VOLTAMMETRIC DETERMINATION OF STABILITY CONSTANTS OF IRON(III) - GLYCINE COMPLEXES IN WATER SOLUTION

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ABSTRACT

Determination of the stability constants of dissolved iron(III) - glycine system in water solution (I = 0.6 mol L^{-1} in $NaClO_4$, pH = 7.3 at 25±1 ºC) using differential pulse cathodic voltammetry (DPCV) and cyclic voltammetry (CV) was performed out on a static mercury drop electrode (SMDE). By choosing voltammetry as analytical tool, measurements with lower iron(III) concentrations (10^{-5} mol L^{-1}), at the pH = 7.3 were enabled, which ensured the formation of higher coordination (1 : 2 and 1 : 3) complexes of iron(III) - glycine system. The added concentration of iron(III) ions was 2.5×10^{-5} mol L^{-1} and the concentrations of total glycine varied from 0.1 to 0.5 mol L^{-1}. Since iron(III) reduction in glycine system, with the techniques employed, was found to be one-electron reversible process, it was concluded that this system contained labile iron(III) complexes. Thus, it was possible to determine stability constants. The stability constants of $[Fe(Gly)_2]^+$ and $Fe(Gly)_3$ complexes, which had not been reported in the literature so far, were found to be log β_{23} = 17.21±0.03 and log β_{33} = 20.19±0.02, respectively. According to the constants found, chemical distribution of iron(III) in glycine water solution, as a function of pH, was calculated and proposed.

Keywords: iron(III)-glycine complexes, stability constants, voltammetry, water solution.

1. INTRODUCTION

Iron is one of the most abundant elements in the earth's crust. However, very low concentrations (< 10^{-9} mol L^{-1}) of dissolved iron(III) organic complexes are present in natural waters owing to low solubility of its thermodynamically stable +3 oxidation state [1-3]. Dissolved iron(III) as an organic complex is very important for a large variety of biological and chemical processes in natural waters [4,5], especially for phytoplankton growth. According to numerous researches, iron is an element that regulates ecosystem structure and the rate of primary production in large areas of oceans [2,6-9]. It is known that some naturally occurring substances, namely α-amino-acids, form complexes with the ions of heavy metals [10]. Although the metals in these complexes no longer react as simple inorganic ions, the complexes are in equilibrium with a proportion of inorganic ions from which they were formed. Hence, it may be practical to think of cells and tissues of all kinds as areas in which traces of metallic ions are competed for by various complex-forming agents present. Accordingly, it would be desirable to know quantitatively the avidity of biologically significant ions of heavy metals such as iron(III) for complex-forming agents such as α-amino-acids [10-12]. We started this task with glycine, the simplest α-amino-acid.

Stability constant of iron(III) with glycine for the complex $[FeGly]^{2+}$ has so far been mentioned in only a few papers [11-14], which is due to markedly expressed hydrolysis of Fe^{3+} ion and formation of binuclear and polinuclear complexes with organic and inorganic ligands [11,12]. The mentioned stability constant has been determined by the measurements with redox electrodes [11] and redox electrodes and pH-measurements [12]. They were determined with relatively high Fe^{3+} ions concentrations (> 10^{-3} mol L^{-1}) which favours the formation of polinuclear complexes [15], under very acidic conditions (pH < 3) to avoid hydrolysis. This is the main reason why only the stability constant [11-14] for the complex $[Fe(Gly)]^{2+}$ has been calculated so far. Practically, there exist no papers dealing with the analysis of iron(III) - glycine

system in water solution by voltammetry, only paper treating glycine as auxiliary complexing agent was found [16]. The main reasons for this are strong iron(III) hydrolyzing capacitiy, as well as strong glycine protonation constants [13,14] which suppose a use of large excess of glycine in order to both enable the formation of iron(III) - glycine complexes and to observe the voltammetric signals of its oxido-reduction processes. Glycine has been voltammetrically investigated much more in the complexes with other metal ions such as cadmium(II) [17] and zinc(II) [18], where hydrolysis does not take place in such extent.

Choosing voltammetry allowed the work with lower iron(III) concentrations, while selecting the suitable experimental conditions at higher pH values facilitated the formation of higher coordination complexes (1:2 and 1:3) of iron(III) - glycine system. All of these made it possible to determine the stability constants and to calculate chemical distribution of iron(III) species.

2. EXPERIMENTAL

2.1 Equipment

The experiments were performed using an μAUTOLAB multimode polarograph controlled by GPES 4.5, General Purpose Electrochemical System software package through a personal computer with data acquisition routine (ECO Chemie, Utrecht, The Netherlands). Repetitive voltammetric measurements for each glycine concentration were automatically controlled with a homemade computer program in order to achieve good statistics of the repeated measurements, i.e. to achieve lower confidence interval.

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

The measurements were performed in a 50 cm^3 electroanalytical quartz cell at 25±1 ºC. 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 [19]. The size of the mercury drop was medium, with an area of 1.55 mm^2. An Ag/AgCl electrode with saturated NaCl, and a platinum wire, were used as a reference and a counter electrode, respectively.

Electrochemical techniques used were differential pulse cathodic voltammetry (DPCV) applied under the selected conditions of pulse amplitude (a) = 25 mV, potential step increment (E_{inc}) = 2 mV, time between the pulses (t_{int}) = 0.2 s, pulse duration (t_p) = 0.05 s, and cyclic voltammetry (CV) with E_{inc} = 2 mV and scan rate (v) = 0.1 V s^{-1}.

2.2. Chemicals and solutions

The stock solutions of 10^{-2} mol L^{-1} of $Fe(NO_3)_3 \times 9H_20$ (p.a., Kemika, Zagreb, Croatia), 10^{-1} and 10^{-2} mol L^{-1} of glycine (H_2NCH_2COOH) (Merck, Darmstadt, Germany), and 7.13 mol L^{-1} of $NaClO_4$ (p.a., Fluka Chemie, Buchs, Switzerland) were prepared. All chemicals used were prepared in distilled, deionised water from a Milli-Q system (Millipore corp., Bedford, USA).

Prior to electrolysis, the solution (7.13 mol L^{-1}) was pretreated overnight with active carbon and filtered through 0.22 μM Millipore filters (Millipore corp.).

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

Five solutions of different glycine and perchlorate concentrations were made in order to maintain the ionic strength of 0.6 mol L^{-1} according to the model (0.6-X) mol L^{-1} $NaClO_4$ + X mol L^{-1} of total glycine, where X = 0.1, 0.2, 0.3, 0.4 and 0.5.

After the solution (20 cm^3) was prepared in an electroanalytical cell, prior to electrochemical measurements, it was deaerated by bubbling with an extra pure nitrogen for about 15 minutes. Then, repetitive voltammetric scans started immediately after the addition of 2.5×10^{-5} mol L^{-1} of iron(III) ions in order to decrease iron(III) hydrolysis effects.

3. RESULTS AND DISCUSSION

3.1. Choosing suitable parameters

In order to obtain the characterization of dissolved and complexed iron(III) behaviour in water solution, experiments with Fe(III) - Gly systems of various concentration ratios were performed. Electrochemical measurements of the redox system Fe(III)-Gly were performed in a model solution of $NaClO_4$, pH = 7.3, ionic strength = 0.6 mol L^{-1} at 25±1 ºC. The added concentration of dissolved iron(III) was 2.5×10^{-5} mol L^{-1} and total glycine concentrations were 0.1, 0.2, 0.3, 0.4 and 0.5 mol L^{-1}. Experiments have not been performed below pH = 6.5 since the concentration of the active glycine form diminishes with lower pH values. As a result, iron(III)-glycine reduction signal shifts to more positive values and is masked by a steep baseline (Fig. 1, voltamograms 2 and 3).

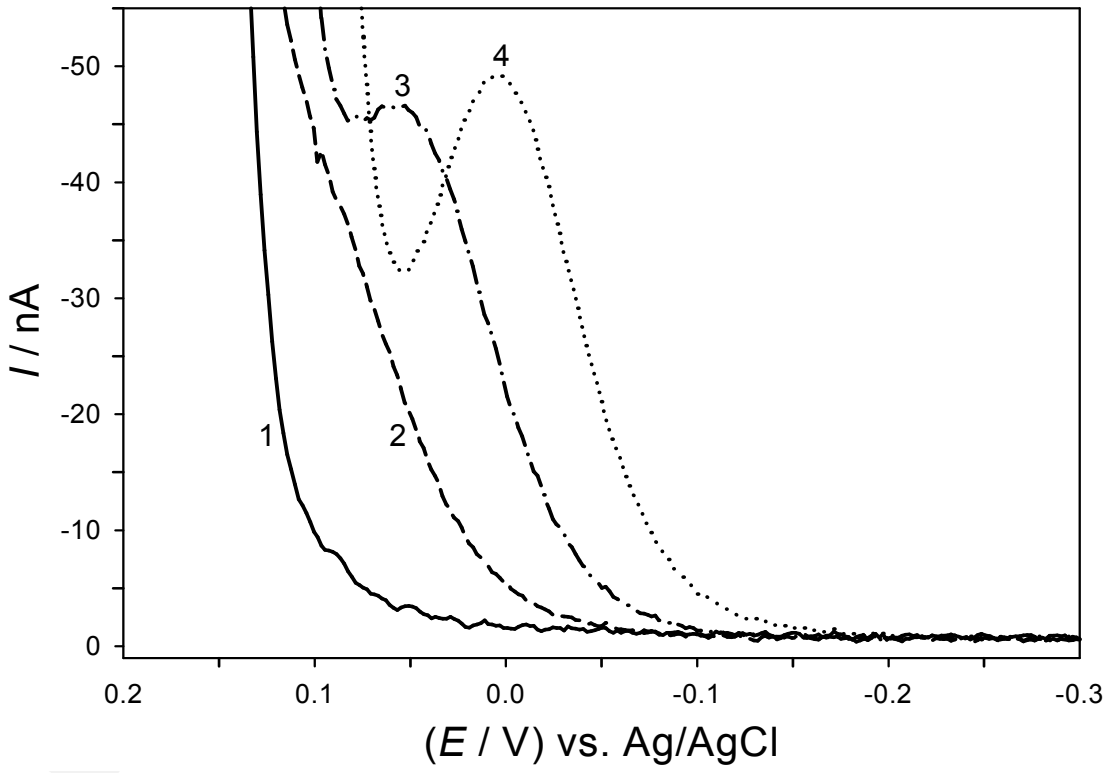

Figure 1. Voltamograms of iron(III) one-electron reduction. $[Fe^{3+}]_{added} = 2.5\times10^{-5}$ mol L^{-1}, $[Gly]_{tot}$ = 0.5 mol L^{-1}, I = 0.6 mol L^{-1} in $NaClO_4$ at 25±1 ºC. Line 1: no iron added, pH = 6.0; line 2: pH = 6.0; line 3: pH = 6.5; line 4: pH = 7.0. Technique: DPCV; E_{inc} = 2 mV; a = 25 mV; t_p = 0.05 s; t_{int} = 0.2 s.

Above the pH = 8.0, iron(III) hydrolysis is highly pronounced regardless of glycine concentration, so the pH of 7.3 has been chosen for experimental work. Also, iron(III)

concentrations higher than 2.5×10^{-5} mol L^{-1} would promote the process of hydrolysis [2].

3.2. Determination of the new stability constants

A solution of 2.5×10^{-5} mol L^{-1} Fe(III) ions in glycine at the pH 7.3, $I = 0.6$ mol L^{-1} in $NaClO_4$, measured by DPCV expresses a reduction peak (Fig. 2, voltamograms 1-5), corresponding to the reduction of Fe(III)-glycine complexes which appear around -0.02V vs. Ag/AgCl.

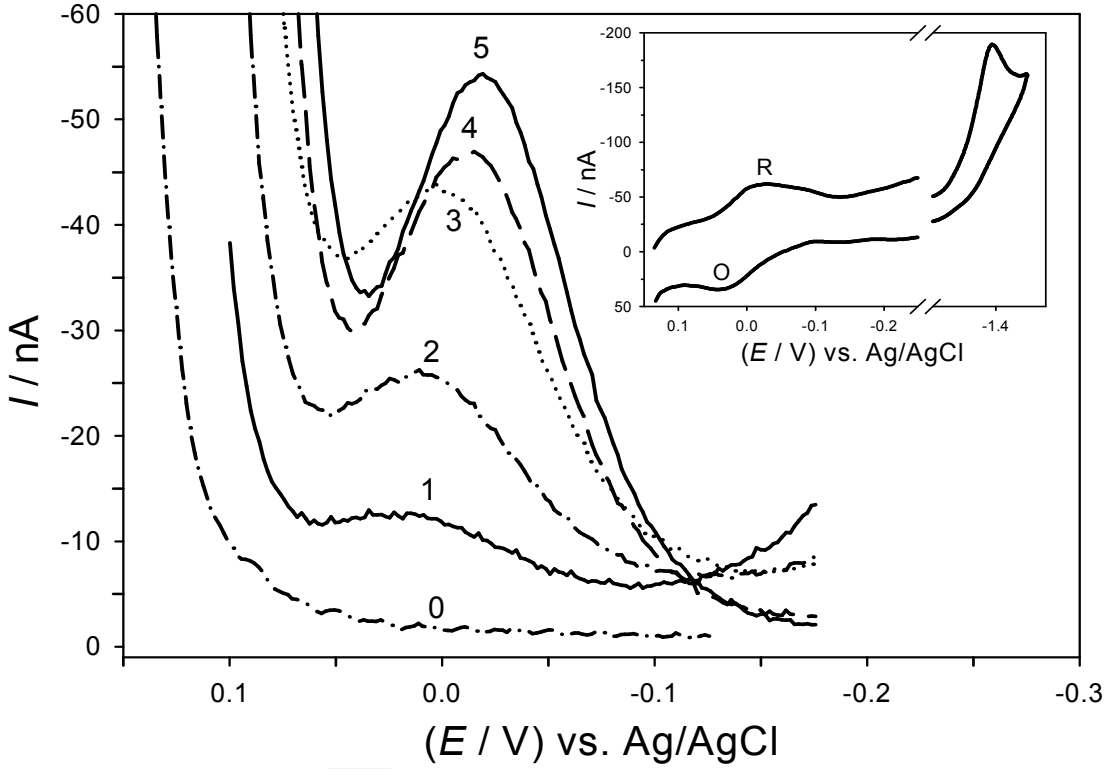

Figure 2. Voltamograms of iron(III) one-electron reduction (first voltamograms scanned 5 seconds after iron(III) addition). $[Fe^{3+}]_{added} = 2.5\times10^{-5}$ mol L^{-1}; $I = 0.6$ mol L^{-1} in $NaClO_4$; pH = 7.3 at 25±1 ºC. Line 0: without glycine; line 1: $[Gly]_{tot} = 0.1$ mol L^{-1}; line 2: $[Gly]_{tot} = 0.2$ mol L^{-1}; line 3: $[Gly]_{tot} = 0.3$ mol L^{-1}; line 4: $[Gly]_{tot} = 0.4$ mol L^{-1}; line 5: $[Gly]_{tot} = 0.5$ mol L^{-1}. Technique: DPCV; $E_{inc} = 2$ mV; $a = 25$ mV; $t_p = 0.05$ s; $t_{int} = 0.2$ s. **Inset** - cyclic voltamogram of 2.5×10^{-5} mol L^{-1} Fe^{3+} added in total 0.5 mol L^{-1} glycine ($I = 0.6$ mol L^{-1} in $NaClO_4$); $E_{inc} = 2$ mV, scan rate (v) = 0.1 V s^{-1}.

The peak corresponding to Fe(III)-Gly → Fe(II)-Gly reduction appears to be reversible. In differential pulse voltammetric technique, measurement of the peak half-width and comparing the value with the theory, is probably the simplest way to assess the reversibility of the electrode process. Peak half-width values ($w_{1/2}$) of iron(III)-glycine reduction peaks in Fig. 2 are ~90 mV, which is, according to differential pulse

voltammetric theory [20], indication for one-electron, reversible reduction process at the mercury drop. At small pulse amplitudes (a < 100 mV), $w_{1/2} = 3.52 \times RT/nF$ (at 25 ºC: $w_{1/2} = 90.4/n$ mV, n = number of electrons exchanged). Peak half-widths larger than $90.4/n$ mV indicate quasireversible or irreversible electrode process. Reversible nature of one-electron iron(III) reduction in glycine solution led to the conclusion that this system contained labile iron(III) complexes. Also, cyclic voltammetry of iron(III) glycine system showed the difference of around 60 mV between the reduction (R) and the oxidation (O) peak currents, which clearly indicates reversible character [20] of iron(III) one-electron redox process in glycine solution (Figure 2, Inset). At the CV potential around -1.4 V, iron(II) reduction peak of two-electron irreversible process takes place. The presence of iron(II) is a result of the iron(III) reduction at the mercury electrode.

Voltamogram 0 in Fig. 2 represents the addition of 2.5×10^{-5} mol L^{-1} Fe(III) ions in perchlorate water solution without glycine. There is no reduction peak of iron (III) because of its rapid hydrolysis (formation of iron(III)-hydroxides) and the subsequent precipitation. Consequent repeating of measurements for each glycine concentration of freshly prepared solution showed the kinetics of the iron(III)-Gly exchange for iron(III)-OH complexes and the degradation of iron(III)-glycine. With 0.5 mol L^{-1} of glycine decrease of reduction peaks was not observed, i.e. after 24 hours from iron(III) addition peak heights remained constant, which indicates that the processes of hydrolysis have not taken place in detectable extent. This was not the case with 0.4, 0.3, 0.2 and 0.1 mol L^{-1} of glycine. We were able to record only 16, 15, 12 and 5 consequent scans of iron(III) reduction in 0.4, 0.3, 0.2 and 0.1 mol L^{-1} glycine solutions, respectively (Table 1). As the glycine concentrations became lower (from 0.4 to 0.1 mol L^{-1}), hydrolysis process was predominant over the iron(III) glycine complexes formation, so after the mentioned number of repetitions no further iron(III) reduction peak has been observed. When the concentrations of total glycine were less than 0.1 mol L^{-1}, it was not possible

to measure the Fe(III)-Gly reduction because of a too fast ferri-glycine exchange for hydroxides. This determined the possible range of ligand concentrations, which appeared to be most functional from 0.1 to 0.5 mol L^{-1} of the total glycine added (Fig. 2, voltamograms 1-5). However, peak reduction potentials of the repeated measurements for each glycine concentration did not show any tendency of changing their position (Table 1), despite the decrease of reduction peak, so it could be concluded that a distribution of iron(III) glycine complexes in investigated solution was not changed.

Using the glycine dissociation constants from the literature [11-14]:

$\log K(H_2L^+) = \log ([H_2L]^+/[HL][H]^+) = 2.39 \pm 0.05$ and

$\log K(HL) = \log ([HL]/[L]^-[H]^+) = 9.54 \pm 0.03$, where HL is $C_2H_5NO_2$, the concentrations of the dissociated ("free") ligand $[L]^-$ were calculated for the given pH of the experiment (Table 1). Table 1 presents also the potentials of the reduction peaks obtained by the DPCV measurements along with the statistics of the repeated measurements.

Table 1. Mean values of reduction peak potentials of Fe(III)-Gly complex with 95% confidence interval c.i. and ΔE for n repeated measurements for different glycine concentrations; pH = 7.3, ionic strength I = 0.6 mol L^{-1} in $NaClO_4$, at 25±1 ºC, $[Fe^{3+}]_{added} = 2.5\times10^{-5}$ mol L^{-1}.

$[Gly]_{TOT}$ / mol L^{-1}	$10^3 \times [Gly]_{free}$ / mol L^{-1}	E_p ± c.i. / V vs. Ag/AgCl	ΔE / V	n
0.1	0.53	-0.0078 ± 0.0014	0.5683	5
0.2	1.07	-0.0169 ± 0.0009	0.5774	12
0.3	1.6	-0.0252 ± 0.0004	0.5857	15
0.4	2.14	-0.0305 ± 0.0005	0.5910	16
0.5	2.67	-0.0330 ± 0.0004	0.5935	21

The potential of iron(III) one-electron reversible redox system is given by the Nernst expression [21]:

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

where $E_{½}$ is the half-wave reversible potential, which is calculated from the equation $E_{½} = E_p + a/2$ [20] (E_p is taken from Table 1, a is a pulse amplitude); E^o (0.77 V) is the standard potential for the one-electron reduction of Fe^{3+} free, non-complexed ions; R = 8.314 JK^{-1} mol^{-1}; F = 96500 C mol^{-1} and T = 298 K. Presuming the existence of three iron(III) complexes ($[FeGly]^{2+}$, $[Fe(Gly)_2]^{+}$ and $Fe(Gly)_3$) and taking into account the iron(II)-Gly complexing constants known from the literature [13,14] we proposed the following model:

$$E_{1/2} = E^{\circ} - \frac{RT}{F} \ln \frac{\left(1 + \beta_{13}[Gly] + \beta_{23}[Gly]^2 + \beta_{33}[Gly]^3\right)}{\left(1 + \beta_{12}[Gly] + \beta_{22}[Gly]^2 + \beta_{32}[Gly]^3\right)}$$

where β_{13}, β_{23} and β_{33} are cumulative stability constants for iron(III)-glycine complexes, and β_{12}, β_{22} and β_{32} are cumulative stability constants for iron(II)-glycine complexes.

The value of the standard potential, E^o, for the one-electron reduction of Fe^{3+} free ions vs. hydrogen electrode of 0.77 V [22] was recalculated to Ag/AgCl saturated reference electrode (used in the experiment), which is 0.573 V. Difference between the standard potential and the experimental peak potentials is defined as $E^o - E_{½} = \Delta E$, and ΔE (Table 1) was used in further calculations. A program in Microsoft® Excel 2002 was designed in order to fit the measured data to the proposed model with the fixed values of the previously known constants (Table 2). The best fitting was achieved with:

$$\log \beta_{23} = \frac{[Fe(Gly)_2]^+}{[Fe]^{3+}\left([Gly]^-\right)^2} = 17.21 \pm 0.03 \text{ and}$$

$$\log \beta_{33} = \frac{Fe(Gly)_3}{[Fe]^{3+}\left([Gly]^-\right)^3} = 20.19 \pm 0.02$$

where ± values are 95% confidence intervals.

Table 2. Logarithms of cumulative stability constants [13,14] for iron(III) - glycine and iron (II) - glycine systems. * - experimentally obtained in this work.

	$\log \beta_1$	$\log \beta_2$	$\log \beta_3$
Fe(III) - Gly	8.57	17.21±0.03*	20.19±0.02*
Fe(II) - Gly	3.73	7.65	8.87

Figure 3 shows the fitting curve obtained with the calculated stability constants (Table 2) and the data points measured at the pH = 7.3 for the ΔE vs. log $[Gly]_{free}$.

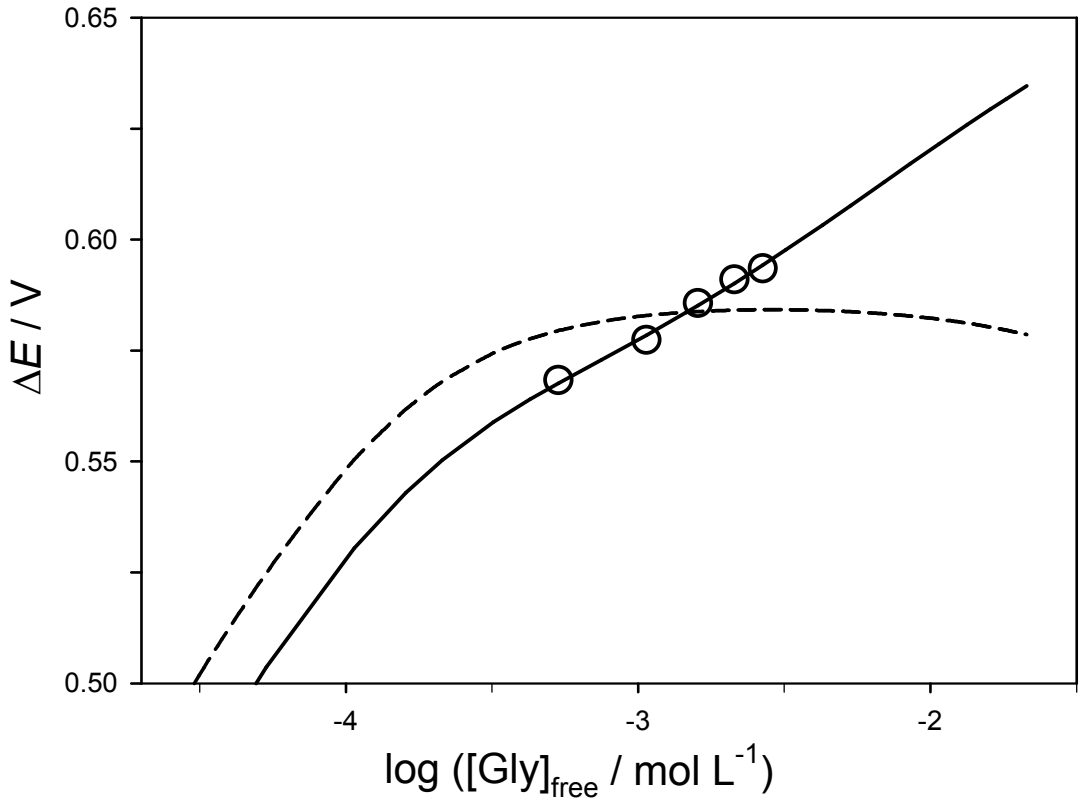

Figure 3. Dependence of ΔE on log $[Gly]_{free}$ for the calculated and literature stability constants (Table 2) - solid line; experimental points (Table 1) - circles. Fitting curve for the Fe(III)-Gly model system of maximum 1:2 coordination - dashed line.

For some transition metals the cumulative stability constants for three ligands of the same species are not reported [13,14], so it is possible that they form complexes with two ligands at the most. To test that possibility for our system, a model with two glycine ligands was tested as well. The best fitting was obtained for the literature value of log β_{13} = 8.57 [13,14] and the calculated log β_{23} = 17.59. The fitting curve is presented in Fig. 3 - dashed line. One look at the slope of the curve is enough to reject two ligand model as a probable one. In favour of that result speaks the conclusion of Perrin [11] that under his published experimental conditions (pH from 0.77 to 3.35 and more than 8×10^{-3} mol L^{-1} of iron(III) ions) no evidence of the complexes higher than 1 : 1 was obtained nor could have not been obtained, while higher ferric complexes (1 : 2 and 1 : 3) might be expected if other experimental conditions were used.

Suitable test found in the literature [10] can confirm the values of the proposed stability constants. Approximate equation $\log \beta_1 = ½(\log \beta_2 - 1)$ enables the comparison of stability constants. When the literature value of the iron(III) - glycine stability constant $\beta_1 = 8.57$ is put in the equation, the obtained $\log \beta_{23}([Fe(Gly)_2]^+)$ is 18.14, which is in a good matching with the proposed constant $\beta_{23}([Fe(Gly)_2]^+) = 17.21 \pm 0.03$. Also, cumulative stability constant of $Fe(oxalate)_3$ complex found in literature [23] is $\beta_{33} = 20.46$, which is almost identical with our calculated $\log \beta_{33} = 20.19 \pm 0.02$ for $Fe(Gly)_3$ complex.

Chemical distribution of iron(III) in glycine water solution, as a function of pH, has been calculated and proposed. The distribution, presented in Fig. 4, was made according to the stability constants found in this work and to the literature values [13,14], all of which are presented in Table 2.

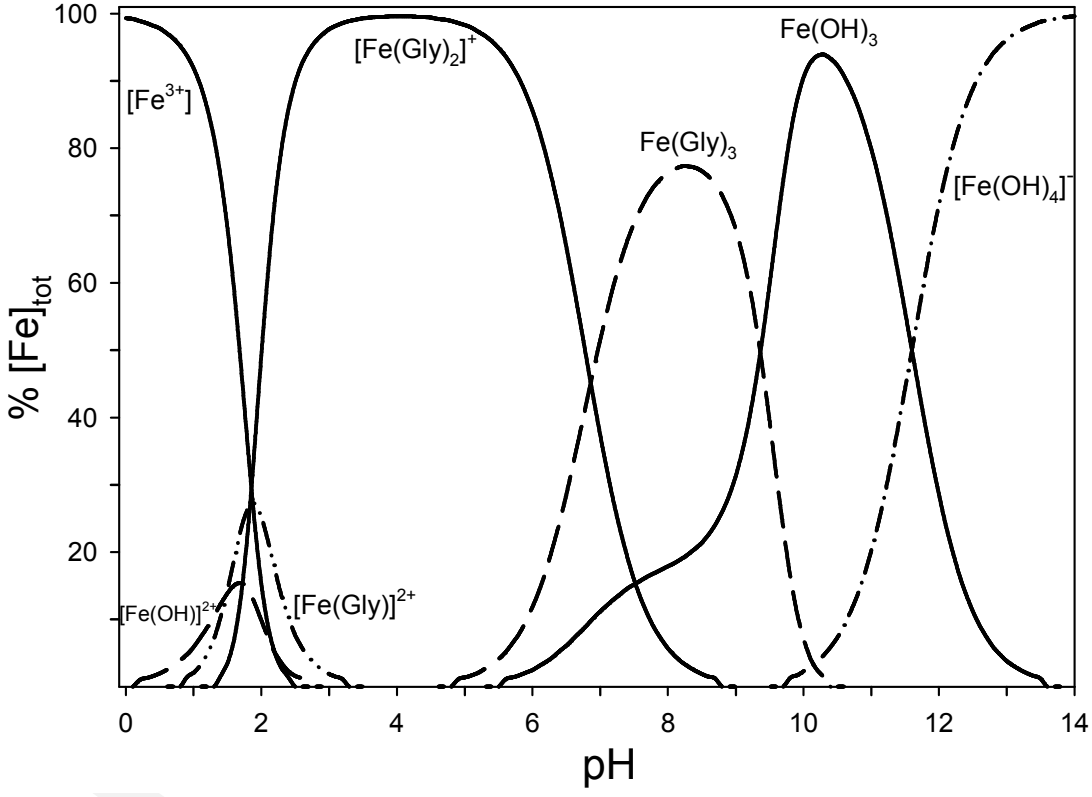

Figure 4. Chemical distribution of iron(III)-glycine system as a function of pH. $[Fe^{3+}]_{added} = 2.5 \times 10^{-5}$ mol L^{-1}, $[Gly]_{tot} = 0.5$ mol L^{-1}, $I = 0.6$ mol L^{-1}. Distribution was calculated by using MINEQL$^+$ computer program [24] with the determined and literature iron(III)-glycine (shown in Table 2) and literature iron(III)-hydroxide stability constants [13].

Calculation was carried out using MINEQL$^+$ chemical equilibrium program [24] with 0.5 mol L^{-1} of glycine and 2.5×10^{-5} mol L^{-1} of iron(III) ions and I = 0.6 mol L^{-1}. As mentioned previously in the paper, experimental conditions at the pH = 7.3 and 0.5 mol L^{-1} of total glycine kept the system in equilibrium where hydrolysis processes were not detected. To achieve better accuracy of the complex system, hydroxide species have been introduced into calculus. One can observe strong influence of iron(III) hydrolysis at the more basic pH values, where $Fe(OH)_3$ and $[Fe(OH)_4]^-$ species are well predominant, which was one of the reasons why we kept our pH at 7.3. It can also easily be seen that at this pH value iron(III) complexes $[Fe(Gly)_2]^+$ and particularly $Fe(Gly)_3$, are predominant as the fractions of total iron(III) in the system, which enabled us to determine the stability constants of ferric complexes of the 1 : 2 and 1 : 3 coordinations.

4. CONCLUSIONS

Choosing voltammetry as an analytical tool for stability constants determination allowed the work with lower concentrations of iron(III) (10^{-5} mol L^{-1}), and higher pH value than those reported previously in the literature, which enabled the formation of higher coordination (1 : 2 and 1 : 3) complexes of the iron(III) - glycine system. The determination of the stability constants of dissolved iron(III) - glycine system in water solution by using differential pulse cathodic voltammetry (DPCV) and cyclic voltammetry (CV) was carried out on a static mercury drop electrode (SMDE). Experimental conditions for the iron(III)-glycine system stability constants determination were found to be the most functional at I = 0.6 mol L^{-1} in $NaClO_4$, pH = 7.3 and 25±1 ºC, where the added concentration of iron(III) ions was 2.5×10^{-5} mol L^{-1} and the concentrations of total glycine varied from 0.1 to 0.5 mol L^{-1}. The investigated labile iron(III) - glycine system shows a one-electron reversible reduction, which allowed to determine stability constants. The stability constants of the $[Fe(Gly)_2]^+$ and $Fe(Gly)_3$ complexes, not mentioned in the literature so far, were found to be log β_{23} =

17.21±0.03 and log β_{33} = 20.19±0.02, respectively. According to the constants found, the chemical distribution of iron(III) complexes with glycine (2.5×10^{-5} mol L^{-1} Fe(III) ions and 0.5 mol L^{-1} of the total glycine at I = 0.6 mol L^{-1}), as a function of pH, has been calculated and proposed.

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