KINETICS OF IRON(III) HYDROLYSIS AND PRECIPITATION IN AQUEOUS GLYCINE SOLUTIONS ASSESSED BY VOLTAMMETRY

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Dedicated to the 50th anniversary of rewarding the Nobel prize to Professor Jaroslav Heyrovský.

The kinetics of iron(III) hydrolysis and precipitation in aqueous glycine solutions were studied by cathodic voltammetry with a mercury drop electrode. The kinetics was controlled by changing ionic strength (I), pH and glycine concentration. Voltammetric measurements clearly showed formation and dissociation of a soluble Fe(III)–glycine complex, formation of iron(III) hydroxide and its precipitation. The rate constants of iron(III) hydroxide precipitation were assessed. The precipitation is first-order with respect to dissolved inorganic iron(III). The calculated rate constants of iron(III) precipitation varied from 0.18×10^{-5} s^{-1} (at 0.2 M total glycine, pH 7.30, $I = 0.6$ mol dm^{-3}) to 2.22×10^{-3} s^{-1} (at 0.1 M total glycine, pH 7.30, $I = 0.2$ mol dm^{-3}). At 0.5 M total glycine and $I = 0.6$ mol dm^{-3}, the iron(III) precipitation was not observed.

Keywords: Iron(III); Kinetics; Hydrolysis; Precipitation; Rate constants; Glycine; Voltammetry; Electrochemistry.

The low solubility of the thermodynamically stable iron(III) is the reason of less than nanomolar Fe^{3+} concentration in natural aquatic systems, although iron is one of the most abundant elements in the Earth crust[1–3]. In natural water columns iron(III) is mostly present as dissolved organic complexes at very low concentrations. However, iron(III) in a soluble form is crucial in many biological and chemical processes in natural waters, such as phytoplankton growth[4–9]. This motivates the research about how to maintain a desirable amount of iron(III) in dissolved and bioavailable form in aquatic system during a defined period of time.

The bioavailable concentration of iron in natural aquatic systems is strongly influenced by hydrolysis and subsequent precipitation[10]. Several results on thermodynamic properties and solubility of iron(III) precipita-

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tion products have been published so far[1,3,11,12]. However, the results of iron(III) precipitation have not been published to an appreciable extent; their number has been growing especially during the last decade[13–18]. By measuring the pH changes caused by iron(III) hydrolysis, Grundl and Delwiche[14] described that iron(III) precipitation proceeded at two distinct rates, both being of the first order. The rate-controlling step was found to be precipitation of the Fe(III) solid from $Fe(OH)_3$. The first-order rate constant of the formation of colloidal iron was determined by chemiluminescence[15]. Investigation of iron(III) hydrolysis and precipitation were undertaken and the corresponding rate constants were obtained using spectrophotometry[16]. Also, spectrophotometric investigations revealed the influence of pH on Fe(III) precipitation[17] and described the effects of divalent cations on the kinetics of Fe(III) complexation with organic ligands[18].

Glycine is the simplest amino acid (α-aminocarboxylic acid), with a single proton as an uncharged polar group. At 25 °C and $I = 0.5$ mol dm^{-3}, pK values are 2.39 and 9.54 with the isoelectric point at pH 5.97. Therefore, between pH 2.39 and 9.54 glycine exists predominantly as zwitterion, $H_3N^+–CH_2–COO^–$, rather than undissociated molecule[19,20].

Recently, electrochemical studies by cathodic differential pulse voltammetry (DPV) in our Laboratory described the iron(III) complexation with glycine[21], nitrilotriacetic acid (NTA)[22] and with mixed ligands[23]. Subsequent hydrolysis was observed but not described in detail. The technique is sufficiently sensitive and applicable to inorganic iron(III) characterization.

In this study, we examine the chemical kinetics of iron(III) hydrolysis and precipitation in aqueous solutions containing glycine by cathodic DPV. Proper choice of experimental conditions enabled us to observe the formation of dissolved iron(III) complexes with glycine and $OH^–$, their competition resulting in dissociation of Fe(III)–glycine and, subsequently, iron(III) hydroxide precipitation.

EXPERIMENTAL

Equipment

The voltammetric experiments were performed using an μAUTOLAB multimode potentiostat controlled by GPES 4.5, a general purpose electrochemical system software package through a personal computer with data acquisition routine (Eco Chemie, Utrecht, The Netherlands). Repeated voltammetric measurements for each glycine concentration were automatically controlled via the project mode of GPES 4.5 software in order to achieve exact time intervals between measurements and, consequently, smaller confidence intervals of the experimental results. The 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, USA) with a modified holder of electrode components[24]. The mercury drop had an area of 1.55 mm^2. An Ag|AgCl electrode bridged by a saturated NaCl solution, and a platinum wire, were used as a reference and an auxiliary electrode, respectively. Cathodic DPV was applied under the following conditions: pulse amplitude 25 mV, potential step increment (E_{inc}) 2 mV, time between the pulses (t_{int}) 0.2 s and pulse duration (t_p) 0.05 s. pH of the solutions was measured with a glass electrode connected to an ATI Orion PerpHecT meter, Model 320 (Cambridge, MA, USA). Potentiostatic electrolysis was performed using an EG&G PAR Model 273 potentiostat.

Chemicals and Solutions

A stock solutions of 10^{-2} M $Fe(NO_3)_3 \cdot 9H_2O$ (p.a., Kemika, Zagreb, Croatia), 10^{-1} and 10^{-2} M glycine (Merck, Darmstadt, Germany), and 7.13 M $NaClO_4$ (p.a., Fluka Chemie, Buchs, Switzerland) were prepared. All chemicals used were prepared with Milli-Q water.

The blank concentration of the dissolved trace metals in the stock of supporting electrolyte ($NaClO_4$), which could be a source of error, was diminished by potentiostatic electrolysis (reduction). The electrolysis was carried out at –1.25 V for at least 4 h under a N_2 atmosphere. Prior to electrolysis, the 7.13 M $NaClO_4$ stock solution was pretreated overnight with active carbon and filtered through 0.22 μm Millipore filters (Millipore Corp., Bedford, USA).

Aqueous solutions at different perchlorate and glycine concentrations were prepared to maintain the ionic strengths 0.2, 0.3 and 0.6 mol dm^{-3} according to the model ($I - X$) M $NaClO_4$ + X M total glycine, where X = 0.1, 0.2 and 0.5. At pH 7.3, all the three ionic strengths were measured, while at pH 8.0 only 0.2 and 0.3 mol dm^{-3}. pH was maintained by addition of dilute $HClO_4$ (SupraPur®) or NaOH (p.a., Merck). Aqueous glycine solution (20 cm^3) was placed in the electroanalytical cell, pH was adjusted and the solution was deaerated by bubbling with extrapure nitrogen for about 15 min. Then, repeated voltammetric scans started immediately after addition of 2.5×10^{-5} M Fe(III).

RESULTS AND DISCUSSION

Electrochemical Characterization

In order to characterize kinetics of iron(III) hydroxide precipitation in aqueous solutions, with glycine as a ligand and $NaClO_4$ as a basic electrolyte (which does not react with iron(III)), voltammetric experiments at different ligand/metal ratios were performed at ionic strengths of 0.2, 0.3 and 0.6 mol dm^{-3} at pH 7.30 ± 0.01 and 8.00 ± 0.01 and temperature 25 ± 1 °C. The optimum iron(III) concentration used in experiments was 2.5×10^{-5} mol dm^{-3}; at lower concentrations, the iron(III) reduction signal was insufficient for correct estimation. On the other hand, iron(III) concentrations higher than 2.5×10^{-5} mol dm^{-3} would extremely promote the hydrolysis[2]. Total concentrations of glycine were 0.1, 0.2 and 0.5 mol dm^{-3}. Since the concentration of free glycine (dissociated, negatively charged) considerably diminishes at more acidic pH, the experiments were not performed below pH 7.30. At lower pH, the Fe(III)–glycine reduction signal shifts to more positive values and is masked by a steep baseline which is a part of the reduction signal of a mercury complex with chloride traces due to a small chloride leakage from the reference electrode. Above pH 9.0, iron(III) hydrolysis and subsequent precipitation are pronounced, regardless of free glycine concentration[21–23]. So, pH 7.30 (blood and physiological solution) and pH 8.00 (sea water) were chosen for experiments with various glycine concentrations. The glycine dissociation constant, $\log K_{HL} = \log([HL]/[L]^-[H]^+)$, where HL is $C_2H_5NO_2$, was estimated for $I = 0.2$, 0.3 and 0.6 mol dm^{-3} by fitting the literature constants[19,20,25,26] 9.778, 9.58, 9.54, 9.66 and 9.93 determined at ionic strengths 0, 0.1, 0.5, 1 and 3 mol dm^{-3}, respectively. The $\log K_{HL}$ versus square root of I dependence was fitted with the second-order polynomial $\log K_{HL} = 0.396I - 0.539\sqrt{I} + 9.751$, with standard errors of parameters of 9.27×10^{-2}, 1.79×10^{-1} and 6.52×10^{-2}, respectively. The obtained values of $\log K_{HL}$ were 9.589, 9.575 and 9.571 for $I = 0.2$, 0.3 and 0.6 mol dm^{-3}, respectively. These values were used for subsequent calculations of free glycine concentrations. The second dissociation constant $\log K_{H2L}{}^+ = \log([H_2L]^+/[HL][H]^+)$ is 2.39 ± 0.05 (refs[19,20,25,26]). The concentrations of the free, dissociated ligand $[L]^-$ were calculated using the MINEQL$^+$ chemical equilibrium program[27] for the given pH (Table I).

A solution of 2.5×10^{-5} M Fe(III) ions in 0.1 M glycine at pH 7.30, I = 0.6 mol dm^{-3} in $NaClO_4$, measured by cathodic DPV, exhibits three groups of reduction peaks (Fig. 1). The most representative reduction voltam-

TABLE I
Rate constants (k) of iron(III) precipitation obtained in this work at various total (tot) and dissociated (free) glycine concentrations; added $[Fe^{3+}] = 2.5 \times 10^{-5}$ mol dm^{-3}; 95% confidence interval (c.i.)

pH	I, mol dm^{-3}	$[Gly_{tot}]$, mol dm^{-3}	$[Gly_{free}]$, mol dm^{-3}	k ± c.i., 10^{-5} s^{-1}
7.30	0.2	0.1	5.10×10^{-4}	222.00 ± 17.00
	0.6	0.1	5.34×10^{-4}	27.83 ± 0.50
	0.3	0.2	1.04×10^{-3}	36.33 ± 1.33
	0.6	0.2	1.07×10^{-3}	0.18 ± 0.03
8.00	0.2	0.1	2.51×10^{-3}	41.67 ± 5.00
	0.3	0.2	5.13×10^{-3}	3.83 ± 1.00

mograms shown in Fig. 1 were chosen from a total of 52 successive scans. At the most positive potential (near 0.0 V vs Ag|AgCl), the peaks correspond to the one-electron reduction of Fe(III)–glycine complexes and follows the electrode half reaction

$$[Fe^{3+}(Gly^-)_n]^{3-n} + e \quad \rightarrow \quad [Fe^{2+}(Gly^-)_{n-1}]^{2-(n-1)} + Gly^- \,. \qquad (1)$$

Around –0.3 V, one-electron reduction of iron(III) hydroxide occurs, following the half reaction

$$[Fe^{3+}(OH^-)_n]^{3-n} + e \quad \rightarrow \quad Fe^{2+} + n\ OH^- \,. \qquad (2)$$

The most negative cathodic peaks (around –1.35 V) represent two-electron reduction of Fe(II)–glycine complexes formed by iron(III) reduction[21–23], with the half reaction

$$[Fe^{2+}(Gly^-)_n]^{2-n} + 2\ e \quad \rightarrow \quad Fe^0 + n\ Gly^- \,. \qquad (3)$$

The cathodic peak corresponding to the one-electron reduction of Fe(III)–glycine complexes is reversible. It shifts to negative values with in-

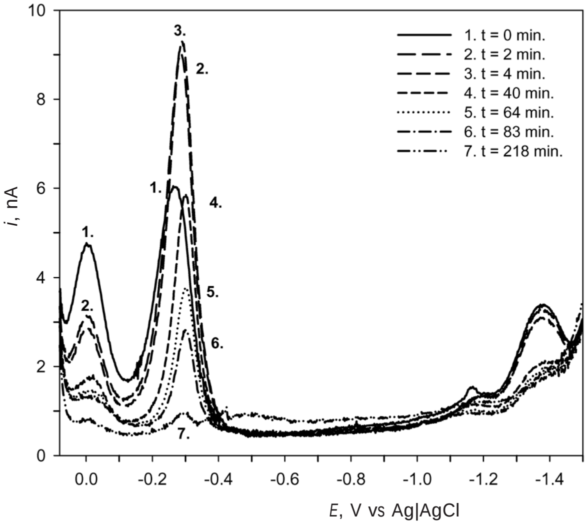

FIG. 1
Voltammograms of iron(III) reduction. $[Fe^{3+}] = 2.5 \times 10^{-5}$ mol dm^{-3}, $[Gly]_{tot} = 0.1$ mol dm^{-3}, $I = 0.6$ mol dm^{-3} ($NaClO_4$) at 25 ± 1 °C, pH 7.30 ± 0.01. Cathodic DPV parameters: $E_{inc} = 2$ mV, $a = 25$ mV, $t_p = 0.05$ s, $t_{int} = 0.2$ s

creasing the free ligand concentration. Peak half-width values ($w_{1/2}$) of Fe(III)–glycine reduction peaks in Fig. 1 are ca. 90 mV. This is an indication of one-electron reversible reduction at the mercury drop, according to the differential pulse voltammetric theory[28]. The reversible nature of one-electron iron(III) reduction in a glycine solution led us to conclude that this system contained labile iron(III) complexes, which helped to design the experiment necessary for assessment of their chemical kinetics. This electrode reaction is diffusion-controlled. That is not the case of reduction peaks around –0.3 V which correspond to one-electron iron(III) hydroxide reduction[21–23,29]. The cathodic peaks were influenced by adsorption of the iron(III) hydroxide complex at the mercury drop electrode. In addition, one-electron reduction of iron(III) hydroxide complex exhibits an irreversible nature, indicating stable complexes in aqueous solution[21,28,29].

The voltammogram 1 in Fig. 1 shows the iron(III) reduction immediately after the addition of 2.5×10^{-5} M Fe(III), at $t = 0$ min. The peaks of the Fe(III)–glycine complex reduction (at ~0 V vs Ag|AgCl) started to diminish with time, indicating fast dissociation of the Fe(III)–glycine complex, while the iron(III) hydroxide reduction peaks (at ca. –0.3 V vs Ag|AgCl) representing iron(III) hydrolysis, reached a maximum in 4 min after the addition of iron (at 0.1 M total glycine) and subsequently decreased, having indicated that precipitation had taken place.

In solutions with lower glycine concentrations, iron(III) hydrolysis and precipitation dominate the Fe(III)–glycine complex formation. Hence, below 0.1 M total glycine it was not possible to measure the Fe(III)–glycine reduction because the glycine exchange for the OH^- group was too fast. This determined the possible range of ligand concentrations to be used in the experiment, viz. 0.1 to 0.5 M total glycine. The Fe(III)–glycine reduction potentials in the voltammograms that were repeated for each glycine concentration, did not show any tendency to shifting. This has proven that the distribution of Fe(III)–glycine complexes did not change during the experiment[21,23,28]. However, Figs 1 and 2a clearly show the shift of peak potentials of one-electron reduction of iron(III) hydroxide with time. Within the first 45 min after the addition of iron ($[\mathrm{Gly}]_{\mathrm{tot}} = 0.1$ mol dm^{-3}; Fig. 2a, ●), the peak potential shifted from –0.27 to –0.30 V and remained constant for 106 min. This implies the formation of various iron(III) hydroxide species in the bulk of the solution during the experiment, which requires a higher energy for reduction at the electrode. With higher concentrations of total glycine (0.2 and 0.5 mol dm^{-3}), reduction peak potentials of dissolved iron(III) hydroxide complexes shifted towards negative values during the experiment (Fig. 2a, ○ and ▼). At the same time, iron(III) hydrolysis

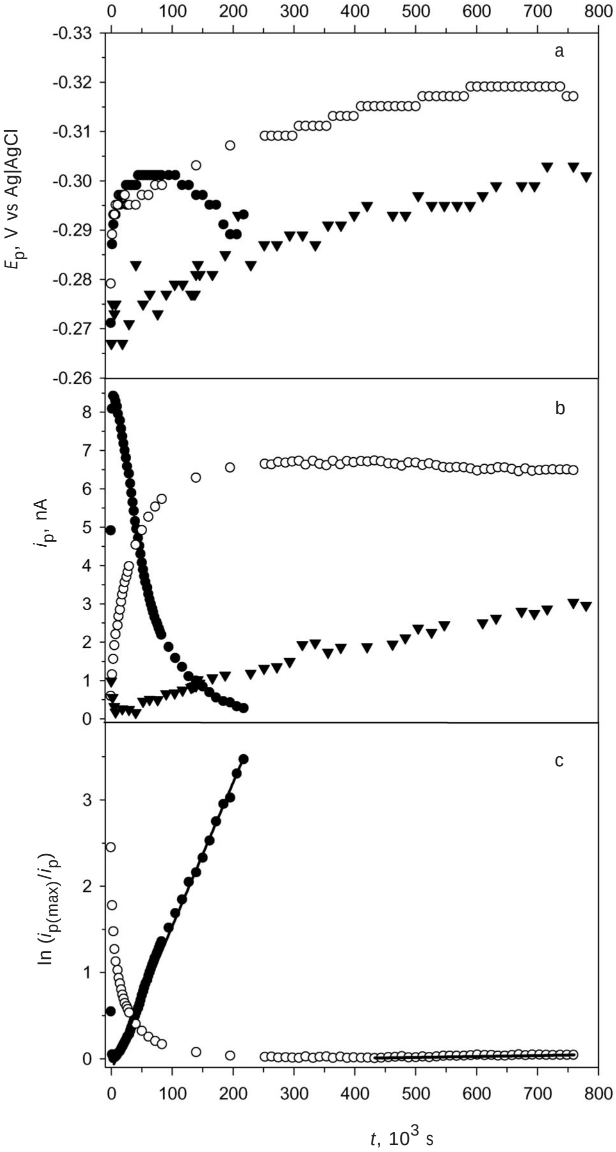

FIG. 2

Dependence of electrochemical parameters versus experimental time for the reduction of iron(III) hydroxide: reduction potentials (a), reduction peak currents (b), natural logarithms of the ratio of maximum peak current to peak current (c). $[Fe^{3+}] = 2.5 \times 10^{-5}$ mol dm^{-3}, $I = 0.6$ mol dm^{-3} ($NaClO_4$) at 25 ± 1 °C, pH 7.30 ± 0.01. $[Gly]_{tot}$ = 0.1 (●), 0.2 (○), 0.5 (▼) mol dm^{-3}

and subsequent precipitation are slowed down, i.e., with 0.2 M total glycine, reduction peaks of iron(III) hydroxide started to diminish 440 min after addition of iron(III) (Fig. 2b, ○). This indicates iron(III) precipitation. With 0.5 M total glycine (Fig. 2b, ▼), peak currents of iron(III) hydroxide reduction were constantly increasing during the experiment, implying that the iron(III) precipitation slowed down. The dependence of the reaction rate on ligand concentration should be predominately attributable to inhibition of iron(III) hydrolysis by glycine complexation[1,12].

Determination of Rate Constants

We assumed that the precipitation of iron(III) is of the first order[14–17] with respect to dissolved inorganic iron(III), in the applied pH range mainly present as $Fe(OH)_3(aq)$:

$$Fe(OH)_3(aq) \rightarrow Fe(OH)_3(s) \, . \tag{4}$$

Precipitation of Fe(III) is expected to yield iron(III) hydroxides of colloidal nature[13]. The general equation for a first-order chemical reaction is $dx/dt = k(a - x)$, and after integration

$$\ln\,(a/(a - x)) = kt \tag{5}$$

where a is the maximum concentration of dissolved inorganic iron(III) (the maximum current of the reduction peak of dissolved iron(III) hydroxide, $i_{p(max)}$), x is a decrement of the analyte and $a - x$ is the peak current height (i_p) at time t, which is proportional to the remaining concentration of dissolved iron(III) hydroxide in the analyzed solution at time t. Equation (*5*), when leading to linearization of data, confirms the proposed model of reaction kinetics. The slope k of the best-fit line through the data points represents the rate constant (Figs 2c and 3b). The precipitation of iron(III) is a first-order reaction with respect to dissolved inorganic iron(III), which satisfied our model for first-order rate constants. As under certain conditions we measured both the formation and precipitation of dissolved iron(III), only the data for the decreasing peak were included into the fitting.

Logarithmic transformation of decreasing reduction currents of iron(III) hydroxide (Figs 2b and 3a) with 0.1 and 0.2 M glycine resulted in a linear dependence on experimental time (Figs 2c and 3b). Higher glycine concentration in aqueous solution at pH 7.30 and I = 0.6 mol dm^{-3} slows both the process of iron(III) hydrolysis and precipitation (Fig. 2b, ▼), which is in good agreement with published results[1,12]. The resulting logarithmic slopes for our model of first-order rate constants (Fig. 2c) differ significantly. With the aforementioned conditions, increasing the glycine concentration from 0.1 (●) to 0.2 (○) mol dm^{-3} the precipitation slowed down. Thus, the rate constant decreased by two orders of magnitude, viz. 154-fold, from 27.83×10^{-5} s^{-1} for 0.1 M glycine down to 0.18×10^{-5} s^{-1} for 0.2 M glycine. The calculated rate constants with confidence intervals (c.i.) for 95% probability are given in Table I.

Ionic strength has a direct influence on rate constants, which can be seen in Table I and in Figs 2c (○) and 3b (●), both for 0.2 M total glycine. The change in ionic strength from 0.3 to 0.6 mol dm^{-3} at pH 7.30 slowed down the iron(III) precipitation and the rate constant decreased for 200 times, from 36.33×10^{-5} to 0.18×10^{-5} s^{-1} (Table I). At the same pH (7.30) with 0.1 M total glycine, the change was less prominent, the ionic strength varying from 0.2 to 0.6 mol dm^{-3}. This resulted in slower iron(III) precipitation and an 8 times lower rate constant, from 222.00×10^{-5} to 27.83×10^{-5} s^{-1} (Table I). The obtained results are in agreement with those of Byrne et al.[1,12], where iron(III) hydrolysis was suppressed by an ionic strength increase from $I = 0$ to 1 mol dm^{-3} ($NaClO_4$).

The influence of pH on iron(III) hydrolysis and precipitation is presented in Fig. 3, while the obtained rate constants are shown in Table I. Figure 3 gives experimental results (reduction currents (Fig. 3a), logarithmic dependence (Fig. 3b)) with added Fe(III) to 2.5×10^{-5} mol dm^{-3} and glycine to 0.2 mol dm^{-3}, $I = 0.3$ mol dm^{-3} at pH 7.3 (●) and pH 8.0 (○). It is evident that hydrolysis and precipitation were faster at pH 7.3. The maximum reduction current ($i_{p(max)}$), which is a in Eq. (5), i.e., the maximum concentration of dissolved inorganic iron(III) at pH 7.3, was recorded after 11 min, while at higher pH, the maximum was recorded 31 min after the addition of iron(III). Accordingly, logarithmic analysis gave a steeper slope for pH 7.3 (●) compared with pH 8.0 (○); the calculated rate constants were 36.33×10^{-5} and 3.83×10^{-5} s^{-1}, respectively (Fig. 3b, Table I). So, the pH change from 8.0 to 7.3 resulted in a 9.5-fold increase in the rate constant. Furthermore, with 0.1 M glycine, the rate constant increased 5.3 times, from 41.66×10^{-5} to 222.00×10^{-5} s^{-1} (Table I). Almost 5 times higher free glycine concentration at the same ionic strength at a higher pH (Table I) resulted in stronger iron(III) complexation with glycine compared with the OH^- group. Hence, the dependence of the rate constant on pH was due to inhibition of iron(III) hydrolysis by ligand complexation[12,17]. Moreover, at pH 8.0, $Fe(OH)_3$ is a significant iron(III) hydroxide species, which shows a relatively high water loss rate[17,30,31]. Therefore, the kinetics of Fe(III)–glycine complex formation is promoted compared with hydrolysis and precipitation[3,11,17,21–23,30,32].

The presented results obtained by cathodic DPV described specific experimental conditions, where the iron(III) precipitation rate in aqueous solutions could be controlled by changing the concentration of ligand (glycine) from 0.1 to 0.5 mol dm^{-3}, ionic strength from 0.2 to 0.6 mol dm^{-3} and pH from 7.3 to 8.0. By increasing the ionic strength, pH or glycine concen-

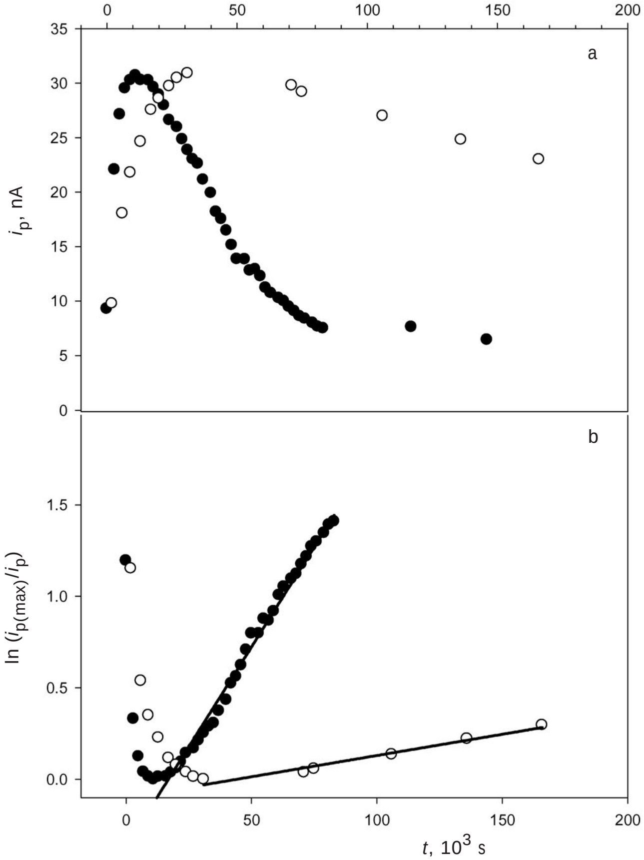

FIG. 3

Dependence of electrochemical parameters versus experimental time for the reduction of iron(III) hydroxide: reduction peak currents (a), natural logarithms of the ratio of maximum peak current to peak current (b). $[Fe^{3+}] = 2.5 \times 10^{-5}$ mol dm^{-3}, $[Gly]_{tot} = 0.2$ mol dm^{-3}, $I = 0.3$ mol dm^{-3} ($NaClO_4$) at 25 ± 1 °C. pH 7.30 ± 0.01 (●), 8.00 ± 0.01 (○)

tration, the rate of iron(III) precipitation decreases. This enables the control of iron(III) hydroxide precipitation rate constants in the range of three orders of magnitude, while for a total glycine concentration of 0.5 mol dm^{-3} at I = 0.6 mol dm^{-3}, iron(III) precipitation was not observed during the experiment. The obtained results, on confirmation and application to natural water systems, could be useful for further understanding of the role of iron in various important biogeochemical processes and its interaction with aquatic organisms, such as in regulation of phytoplankton growth.

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