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INFLUENCE OF CONCENTRATION PARAMETERS OF THE HOMOGENEOUS SYSTEM Fe(II)-Fe(III)-GLICINE-Na(H)ClO$_4$-H$_2$O ON THE COMPOSITION OF THE COMPLEXES FORMED

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Abstract: *We studied the complexation processes in the system Fe(II) - Fe(III) - glycine - Na(H)ClO$_4$ - H$_2$O at temperature 308.16 K, solution ionic strength 0.75(Na(H)ClO$_4$), $C_{Fe(III)} = C_{Fe(II)} = 1\text{-}10^{-3}$ and $C_{Gly} = 3\cdot10^{-3}$ mol/l in the pH range 0.5-8.5 by the Clark-Nikolsky method. Therefore, we obtain an experimental curves of system EMF dependence on concentration parameters: pH, $pC_{Fe(III)}$, $pC_{Fe(II)}$, pC_L. We also obtain the formation of the studied system coordination compounds of* ***Fe(III)*** *composition: $[FeHL(H_2O)_5]^{3+}$, $[Fe(HL)_2(H_2O)_4]^{3+}$, $[Fe_2(HL)_2(OH)_2(H_2O)_8]^{4+}$, $[Fe^{III}Fe^{II}(HL)_2(OH)_2(H_2O)_8]^{3+}$, as well as* ***Fe(II):*** *$[Fe(HL)(H_2O)_5]^{2+}$, $[Fe(HL)(OH)((H_2O)_4]^{+}$, $[Fe^{II}Fe^{III}(HL)_2(OH)_2(H_2O)_8]^{3+}$. To calculate the constants of complex formation we used the method of successive approximation of the theoretical and experimental oxidation functions using the Excel program.*

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Introduction

Glycine is a bidentate biologically active ligand. It can co-ordinate at the amino and carboxylic groups to form homonuclear, biuclear and heteronuclear complexes with metal ions [1].

The study of the protolytic properties of glycine under experimental conditions of the formation of coordination compounds and the construction of the distribution diagram of the amino acid ionic forms shows that the cationic form of glycine $(NH_3CH_2COOH)^+$ is present in solution only in mixture with bipolar ion $(NH_3CH_2COO)^{\pm}$ at any pH<4.0, in the range of pH>4.0 it exists as a zwitter ion and at pH>9.0 as the anion $(NH_2CH_2COO)^-$ [2].

We have shown by potentiometry at a solution ionic strength of 0.01 mol/l and at high pH values the formation of complexes of the composition $[FeL]^+$ and $[FeL_2]^0$, where L^- is the glycinate ion [3]. We calculated step constants of instability equal to $5.0\cdot10^{-5}$ and $3.0\cdot10^{-4}$, respectively.

In [4] the formation of glycinate iron (II) complexes was shown for the Fe^{II}–Fe^{III}–Gly system at ionic strength 0.5 mol/l and in a wide range of pH = 1.4-10.6, $C_{Fe(II)} = C_{Fe(III)} = 1\cdot10^{-4}$; $C_{Gly} = 1\cdot10^{-2}$ mol/l: $[FeHL(H_2O)_5]^{2+}$ ($\lg\beta$ = -0.70±0.04), $[FeL(H_2O)_4]^+$ ($\lg\beta$ = 6.00±0.02), $[Fe_2(L)_4(OH)_2(H_2O)_6]^{2-}$ ($\lg\beta$ = 3.98±0.02), $[Fe(OH)(H_2O)_5]^+$ ($\lg\beta$ = -9.50±0.03), and iron (III): $[FeOH]^{2+}$ ($\lg\beta$ = -2,70±0,02), $[FeHL]^{3+}$ ($\lg\beta$ = 1,00±0,04), $[Fe(HL)_2]^{3+}$ ($\lg\beta$ = 0,70±0,04), $[Fe(HL)_2OH]^{2+}$ ($\lg\beta$ = 1,20±0,03), $[Fe_3L_6(OH)_2]^+$ ($\lg\beta$ = 42,00±0,02), $[Fe_2L_4(OH)_2]^0$ ($\lg\beta$ = 3,28±0,02), $[Fe(OH)_2]^+$ ($\lg\beta$ = -4,59±0,04).

The formation of glycinate complexes of trivalent iron with a zwitter ion of composition is shown at an ionic strength of 1.0 mol/l and a temperature of 298 K: $[Fe(HL^{\pm})]^{3+}$ ($\lg\beta$ = 1.47), $[Fe(HL^{\pm})_2]^{3+}$ ($\lg\beta$ = 3.49), $[Fe(HL^{\pm})A]^{2+}$ ($\lg\beta$ = 0.32) [5].

The purpose of this study is to investigate the complexation processes in the system Fe(II) - Fe(III) - glycine - $Na(H)ClO_4$ - H_2O at temperature 308.16 K and solution ionic strength I = 0.75 mol/l.

Experimental part

The Clark-Nikolsky oxidation potential method was used to study the formation of glycinate iron (II) and iron (III) complexes [6-8]. In our experiments we used Fe(III) and Fe(II) perchlorates. Their initial concentrations were determined by trilometric and bichromatometric methods, respectively [9, 10]. We verified the concentration of the initial equimolecular mixture of Fe(II) and Fe(III) perchlorates by a bichromatometric method by reducing Fe(III) to Fe(II), and using a Johnson reducer [11]. We determined the concentration of $NaClO_4$ prepurified by recrystallization by weight method [12]. The chloric acid $HClO_4$ of the "chemically pure" grade was used without pre-treatment. We obtained the concentration of sodium hydroxide by direct titration with 0.1 M hydrochloric acid HCl solution from fixonal [13].

According to the method of oxredmetry [6-8] it is necessary to obtain experimental dependences of the electromotive force (E, mV) on the following concentration variables: **pH**(-lg$h$), $\mathbf{p}\boldsymbol{C}_{\mathbf{Fe(III)}}$(-lg$C_{Fe(III)}$), $\mathbf{p}\boldsymbol{C}_{\mathbf{Fe(II)}}$(-lg$C_{Fe(II)}$) and $\mathbf{p}\boldsymbol{C}_{\boldsymbol{L}}$(-lg$C_{HL}$), where h is the activity of hydrogen ions; $C_{Fe(III)}$ is the concentration of the oxidized form of the metal; $C_{Fe(II)}$ is the concentration of the reduced form of the metal, and C_{HL} is the concentration of glycine.

The experimental procedure is to measure the EMF of galvanic elements I and II.

$$Pt/Fe^{2+}, Fe^{3+}, Gly, H_2O//Cl^-, AgCl\ /Ag(I)$$
$$Pt/Fe^{2+}, Fe^{3+}, Gly, H_2O/glass/0{,}1\text{н}\ HCl/AgCl\ /Ag(II)$$

We measured the EMF of the galvanic cells on an EV-74 ionometer with an accuracy of ±1 mV. We monitored the pH values of the solutions with a glass electrode using a calibration curve. The values of the standard potential of the silver chloride electrode were taken from the reference book [14] and the calculated value $\nu = 2.303RT/F$ at 308.16 K is 59.16 mV.

Discussion of the results of the study

The oxredmetry method is widely used in the study of complexation reactions [4, 15-17].

The complexation reaction of Fe (II) and Fe (III) with all forms of glycine, taking into account hydrolytic processes, can be represented as

$$q\mathrm{Fe(H_2O)_6}^{3+} + x\mathrm{L}^- + (s\text{-}k)\mathrm{H_3O^+} + (y\text{-}x\text{-}s)\mathrm{H_2O} = \mathrm{Fe}_q\mathrm{H}_s\mathrm{L}_x\mathrm{(OH)}_y + \mathrm{(H_2O)}_n{}^{(3q+s-y-x)} \qquad (1)$$

$$p\mathrm{Fe(H_2O)_6}^{2+} + l\mathrm{L}^- + (\mathrm{l}\text{-}\upsilon)\mathrm{H_3O^+} + (\upsilon\text{-}l\text{-}s)\mathrm{H_2O} = \mathrm{Fe}_p\mathrm{H}_s\mathrm{L}_l\mathrm{(OH)}_\upsilon + \mathrm{(H_2O)}_n{}^{(2p+s-\upsilon-l)}, \qquad (2)$$

where q is the iron (III) complex nuclearity; l is the number of ligands; s is the number of protonated ligand groups in the complex; k is the number of coordinated OH^--groups; p is the iron (II) complex nuclearity; υ is the number of coordinated OH^--groups. These particles are basic because they all coexist in the system under study, and influence each other.

In order to determine the composition of complexes formed in the system under study as well as the values of basic particles (q, p, s, l, k) according to the theory of oxredmetry method, we obtained experimental dependencies of EMF (E, mV) on pH of the solution at ionic strength 0.75 mol/l and different concentrations of Fe (Fig. 1).

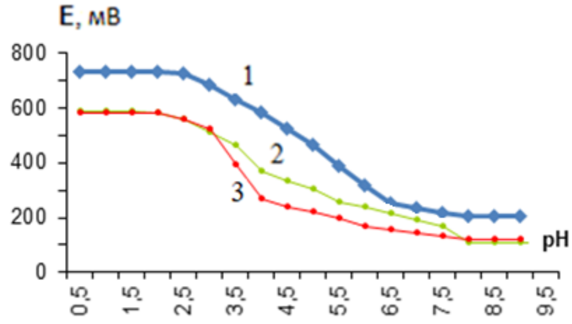

Fig. 1. The dependence of EMF on pH in the system: Fe(II) – Fe(III) – Glycine – $Na(H)ClO_4$ – H_2O at the temperature 308.16 K and the ionic strength of the solution 0,75; $C_{Fe(III)} = C_{Fe(II)} = 1\cdot10^{-3}$. The curves relate to: 1 - $C_{Fe(III)} = C_{Fe(II)} = 1\cdot10^{-4}$; 2 - $C_{Gly} = 3\cdot10^{-3}$; 3 - $C_{Gly} = 5\cdot10^{-3}$ mol/l

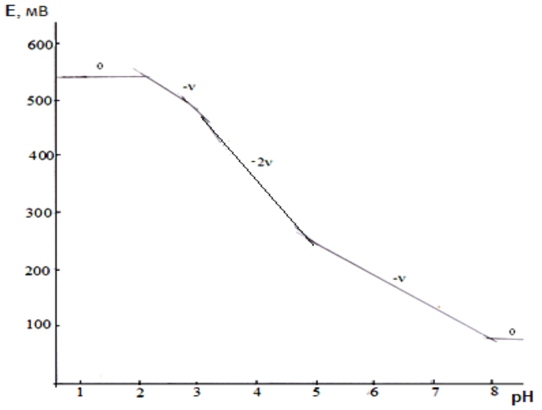

Fig. 2. The dependence of EMF (E, mV) on pH for the system Fe(II) – Fe(III) – Gly – H_2O at $C_{Fe(II)} = C_{Fe(III)} = 1\cdot10^{-3}$, $C_{Gly} = 3\cdot10^{-3}$ and $I = 0.75$ mol/l.

The results show that the system's EMF does not change with an increase in pH to 2.0. According to the oxredmetry theory of the method, there is no complexation process. The system's EMF then decreases. According to the Nernst equation, this indicates the occurrence of a complexation process, which takes place up to a pH of about 9.0. It should be noted that as the concentration of Fe (III) decreases, some of the metal in the oxidized form is consumed to form the complex, the amount of free metal decreases and the electrode potential (EMF as well) decreases. On the other hand, as the concentration of the reduced metal form decreases, the electrode potential increases according to the Nernst equation and the system EMF increases (curves 1-3, Fig. 1).

In all experimental dependences obtained E on pH, slopes are formed, which, according to the theory of oxredmetry, correspond to the successive formation of linear areas with tangents of angle: 0, -ν, -2ν, -ν, 0, indicating a stepwise complexation of Fe(III) and Fe(II) (Fig. 2).

These dependencies allow the total number of hydroxyl and glycinate coordinated ligands around the central complexing ion to be determined.

We found that the process of complexation in the studied system is stepwise and proceeds in a wide pH range from 2.0 to 9.0. The system then becomes unstable, and the system's EMF drops sharply.

Experimental curves for the dependence of EMF on the concentration index of the oxidized form of iron (pC_{ox}) were obtained. They are linear with a slope of - ν (curves 1, 3-4, Fig. 3) and -ν/2 (curve 2, Fig. 3). According to the theory of the method, it indicates the formation of mono- and bi-nuclear Fe (III) coordination compounds in the solutions under study.

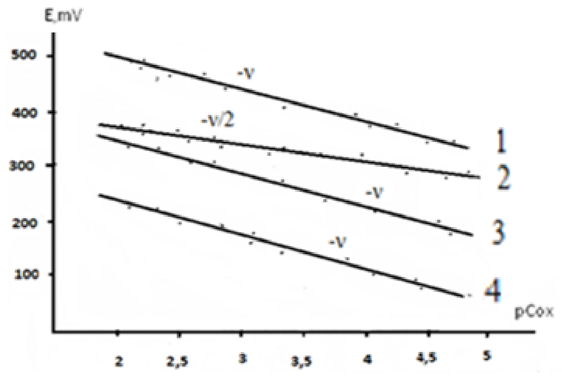

Fig. 3. The dependence of EMF (E, mV) on $pC_{Fe\ (III)}$ for the system Fe (II) – Fe (III) – Gly – H_2O at $T = 308.16$ K; $I = 0.75$ and $C_{Gly} = 3 \cdot 10^{-3}$ mol/l. The curves relate to pH: 1 – 3.0; 2 – 4.5; 3 – 6.0; 4 – 8.0

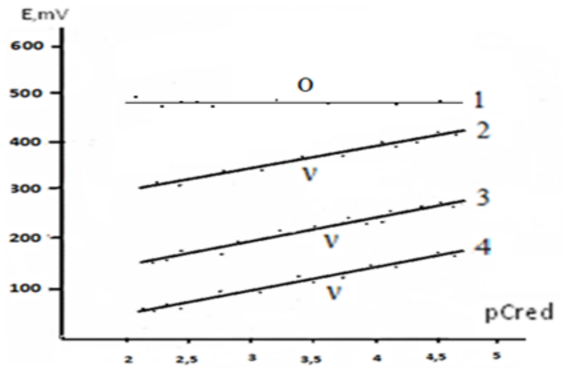

Fig. 4. The dependence of EMF (E, mV) on $pC_{Fe\ (II)}$ for the system Fe(II) – Fe(III) – Gly – H_2O at $T = 308.16$ K; $I = 0.75$ and $C_{Gly} = 3 \cdot 10^{-3}$ mol/l. The curves relate to pH: 1 – 3.0; 2 – 4.5; 3 – 6.0; 4 – 8.0

Through the experimental points of E-pC_{red} dependences at different pH we can draw one linear section with the angle coefficient ν, which corresponds to the formation of mononuclear iron (II) coordination bonds in the whole studied pH interval (Fig. 4).

The number of glycine molecules entering the inner coordination sphere as ligands was established from a combined consideration of the experimental E-pC_L dependences (Fig. 5).

In the curves shown (see Fig. 5), depending on the pH and glycine concentration, straight lines can be identified with the angular coefficients ν, 2ν. A comparison of these slopes with the theory of the method shows that one and two ligands can be included in the coordination compounds as the concentration of glycine increases.

The composition of the resulting coordination compounds was established by analyzing the slopes of the experimental curves and the stoichiometric matrix of their angle coefficient values (Tables 1, 2).

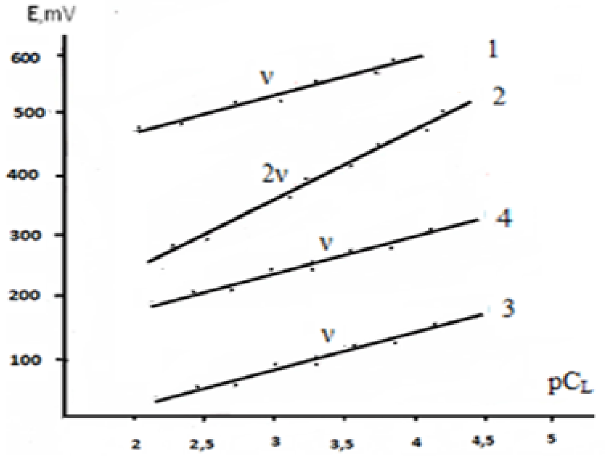

Fig. 5. The dependence of EMF (E, mV) on pC_L for the system Fe(II) – Fe(III) – Gly – H_2O at $T = 308.16$ K; $I = 0.75$ and $C_{Gly} = 3 \cdot 10^{-3}$ mol/l. The curves relate to pH: 1 – 3.0; 2 – 4.5; 3 – 6.0; 4 – 8.0

Table 1. Experimental values of angular coefficients of EMF dependences on concentration variables of Fe(II) – Fe(III) – glycine – water system for complexes **Fe(III)** at T = 308.16 K, I = 0.75; $C_{Fe(II)} = C_{Fe(III)} = 1 \cdot 10^{-3}$ and $C_{Gly} = 3 \cdot 10^{-3}$ mol/l

№, item n/a	Linear area on Ph scale	The slope of the EMF dependence on the concentration parameters				Composition of the compounds
		pH	pC_{ox}	pC_{red}	pC_L	
1	0.5–2.2	-	-	-	-	$[Fe(H_2O)_6]^{3+}$
2	2.0–3.5	-ν	-ν	-	ν	$[FeHL(H_2O)_5]^{3+}$
3	3.5–5.0	-2ν	-ν	-	2ν	$[Fe(HL)_2(H_2O)_4]^{3+}$
4	5.0–6.8	-2ν	-ν/2	-	ν	$[Fe_2(HL)_2(OH)_2(H_2O)_8]^{4+}$
5	6.8–8.5	-2ν	-ν	ν	ν	$[Fe^{III}Fe^{II}(HL)_2(OH)_2(H_2O)_8]^{3+}$

Table 2. Experimental values of angular coefficients of EMF dependences on concentration variables of Fe(II) – Fe(III) – glycine – water system for complexes **Fe(II)** at T = 308.16 K, I = 0.75; $C_{Fe(II)} = C_{Fe(III)} = 1 \cdot 10^{-3}$ and $C_{Gly} = 3 \cdot 10^{-3}$ mol/l

№, item n/a	Linear area on Ph scale	The slope of the EMF dependence on the concentration parameters				Composition of the compounds
		pH	pC_{ox}	pC_{red}	pC_L	
1	0.5–3.5	-	-	-	-	$[Fe(H_2O)_6]^{2+}$
2	3.5–5.8	-2ν	-	ν	ν	$[Fe(HL)(H_2O)_5]^{2+}$
3	5.8–7.0	-2ν	-	ν	ν	$[Fe(HL)(OH)((H_2O)_4]^{+}$
4	7.2–8.5	-2ν	-ν	ν	ν	$[Fe^{II}Fe^{III}(HL)_2(OH)_2(H_2O)_8]^{3+}$

Based on the stoichiometric matrix, taking into account the first derivative of the general equation of the oxidation potential of the system from the concentration parameters, we made a chemical model of the equilibria existing in the system under study (Table 3).

Table 3. Chemical model of the ionic equilibrium system Fe(II) – Fe(III) – glycine – water at T = 308.16 K, I = 0.75; $C_{Fe(II)} = C_{Fe(III)} = 1 \cdot 10^{-3}$ и $C_{Gly} = 3 \cdot 10^{-3}$ mol/l

№, item n/a	Numerical valuesof model parameters					Composition of the compounds
	g	*p*	*s*	*l*	*k*	
	Fe(III)	Fe(II)	H	L	OH	
1	1	0	1	1	0	$[FeHL(H_2O)_5]^{3+}$
2	1	0	2	2	0	$[Fe(HL)_2(H_2O)_4]^{3+}$
3	2	0	2	2	2	$[Fe_2(HL)_2(OH)_2(H_2O)_8]^{4+}$
4	1	1	2	2	2	$[Fe^{III}Fe^{II}(HL)_2(OH)_2(H_2O)_8]^{3+}$
5	0	1	1	1	0	$[Fe(HL)(H_2O)_5]^{2+}$
6	0	1	1	1	1	$[Fe(HL)(OH)((H_2O)_4]^{+}$
7	1	1	2	2	2	$[Fe^{II}Fe^{III}(HL)_2(OH)_2(H_2O)_8]^{3+}$

The chemical models can be used for computer programming and calculation of model parameters of complex compound formation reactions: formation constants, molar fractions, maximum accumulation rates, and dominance areas.

Conclusions

1. Complexation processes in the Fe(II) – Fe(III) – glycine – water system were studied by the Clark-Nikolsky oxredmetry method at T = 308.16 K, I = 0.75; $C_{Fe(II)} = C_{Fe(III)} = 1 \cdot 10^{-3}$, $C_{Fe(II)} = C_{Fe(III)} = 1 \cdot 10^{-4}$ and $C_{Gly} = 3 \cdot 10^{-3}$, $C_{Gly} = 5 \cdot 10^{-3}$ mol/l.

2. We found that the process of complexation in the system under study is stepwise and proceeds in a wide pH range from 2.0 to 9.0. The system then becomes unstable, and the system's EMF drops sharply.

3. Experimental dependencies of the system EMF on concentration parameters pH, pC_{ox}, pC_{red}, pC_L, were obtained, a stoichiometric matrix (mathematical model) of numerical values of their slopes was composed, and their analysis allowed us to determine the composition of the forming complexes.

4. It is shown that in the system under study coordination compounds of **Fe(III)** composition are formed: $[FeHL(H_2O)_5]^{3+}$, $[Fe(HL)_2(H_2O)_4]^{3+}$, $[Fe_2(HL)_2(OH)_2(H_2O)_8]^{4+}$, $[Fe^{III}Fe^{II}(HL)_2(OH)_2(H_2O)_8]^{3+}$, а также **Fe(II):** $[Fe(HL)(H_2O)_5]^{2+}$, $[Fe(HL)(OH)((H_2O)_4]^{+}$, $[Fe^{II}Fe^{III}(HL)_2(OH)_2(H_2O)_8]^{3+}$.

5. We have found that increasing the pH to a neutral condition increases the possibility of formation of mixed ligand hydroxocomplexes of both **Fe(III)** and **Fe(II),** which is not observed in an acidic environment.

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