ISSN 0036-0236, Russian Journal of Inorganic Chemistry, 2018, Vol. 63, No. 4, pp. 561–566. © Pleiades Publishing, Ltd., 2018.
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The Effect of Concentration Parameters on Complexation in the Iron(0)–Iron(II)–Glycine–Water System

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Received June 24, 2016

Abstract—The processes of formation of iron(II) complexes in aqueous glycine solutions in the pH range of 1.0–8.0 at 298 K and ionic strength of 1 mol/L ($NaClO_4$) are studied using Clark and Nikolskii's oxidation potential method. The type and number of coordinated ligands, the nuclearity, and the total composition of the resulting complexes are determined. The following complex species are formed in the investigated system: $[Fe(OH)(H_2O)_5]^+$, $[FeHL(H_2O)_5]^{2+}$, $[Fe(HL)(OH)(H_2O)_4]^+$, $[Fe(OH)_2(H_2O)_4]^0$, $[Fe_2(HL)_2(OH)_2(H_2O)_8]^{2+}$, and $[Fe(HL)_2(H_2O)_4]^{2+}$. Their formation constants are calculated by the successive iterations method using Yusupov's theoretical and experimental oxidation function. The model parameters of the resulting coordination compounds are determined.

DOI: 10.1134/S0036023618040083

Glycine is the simplest aliphatic amino acid. It is known from the literature [1, 2] that glycine exists as a zwitterion (10%) and a cation (90%) at pH 1.2; as a zwitterion $HL^{\pm}$ at pH 3.3–8.9; and predominantly exists as an anion L^- at pH $\geq$ 10.9.

We studied glycine dissociation by pH-metric titration under the concentration conditions of Fe(II) complexation and determined its ionization constants: $pK_{a1} = 2.20 \pm 0.04$ and $pK_{a2} = 9.60 \pm 0.04$ [3], which were further used to calculate the formation constants of the resulting coordination compounds.

The data on composition of Fe(II)–glycine complexes are sparse; the literature data mostly refer to a limited range of concentrations. For example, formation of complexes of composition $[FeL]^+$ and $[FeL_2]^0$ (where L^- is the glycinate ion) was detected potentiometrically [4]. The calculated stepwise instability constants are 5.0×10^{-5} and 3.0×10^{-4}, respectively. The following iron(II)–glycinate complexes were shown to be formed in the Fe(II)–Fe(III)–Gly system at ionic strength of 0.5 mol/L in the pH range of 1.4–10.6, $C_{Fe(II)} = C_{Fe(III)} = 1 \times 10^{-4}$, CGly = 1×10^{-2} mol/L: $[FeHL(H_2O)_5]^{2+}$ ($\log\beta = -0.70 \pm 0.04$), $[FeL(H_2O)_4]^+$ ($\log\beta = 6.00 \pm 0.02$), $[Fe_2(L)_4(OH)_2(H_2O)_6]^{2-}$ ($\log\beta = 3.98 \pm 0.02$), and $[Fe(OH)(H_2O)_5]^+$ ($\log\beta = -9.50 \pm 0.03$) [5].

No other data on iron(II)–glycine complexes have been found in literature. There are studies focused on synthesis of platinum(II) complexes with α-amino acids (LH): glycine, alanine, and valine [6], as well as manganese(II) complexes with glycine(L), leucine (L'), and β-alanine (L'') [7]. Salishcheva et al. [6] reported the formation of a binuclear complex $[Pt_2(L)_2(NH_3)_4](NO_3)_2]$, where platinum atoms were bound via amino acid ligands. Osmanov [7] reported the formation of mixed ligand complexes $[MnCl_2(LL')] \cdot 2H_2O$, $[MnCl_2(LL'')] \cdot 2H_2O$, and $[MnCl_2(L'L'')] \cdot 2H_2O$ in neutral media.

We would like to mention that iron(II) complexes are of the greatest practical importance as they exhibit the strongest biological, physiological, and pharmaceutical properties. In this connection, studying complexation in the iron(0)–iron(II)–glycine–water system under various concentration conditions is relevant both in fundamental and practical context. We used Clark and Nikolskii's oxidation potential method [6], which has earlier been applied for other systems [5, 8–11].

EXPERIMENTAL

Iron(II) perchlorate prepared using the procedure described in [12] was used as an initial component. Concentration of Fe(II) ions was determined by titration with 0.1 N $K_2Cr_2O_7$ standard solution in the presence of sodium diphenylamine sulfonate as an indicator [13]. Aminoacetic acid of pure for analysis grade was used without additional purification. $NaClO_4$ salt was purified by recrystallization from saturated aqueous solution. Perchloric acid $HClO_4$ of chemical purity grade was used without preliminary purification. NaOH concentration was determined by direct

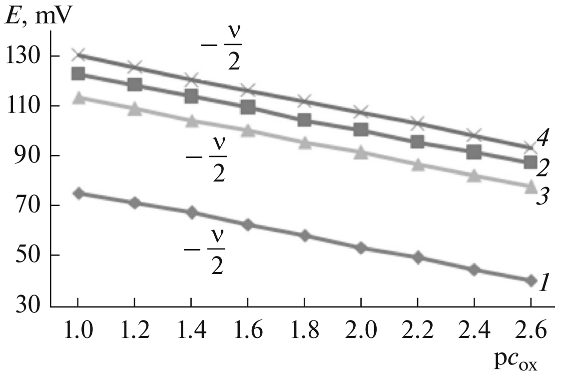

Fig. 1. EMF (E, mV) versus pc_{ox} for the Fe(II)–Gly–H_2O system at 298 K, I = 1.0; $c_{Gly} = 1 \times 10^{-3}$ mol/L. (*1*) $c_{Fe(II)} = 1 \times 10^{-3}$ (voltaic cell), $c_{Fe(II)} = 2 \times 10^{-2}$ (burette) mol/L, pH 3; (*2*) $c_{Fe(II)} = 1 \times 10^{-4}$ (voltaic cell), $c_{Fe(II)} = 2 \times 10^{-2}$ (burette) mol/L, pH 4; (*3*) $c_{Fe(II)} = 1 \times 10^{-5}$ (voltaic cell), $c_{Fe(II)} = 2 \times 10^{-2}$ mol/L, pH 5; and (*4*) $c_{Fe(II)} = 1 \times 10^{-6}$ (voltaic cell), $c_{Fe(II)} = 2 \times 10^{-2}$ (burette) mol/L, pH 6.

titration with 0.1 M HCl solution in the presence of phenolphthalein indicator. The titer of NaOH solution was determined using succinic acid [14].

The EMF of voltaic cells was measured with an EV-74 ion meter with an accuracy of 1–3 mV. The pH value in the system under study was monitored using a glass electrode precalibrated using standard buffer solutions; measurement accuracy was 0.05 pH units. The potential of silver/silver chloride electrode and the $\nu = 2.303RT/F$ value at 298 K were taken from a handbook [15]. Before each experiment, the solutions with immersed electrodes and connecting vessels were thermostated for 30 min under a flow of purified nitrogen.

The EMF was measured for the following voltaic cells:

Fe^0/test solution//Cl^-,AgCl/Ag (I),

Ag,AgCl/HCl/glass/test solution//KCl/AgCl,Ag (II).

The metal electrode used was stainless steel resistant to corrosion in air, water, and some aggressive media. The electrode was made of low-carbon steel 10.

The electrode structure was determined by microstructural analysis using an MIM-7 metallographic microscope. The electrode consists of perlite (a mechanical mixture of soft lamellae or grains of cementite and ferrite containing 0.8% C, which is known as eutectoid steel) and ferrite (Fe–C interstitial solid solution). The ratio between the electrode components was 1 : 9 (10% perlite and 90% ferrite). Carbon content in perlite and ferrite was 0.8 and 0.02%, respectively. The total carbon content was calculated using the formula:

$$\begin{aligned} C &= (F_f 0.02 + F_p 0.8)/100 \\ &= (90 \times 0.02 + 10 \times 0.8)/100 = 0.098\%, \end{aligned}$$

where F_f is the cross-sectional area of ferrite and F_p is the cross-sectional area of perlite. The electrode grade was verified by calculating the carbon content in it.

RESULTS AND DISCUSSION

The reaction of complexation of iron(II) with all glycine species, with allowance for hydrolysis, can be shown using the equation:

$$\begin{aligned} &q[Fe(H_2O)_6]^{2+} + lH_sL + kH_2O \\ &= [Fe_q(H_sL)l(OH)k(H_2O)_j]^{2q-k-l+s} \qquad (1) \\ &+ kH_3O + lH_2O, \end{aligned}$$

where q is the nuclearity of iron(II) complexes; l is the number of ligands (L^-), k is the number of coordinated OH groups; and s is the number of protons in the complex.

Taking into account Eq. (1) and the expression for equilibrium constants, the equation for the electromotive force for the voltaic cell is written as:

$$\begin{aligned} E &= E^0 + \frac{\nu}{2}\log c_0 \\ &+ \frac{\nu}{2}\log\sum_1^q\sum_0^s\sum_0^l\sum_0^k q\beta_{qslk}^{\frac{1}{q}} G_{qslk}^{\frac{q-1}{q}}\left[H_sL^{n-}\right]^{\frac{1}{q}} h^{-\frac{k}{q}}, \end{aligned} \qquad (2)$$

where G_{qslk} is the equilibrium concentration of a coordination compound; β_{qslk} is the overall formation constant of these compounds; and h is the activity of hydrogen ions.

The nuclearity (q) of the resulting coordination compound according to the oxidation potential theory [8–11, 16] was determined by analyzing the experimental dependence between EMF (E) of a voltaic cell and exponent of Fe^{2+} ion concentration ($pc_{ox} = -\log c_{Fe(II)}$) (Fig. 1).

The angular coefficient of these linear dependences is equal to $-\nu/2$. On the basis of the theory of redoxmetry and the equation of partial derivative (3) ($q = 1$), a conclusion can be drawn that mononuclear iron(II) complexes were formed at all analyzed pH values of the solutions.

$$\left(\frac{\partial E}{\partial pc_{ox}}\right)_{pc_{L,pH}} = -\frac{\nu}{2q}. \qquad (3)$$

An analysis of partial derivatives of the dependence between EMF of a voltaic cell and the exponent of glycine concentration pcL ($pc_L = -\log c_{Gly}$) (4) made it possible to determine the number of protonated ligands (sl) in iron(II) complexes.

$$\left(\frac{\partial E}{\partial pc_L}\right)_{pc_{ox,pH}} = \frac{\nu sl}{2q}. \qquad (4)$$

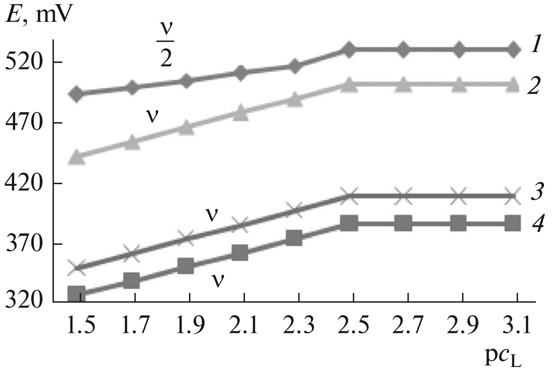

Fig. 2. EMF (E, mV) versus pc_L for the Fe(II)–Gly–H_2O system at 298 K, $I = 1.0$; $c_{Gly} = 5 \times 10^{-4}$ (voltaic cell), $c_{Gly} = 6 \times 10^{-3}$ (burette), $c_{Fe(II)} = 1 \times 10^{-4}$ mol/L. (*1*) pH 3, (*2*) pH 4, (*3*) pH 5, and (*4*) pH 6.

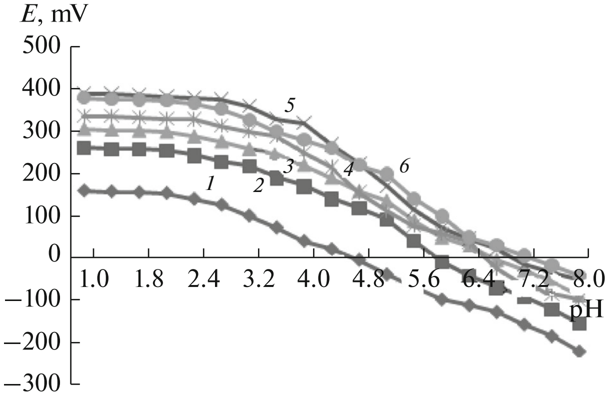

Fig. 3. EMF (E, mV) versus pH for the Fe(0)–Fe(II)–Gly–H_2O system at 298 K, $I = 1.0$; $c_{Fe(II)} =$ (*1–3*) 1×10^{-3} and (*4–6*) 1×10^{-4} mol/L; $c_{Gly} =$ (*1, 4*) 1×10^{-3}, (*2, 5*) 2×10^{-3}; and (*3, 6*) 3×10^{-3} mol/L.

A linear segment with a zero slope exists in the range $pc_L = 2.6–3.1$ in the experimental dependences E versus pc_L shown in Fig. 2. It indicates that complexation with glycine does not take place under these concentration conditions.

As glycine concentration increases, one can differentiate linear segments with angular coefficients $+\nu/2$ and $+\nu$. We calculated the numeric sl values according to Eq. (4) at an accurately determined q value. We found that sl is equal to 1 at pH 3.0 and sl is equal to 2 in the pH range 4.0–6.0. Therefore, the inner coordination sphere of the complex contains one or two ligands. The type of ligand depends on pH of the solution.

In order to find the pH ranges of domination of coordination compounds and to determine the possible number of coordinated hydroxyl groups and the type of ligands within the complex, we analyzed the experimental dependences E versus pH according to the theory of the method (Fig. 3).

It follows from Eq. (2) that partial derivative of the EMF–pH curve is written as:

$$\left(\frac{\partial E}{\partial \mathrm{pH}}\right)_{pc_{ox},pc_L} = -\frac{\nu}{2}\left(\frac{sl + k}{q}\right). \qquad (5)$$

One can consecutively differentiate linear segments with angular coefficients 0, $-\nu/2$, $-\nu$, -2ν, and $-\nu$ in the E versus pH curve at iron(II) and glycine concentrations $c_{Fe(II)} = 1 \times 10^{-4}$ mol/L and $c_{Gly} = 3 \times 10^{-3}$ mol/L, respectively. Taking into account the known nuclearity (q) and the number of ligands (sl) (Eqs. (3) and (4)), the possible concentration of OH^- ions (k) within the complexes being formed can be determined from Eq. (5). At the slope of the plot under study -2ν and $-\nu$, the k value is 1 and 2, respectively. For three initial angular coefficients, $k = 0$.

Hence, simultaneous examination of the results of analyzing partial derivatives E of pc_{ox}, pc_L and pH under these concentration conditions allowed us to detect formation of Fe(II) complexes with the following compositions: $[Fe(H_2O)_6]^{2+}$, $[FeHL(H_2O)_5]^{2+}$, $[Fe(HL)_2(H_2O)_4]^{2+}$, $[Fe(HL)(OH)(H_2O)_4]^+$, and $[Fe(OH)_2(H_2O)_4]^0$. Using these data and knowing the pH ranges of existence of the complexes, we built a summary table for the mathematical model of equilibria in the system (Table 1).

Next, we used the data of the stoichiometric matrix to build a chemical model of equilibria in the system with numerical values of nuclearity of metal complexes q, the number of protons in them s, the number

Table 1. Experimental slopes of the EMF versus concentration parameter plots in the Fe(0)–Fe(II)–glycine–water system at 298 K, $I = 1.0$; $c_{Fe(II)} = 1 \times 10^{-4}$ and $c_{Gly} = 3 \times 10^{-3}$ mol/L

Linear pH region	Dependence of EMF on concentration parameters			Tentative composition of the complexes
	pH	pc_{ox}	pc_L	
1.0–2.0	0	–	–	$[Fe(H_2O)_6]^{2+}$
2.0–3.0	$-\nu/2$	$-\nu/2$	$\nu/2$	$[FeHL(H_2O)_5]^{2+}$
3.0–4.5	$-\nu$	$-\nu/2$	ν	$[Fe(HL)(OH)(H_2O)_4]^+$
4.5–6.4	-2ν	$-\nu/2$	ν	$[Fe(HL)_2(H_2O)_4]^{2+}$

Table 2. Chemical model of equilibria in the Fe(0)–Fe(II)–glycine–water system at 298 K, $I = 1.0$; $c_{\mathrm{Fe(II)}} = 1 \times 10^{-4}$ and $c_{\mathrm{Gly}} = 3 \times 10^{-3}$ mol/L

Fe^{2+}	H^+	L^-	OH^-	Composition of the complex	β_{qslk}	Fragments of the equations of oxidation potential of the system
q	*s*	*l*	*k*			
1	0	0	1	$[Fe(OH)(H_2O)_5]^+$	β_{1001}	$\nu\log(h^3 + \beta_{1001}h^2)$
1	1	1	0	$[FeHL(H_2O)_5]^{2+}$	β_{1110}	$\nu\log(h^3 + \beta_{1110}K_1C_{a1}h^2)$
1	2	2	0	$[Fe(HL)_2(H_2O)_4]^{2+}$	β_{1220}	$\nu\log(h^3 + \beta_{1220}K_1^2C_{a1}^2h)$
1	1	1	1	$[Fe(HL)(OH)(H_2O)_4]^+$	β_{1111}	$\nu\log(h^3 + \beta_{1111}K_1C_{a1}h)$
2	2	2	2	$[Fe_2(HL)_2(OH)_2(H_2O)_8]^{2+}$	β_{2222}	$\nu\log(h^3 + 2\beta_{2222}^{1/2}G_{2222}^{1/2}K_1C_{a1}h)$
1	0	0	2	$[Fe(OH)_2(H_2O)_4]^0$	β_{1002}	$\nu\log(h^3 + \beta_{1002}h)$

of coordinated ligands *l* and hydroxyl groups *k* (Table 2). β_{qslk} stands for the overall formation constant, the *qslk* index completely corresponds to the numeric values reported above and shows the composition of the complexes.

Yusupov's oxidation function [17] and the built chemical model were used to calculate the formation constants of coordination compounds. The experimental oxidation function f^0_{exp} was calculated from the results of experimental dependence between the electromotive force *E* and pH (Fig. 3) using the equation:

$$f^0_{\mathrm{exp}} = c_{\mathrm{r}}/c_{\mathrm{o}} \exp\left(E - E^0\right)n/\nu\ , \qquad (6)$$

where *E* is the experimentally measured EMF value, E^0 is the standard EMF value, *n* is the number of electrons involved in the redox reaction, and $\nu = 2.303\ RT/F$.

Next, the f^0_{exp} versus pH plot was constructed (Fig. 4): it consists of four rectilinear segments and corresponds to the total number of complexes being formed.

The agreement between the experimental (f^0_{exp}) and theoretical (f^0_{T}) oxidation functions attests to the validity of the determined compositions of the complexes and their calculated stability constants.

The general expression for the theoretical oxidation function f^0_{T} of the system under study is written as:

$$f^0_{\mathrm{T}} = \frac{c_{\mathrm{r}}}{c_{\mathrm{o}}} \frac{1}{\left\{\sum_1^q \sum_0^s \sum_0^l \sum_0^k q\beta_{qslk}^{\frac{1}{q}} G_{qslk}^{\frac{q-1}{q}} \left[H_sL^{n-}\right]^{\frac{1}{q}} h^{\frac{-k}{q}} \left[M^{(z-e)+}\right]^{\frac{1}{q}}\right\}}. \qquad (7)$$

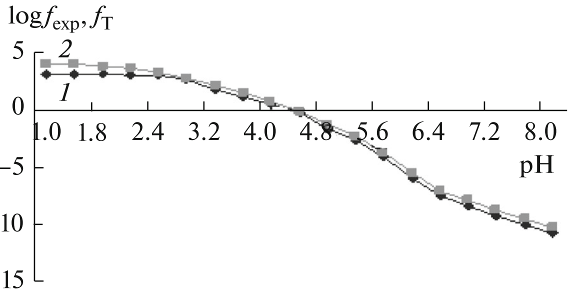

Fig. 4. Logarithmic values of the (*1*) experimental f_{exp} and (*2*) theoretical f_{T} oxidation functions versus pH for the Fe(0)–Fe(II)–Gly system at $c_{\mathrm{Fe(II)}} = 1 \times 10^{-4}$ and $c_{\mathrm{Gly}} = 3 \times 10^{-3}$ mol/L.

The equation of the theoretical oxidation function of the system was obtained using the data from the table showing the chemical model of equilibria (Table 2). Summation of the equations for individual linear segments gave the general expressions for the theoretical oxidation function of the investigated system (Eq. (8)):

$$f^0_{\mathrm{T}} = \frac{10^4}{\left\{\sum_1^q \sum_0^s \sum_0^l \sum_0^k q\beta_{qslk}^{\frac{1}{q}} G_{qslk}^{\frac{q-1}{q}} \left[H_sL^{n-}\right]^{\frac{l}{q}} h^{\frac{-k}{q}}\right\}}. \qquad (8)$$

The values of oxidation functions f^0_{exp} and f^0_{T} are figures with decimal base, so these dependences are shown as logarithms (Fig. 4). The f^0_{T} was calculated using the numeric values of stability constants deter-

Table 3. Model parameters of the coordination compounds in the Fe(0)–Fe(II)–glycine–water system at 298 K, $I = 1.0$; $c_{\mathrm{Fe(II)}} = 1 \times 10^{-4}$ and $c_{\mathrm{Gly}} = 3 \times 10^{-3}$ mol/L

pH range of existence of the complex	Composition of the complex	Maximum degree of accumulation, α, %	pH	Logarithmic formation constant of the complex ($\log\beta_{qslk}$)
1.0–4.0	$[Fe(OH)(H_2O)_5]^+$	10.30	2.4	–2.520 ± 0.05
1.0–4.4	$[FeHL(H_2O)_5]^{2+}$	57.10	2.4	2.900 ± 0.04
2.0–5.2	$[Fe(OH)_2(H_2O)_4]^0$	14.00	4.0	–5.440 ± 0.04
1.8–5.6	$[Fe(HL)(OH)(H_2O)_4]^+$	64.70	4.0	–0.097 ± 0.05
2.4–5.2	$[Fe(HL)_2(H_2O)_4]^{2+}$	6.48	4.0	3.590 ± 0.04
3.6–8.0	$[Fe_2(HL)_2(OH)_2(H_2O)_8]^{2+}$	99.00	6.4	10.860 ± 0.04

mined by solving the equations for linear segments of dependences E versus pH and E versus pC_L in their point of intersection and using the findings reported in [5]. Having made an assumption that the $[Fe_2(HL)_2(OH)_2(H_2O)_8]^{2+}$ complex was formed, we see a good agreement between the f^0_{exp} and f^0_{T} curves, which again attests to validity of the results. The true values of the complex formation constants are found by iterative fitting of f^0_{exp} and f^0_{T} versus pH curves; these true complex formation constants are listed in the table with model parameters (Table 3). All calculations were performed on a PC using the Excel program.

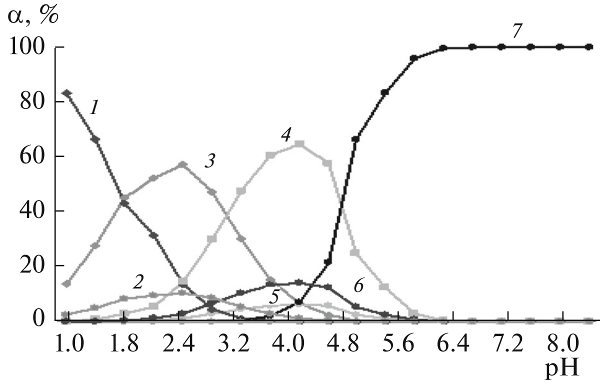

Fig. 5. Degree of accumulation of complexes versus pH for the Fe(II)–Gly–H_2O system at 298 K, $I = 1.0$; $c_{\mathrm{Fe(II)}} = 1 \times 10^{-4}$, $c_{\mathrm{Gly}} = 3 \times 10^{-3}$ mol/L. (*1*) $[Fe(H_2O)_6]^{2+}$; (*2*) $[Fe(OH)(H_2O)_5]^+$, (*3*) $[FeHL(H_2O)_5]^{2+}$; (*4*) $[Fe(HL)(OH)(H_2O)_4]^+$; (*5*) $[Fe(HL)_2(H_2O)_4]^{2+}$, (*6*) $[Fe(OH)_2(H_2O)_4]^0$; and (*7*) $[Fe_2(HL)_2(OH)_2(H_2O)_8]^{2+}$.

The calculations were terminated when the final variant of the degrees of accumulation of complex species (as mole fractions) was calculated and their distribution curve was plotted (Fig. 5).

Molar fractions of complex species in the solutions containing ions of the oxidized metal species α^0_{qslk} were calculated using the equation:

$$\alpha^0_{qslk} = \left[\frac{M_qH_sL_l(OH)_k]^{q+}}{\sum\limits_{1}^{q}\sum\limits_{0}^{s}\sum\limits_{0}^{l}\sum\limits_{0}^{k} q\beta_{qslk}^{\frac{1}{q}}G_{qslk}^{\frac{q-1}{q}}\left[H_sL^{n-}\right]^{\frac{l}{q}}h^{\frac{-k}{q}}}\right]. \quad (9)$$

One can see from the calculated data and the distribution diagram that the complex of composition $[FeHL(H_2O)_5]^{2+}$ with the stability constant 2.90 ± 0.04 is formed in the strongly acidic range; the mixed-ligand hydroxo complex of composition $[Fe(HL)(OH)(H_2O)_4]^+$ is then formed and is subsequently transformed into the most stable dimer with the maximum degree of accumulation of 100%. Hydrolysis dominates over complexation with HL; therefore, the mole fraction of the hydroxo complex is higher than in the case of pure glycine ion, although the formation constant of the mononuclear complex is higher than that of hydroxo complex. Monomeric coordination compounds have the largest range of existence (almost 5.5 pH units); the range of domination of the dimer is pH 3.2–8.0.

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Translated by D. Terpiloversuskaya