5×10^{-4} mol L^{-1} nitrilotriacetate at $v = 0.1$ V s^{-1}.

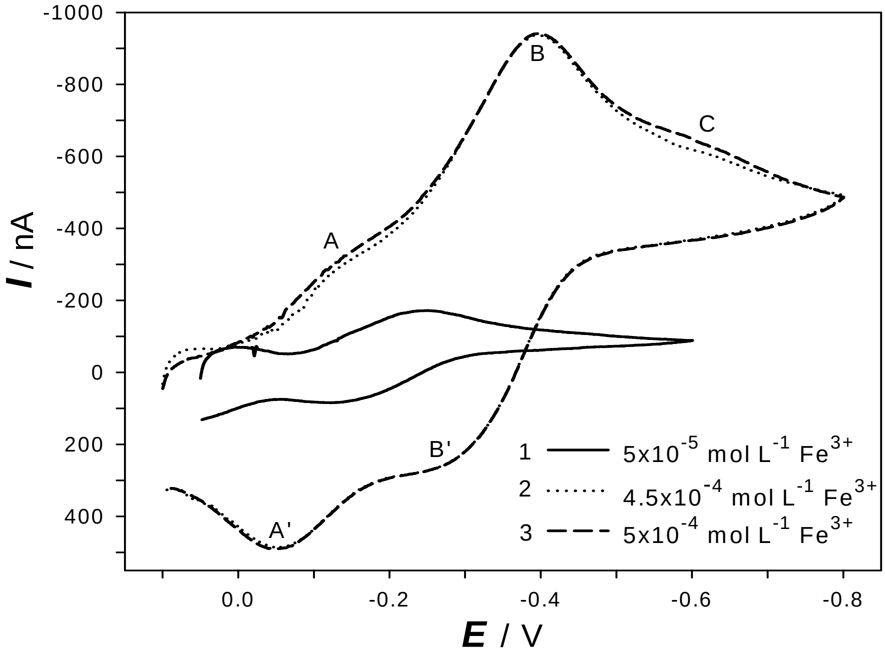

Fig. 4 Cyclic voltammograms of Fe^{3+} - NTA system. 5×10^{-4} mol L^{-1} NTA; 0.1 mol L^{-1} $NaClO_4$; pH = 8.0±0.1; ΔE = 2 mV; v = 0.1 V s^{-1}.

The voltammogram 1 is a result of the addition of a 5×10^{-5} mol L^{-1} ferric ions. Two peaks were observed, the cathodic (reduction) with a negative current values, and the anodic (oxidation) with a positive current values. Those peaks can be attributed to the reduction and the oxidation processes of $[FeOHNTA]^-$ and $[Fe(OH)_2NTA]^{2-}$ mixture. A cathodic peak was recorded at -0.25 V while an anodic peak at -0.16 V. The difference of 90 mV between these two peaks indicates a strong possibility of Fe(III)-NTA-OH system being consistent with the 1-electron quasi-reversible redox reaction mechanism. This is in a good agreement with the reports published elsewhere [9,17,20]. The cyclic voltammograms 2 and 3 presented in Fig. 4, are very similar. They were recorded after the addition of a 4.5×10^{-4} mol L^{-1} and a 5×10^{-4} mol L^{-1} ferric ions, respectively. Three cathodic peaks and only two anodic peaks were observed on each of the two voltammograms. The values of the oxidoreduction peak potentials of the voltammograms 2 and 3 were practically the same. The most positive cathodic peaks (A) at -0.146 V correspond to the 1-electron reduction of the $[Fe(NTA)_2]^{3-}$ inert complex. Its anodic peaks (A') are positioned at -0.055 V which is a shift of 91 mV in a positive direction. Such a shift value suggests the quasi-reversible character of the $[Fe(NTA)_2]^{3-}$ reduction [9,17,20]. The reduction reaction can be expressed as follows:

$$[Fe(NTA)_2]^{3-} + e^- \leftrightarrow [FeNTA]^- + NTA^{3-}, \tag{1}$$

where the ferro complex $[FeNTA]^-$ is the most abundant of all Fe(II) - NTA complexes in the system at the experimental pH = 8.0±0.1, which was calculated using a MINEQL+ chemical equilibrium program [27] and the stability constants from the literature [24,26]: $\log K_1([FeNTA]^-) = 8.83$, $\log \beta_2([Fe(NTA)_2]^{4-}) = 11.98$ and $\log K_1([FeOHNTA]^{2-}) = 12.1$. The highest cathodic peaks (B) at -0.394 V, represent the 1-electron reduction of the $[FeOHNTA]^-$ and $[Fe(OH)_2NTA]^{2-}$ mixture. At -0.290 V, their anodic counterparts (B') are shifted 104 mV more positively, which also corresponds to the one-electron quasi-reversible redox reaction. The behaviour of the cathodic peaks (C) at about -0.55 V is also interesting. As mentioned earlier, these peaks represent the reduction of the binuclear diiron(III) complex $[NTAFeOFeNTA]^{2-}$. They are the only cathodic peaks on the voltammograms 2 and 3 which anodic components are indistinguishable. This probably means that the binuclear diiron(III)-NTA redox process is irreversible under our experimental conditions (pH = 8.0±0.1; $I = 0.1$ mol L^{-1}; 4.5×10^{-4} and 5×10^{-4} mol L^{-1} iron(III) ions; 5×10^{-4} mol L^{-1} nitrilotriacetate; $v = 0.1$ V s^{-1}). This presumption is in disagreement with the report published elsewhere [9] where such a process was found to be quasi-reversible under different experimental conditions (pH = 6; $I = 0.5$ mol L^{-1} of KNO_3; 2×10^{-4} and 2×10^{-3} mol L^{-1} iron(III)-NTA system; $v = 0.5$ V s^{-1}). If one presumes the reduction reaction of the binuclear complex, as follows [19,20]:

$$[NTAFe^{3+}\text{-}O\text{-}Fe^{3+}NTA]^{2-} + e^- \leftrightarrow [NTAFe^{3+}\text{-}O\text{-}Fe^{2+}NTA]^{3-} \tag{2}$$

this reaction is immediately followed by the chemical reaction of hydrolysis:

$$[NTAFe^{3+}\text{-}O\text{-}Fe^{2+}NTA]^{3-} + H_2O \rightarrow [FeOHNTA]^- + [FeOHNTA]^{2-}. \tag{3}$$

A possible explanation for the irreversible mechanism of the reduction of the binuclear complex is that the pH value around 8.0 is preferable for the chemical reaction of hydrolysis

(3). This reaction is enhanced and fast due to the basic pH value enabling the freshly formed reduced binuclear complex $[NTAFe^{3+}\text{-}O\text{-}Fe^{2+}NTA]^{3-}$ to hydrolyse instantly. Therefore, its oxidation is significantly diminished, and the anodic component was not observed. The experiment reported elsewhere [9], carried out at pH = 6, yielded the quasi-reversible character of the binuclear reduction due to a lower pH value which suppressed hydrolysis of the reduced binuclear complex $[NTAFe^{3+}\text{-}O\text{-}Fe^{2+}NTA]^{3-}$, so that its oxidation was observed as the anodic signal on the cyclic voltammogram.

Sampled d.c. polarography

To test and evaluate the character (a number of the electrons involved and the reversibility) of the iron(III)-NTA-OH system redox reaction, a sampled d.c. polarographic technique was applied [25,28-30]. Fig. 5 shows the polarogram of the 5×10^{-5} mol L^{-1} of iron(III) ions and 5×10^{-4} mol L^{-1} nitrilotriacetate in 0.1 $NaClO_4$ mol L^{-1} at pH = 8.0±0.1. Under these conditions, mixed complex $[FeOHNTA]^-$ is highly predominant over $[Fe(OH)_2NTA]^{2-}$ in the solution. The polarographic measurements were carried out in the range from 0.03 V to -0.8 V with the following parameters: drop time (t_d) = 0.5 s and step potential (ΔE) = 2 mV. Under these experimental conditions, only one reduction wave with half-wave potential ($E_{1/2}$) at -0.195 V was detected, which can be related to the reduction of the $[FeOHNTA]^-$ mixed ligand complex. No reduction of the $[Fe(NTA)_2]^{3-}$ and the binuclear $[NTAFe^{3+}\text{-}O\text{-}Fe^{3+}NTA]^{2-}$ was recorded. The sampled d.c. polarographic technique under these conditions is not sensitive enough to register the $[Fe(NTA)_2]^{3-}$ reduction, while its reduction was observed using a differential pulse and cyclic voltammetry.

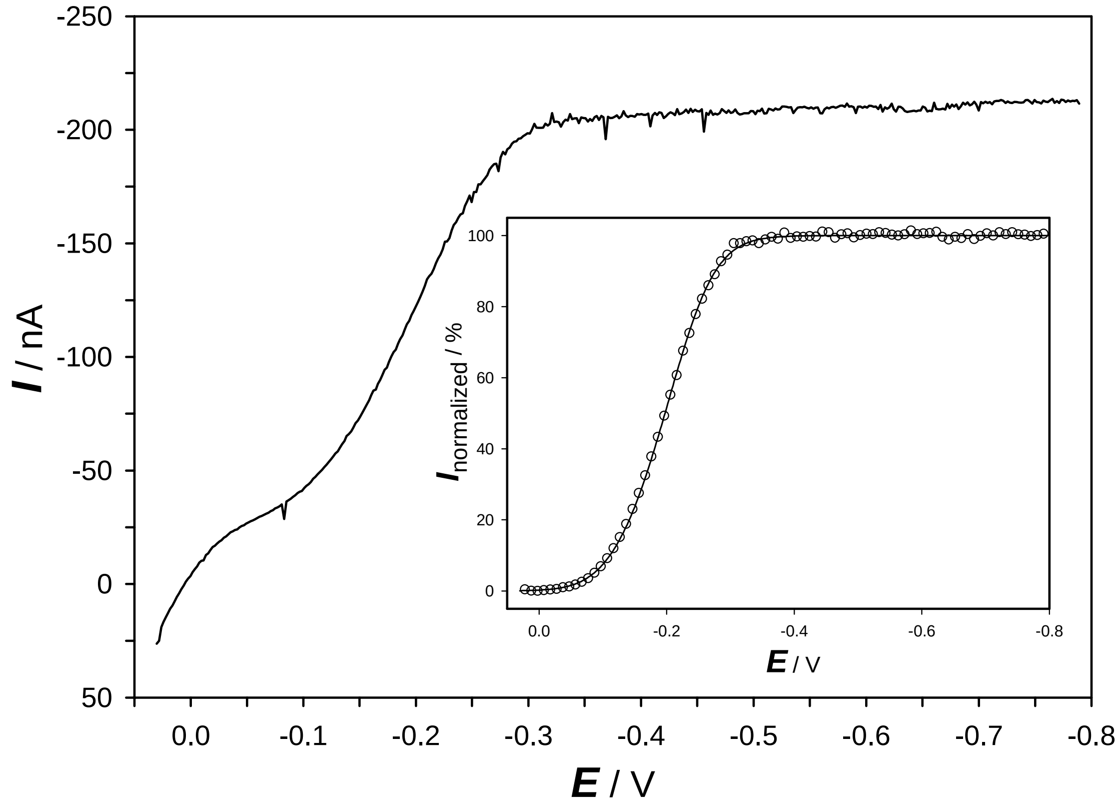

Fig. 5 Sampled d.c. polarogram. 5×10^{-5} mol L^{-1} Fe^{3+}; 5×10^{-4} mol L^{-1} NTA; 0.1 mol L^{-1} $NaClO_4$; pH = 8.0±0.1; ΔE = 2 mV; t_d = 0.5 s. **Inset**: normalized (circles) and simulated (line) polarograms. Simulated electrochemical parameters: $\alpha = 0.46\pm0.05$, $k_s = 1.0\pm0.3 \times10^{-3}$ cm s^{-1}, $E^{0'} = -0.154\pm0.010$ V.

The binuclear diiron(III) $[NTAFe^{3+}\text{-}O\text{-}Fe^{3+}NTA]^{2-}$ complex is sufficiently present in the solution when metal to ligand ratio approaches 1 : 1, but when the ratio is around 1 : 10 or lower, as in this case, the binuclear formation is severely suppressed [8,9,19,20], and its reduction wave was not observed.

To obtain the electrochemical parameters [25,28-30] of the $[FeOHNTA]^-$ reduction, such as a transfer coefficient (α), a rate constant (k_S), and a formal potential ($E^{0'}$) as well as the reversibility of the reaction, the mathematical treatment of the polarographic curve was carried out as described previously in detail [31]. The treatment of the experimental polarographic curve produced a normalized polarogram presented in the inset in Fig. 5, along with the simulated [32] polarogram. A method known as a logarithmic analysis of the polarogram is suitable for testing system reversibility [25,28-32]. It also allows the determination of the transfer coefficient (α) for the non-reversible reactions, which can be evaluated from the expression [25,28-30]:

$$\text{slope} = 0.0591 / \alpha \text{n}$$

where n is a number of the electrons exchanged in the redox reaction (in this case, n = 1). However, as previosly shown [32], the logarithmic analysis is unsuitable method for determining the transfer coefficient (α) for the quasi-reversible reactions. Therefore, α was determined by constructing a simulated polarogram. The simulated polarogram (constructed in an ECDSOFT program) [31,32] was constructed with the following electrochemical parameters: a transfer coefficient (α) = 0.46±0.05, a rate constant (k_s) = $1.0 \pm 0.3 \times 10^{-3}$ cm s^{-1}, and a formal potential ($E^{o\prime}$) = -0.154±0.010 V, and it overlaps very well with the normalized original polarogram (Fig. 5, inset). A good overlap suggests that the reduction of the $[FeOHNTA]^-$ mixed complex shows the 1-electron quasi-reversible character.

CONCLUSIONS

In the frame of our interest in dissolved iron species in natural water systems a research is done in order to characterize the electroactive iron (III) species which were simultaneously measured in a 0.1 mol L^{-1} $NaClO_4$ (I = 0.1 mol L^{-1}) model water solution containing nitrilotriacetate at natural seawater pH of 8.0 ± 0.1. Using various voltammetric techniques (DPCV, CV and sampled d.c. polarography), as well as the data treatment by deconvolution, four iron(III) dissolved species were distinguished: the three of them ($[Fe(NTA)_2]^{3-}$ and mixed ligand complexes $[FeOHNTA]^-$ and $[Fe(OH)_2NTA]^{2-}$) undergo the one-electron quasi-reversible reduction at the mercury drop electrode, while the binuclear diiron(III) complex $[NTAFeOFeNTA]^{2-}$, detected in case when the solution contained more than 4×10^{-4} mol L^{-1} of the added iron(III) ions, showed the one-electron irreversible reduction. In order to give quantification of the results, the calculations with the constants from the literature were done and compared with the potential shifts of the voltammetric peaks. Fitting was obtained by changing the following literature constants: log β_2($[Fe(NTA)_2]^{3-}$) from 24 to 27.2, log β_1($[FeNTA]^{-}$) from 8.9 to 9.2, log β_2($[Fe(NTA)_2]^{4-}$) from 11.89 to 15.7 and log β_2($[Fe(OH)_2NTA]^{3-}$) from 15.63 to 19. Such calculation is only an orientation and is a motive for reconsidering the stability constants values, while in any case it should be corrected for the reversibility part, which was not done at this stage. The $[FeOHNTA]^{-}$ mixed ligand complex electrochemical parameters, such as: a transfer coefficient (α), a rate constant (k_s), a formal potential ($E^{o\prime}$), were found to be 0.46±0.05, $1.0\pm0.3 \times 10^{-3}$ cm s^{-1}, and -0.154±0.010 V, respectively. Finally, these four species well known from literature, have now for the first time been recorded simultaneously, i.e. proved to exist simultaneously under the given conditions. In this case, voltammetry showed more capability than other analytical techniques mentioned elsewhere. The results presented look promising for further investigations of the dissolved iron species in model and natural water systems.

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