



Scientific article

UDC 577.112.386.2 + 541.49 547.11

DOI: 10.52957/2782-1900-2026-7-3-168-179

CYSTEINATE COORDINATION COMPOUNDS OF COPPER (II), MODELS OF THEIR FORMATION PROCESSES

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Keywords:

EMF, complex, copper(II),
cysteine, iteration, formation
constants, mole fractions,
regions of existence,
distribution diagrams.

Abstract. The complexation of copper in aqueous solutions of L-cysteine was studied by the oxidative potential method using a copper amalgam electrode in the pH range of 1.0–8.0 at a temperature of 298 K and an ionic strength of the solution (NaNO₃) of I = 1.00 mol/L. The composition was identified and the stepwise formation constants of the complexes were calculated. The following mononuclear copper(II) compounds [CuCys(H₂O)₃]²⁺; [Cu(Cys)(OH)(H₂O)₂]⁺; [Cu(OH)₂(H₂O)₂]⁰; [Cu(Cys)(L)(H₂O)₂]⁺ are formed in the system. According to the experimental data obtained, the composition, stability, regions of existence, and degrees of accumulation of cysteinate coordination compounds of copper were determined in agreement with the oxidative function and the proposed principle of equilibrium modeling. The calculated model parameters can be used as reference material for the targeted synthesis of complexes and for thermodynamic calculations.

For citation:

Bobonazarzoda G.B., Davlatshoeva Dzh.A., Rakhimova M., Miraminzoda F. Cysteinate coordination compounds of copper (II), models of their formation processes // From Chemistry towards Technology Step-by-Step. 2026. Vol. 7, Iss. 3. P. 168-179. URL: <https://chemintech.ru/en/nauka/issue/7500/view>

Introduction

There are significant quantities of publications in the modern scientific literature are devoted to coordination compounds of metals with organosulfur ligands. Within the extensive class of such compounds, cysteine is one of the most important one. Presented in blood and plasma, L-Cysteine is one of the most significant metal-binding agents in biological fluids. A deficiency of L-cysteine in the body correlates with a number of clinical conditions, including hepatotoxicity, dermatological disorders, growth retardation, and AIDS [1].



Copper, being a key trace element, plays a significant role in maintaining the structural integrity of vascular walls, including the membranes of the spinal cord. In addition, copper ions are necessary for the biosynthesis of melanins. They are responsible for the pigmentation of skin, hair, iris of the eyes, and formation of hemoglobin. Numerous studies have demonstrated that copper complexes possess the ability to restore damaged tissues. In this regard, copper-containing compounds are considered promising medicinal agents [2].

The complexation of Ag^+ ions with L-cysteine anions (Cys^{2-}) was studied by the potentiometric method [3] at 25 °C against a background of 0.1 mol/L KNO_3 . The formation of soluble complexes of the composition AgCys^- ($\lg\beta = 11.14 \pm 0.10$), AgHCys ($\lg\beta = 20.77 \pm 0.06$), Ag_2Cys ($\lg\beta = 20.32 \pm 0.17$), Ag_2HCys^+ ($\lg\beta = 27.28 \pm 0.12$) was found.

Using pH-metric methods [4], solubility determinations and potentiometry with a gold electrode were conducted. Indeed, the equilibria involving cysteinate complexes of gold(I) in aqueous solution at 25 °C and $I = 0.2 \text{ M}$ (NaCl) were studied. The successive protonation constants $\lg K_i \text{H cysteinate } \text{H}_{i-1}\text{Cys}^{i-3} + \text{H}^+ = \text{H}_i\text{Cys}^{i-2}$ are equal ones: 10.10 ($i = 1$), 8.12 ($i = 2$), 1.90 ($i = 3$). The protonation of cysteinate complexes was studied: $\text{Au}(\text{Cys})_2^{3-} + \text{H}^+ = \text{Au}(\text{HCys})(\text{Cys})^{2-}$, $\lg K_{1\text{HAu}} = 9.62$ and $\text{Au}(\text{HCys})(\text{Cys})^{2-} + \text{H}^+ = \text{Au}(\text{Cys})_2^-$, $\lg K_{2\text{HAu}} = 9.01$. The constant of the heterogeneous equilibrium $\text{Au}(\text{HCys})_{\text{solid}} + \text{HCys}^- = \text{Au}(\text{HCys})_2^-$, $K_S = 3.3$, was determined. The standard potential of the complex $\text{Au}(\text{Cys})_2^{3-}$ is $E^0_{1/0} = -0.172 \pm 0.011 \text{ V}$. The complex $\text{Au}(\text{Cys})_2^-$ proved to be close in stability to the complex $\text{Au}(\text{HS})_2^-$.

The purpose of this study is to determine the composition, stability, regions of existence, and degrees of accumulation of cysteinate coordination compounds of copper using the oxidative function and the proposed principle of equilibrium modeling based on experimental data from the redox-metric method.

Experimental part

The redox-metric study was conducted using a copper electrode in accordance with [5, 6]. The copper electrode was made of 'extra-pure' grade metallic copper in the form of a rod pressed into a Teflon tube. Purification of mercury and amalgamation of the electrode were performed in accordance with the recommendations in [7].

For amalgamation, the surface of the copper electrode was polished with fine sandpaper and washed with distilled water. The copper electrode surface prepared in this way was amalgamated by immersing it for some time in pure mercury contained in a vessel. The mercury droplets remaining on the copper plate were rubbed with filter paper until the copper amalgam uniformly covered the entire surface. The mercury used for amalgamation was periodically purified by filtration and decantation with 0.5% nitric acid and water.

The concentration of Cu^{2+} ions was determined by the iodometric method [8–10]. For the preparation of solutions, bidistillate, $\text{Cu}(\text{NO}_3)_2 \cdot 3\text{H}_2\text{O}$ (chemically pure), cysteine manufactured by Reanal (Hungary), analytical-grade NaNO_3 , and HNO_3 prepared from a fixanal were used. The concentration of NaOH was determined by the method described in [11] by direct titration with 0.1 M hydrochloric acid in the presence of the indicator phenolphthalein.



Standardization of the stock and working solutions was performed according to the procedures described in [12]. The EMF of the galvanic cells was measured using an EV-74 ion meter (accuracy $\pm 1-3$ mV). The values of the silver chloride electrode potential and the quantity $v = 2.303RT/F$ at the required temperatures were taken from [13].

To imitate an inert atmosphere and to stir the solutions, gaseous nitrogen purified from O_2 and CO_2 was used.

Calibration of the copper electrode to verify its compliance with the Nernst equation consists in measuring the EMF of the first galvanic cell in a series of solutions containing copper(II) nitrate at various concentrations. The measurement of the oxidative potential of galvanic cells with transference was conducted using a combination of three electrodes: copper and silver chloride electrodes to determine the oxidative potential of the circuit; glass and silver chloride electrodes to determine the pH. The second galvanic cell is necessary for determining the pH of the solution in the electrolytic cell during titration.

The first working solution was added to the cell ($V = 50$ mL). Through it an inert gas was passed to stir the Cu(II) solution. Then, gradually, a calculated amount of 0.1 N HNO_3 and 0.9 N $NaNO_3$ was added to form the required ionic strength and achieve the desired pH value. Repeating the same procedure with the second working solution, the required amount of the second solution was added in small portions to the first, and the EMF of galvanic cells (I) and (II) was measured. The equilibrium value of the oxidative potential was taken to be the value that did not change within 2–3 minutes. The concentrations of copper(II) and cysteine were varied within the pH range of 1.5–1.9, i.e., within the limits of a stable redox system where the formation of insoluble products is not observed.

An assessment of the electrode function of the copper electrode was conducted. It verifies its compliance with the Nernst equation. Copper(II) ions undergo hydrolysis at $pH \leq 6.5$. Therefore, the EMF of the system was measured up to these pH values with strict fixing of their values and the ionic strength using two working solutions with identical pH and ionic strength values but different concentrations of copper(II). The EMF of the galvanic cell composed of copper and silver chloride electrodes was measured using the equation:

$$\varphi_{Cu(II)/Cu(0)} = E - \varphi_{Ag/AgCl,Cl^-}, \quad (1)$$

where E is the EMF of the galvanic cell; $\varphi_{Cu(II)/Cu(0)}$ is the potential of the copper electrode; $\varphi_{Ag/AgCl,Cl^-}$ is the potential of the silver chloride electrode.

Discussion of the results of the study

To determine the composition of copper(II) complexes formed in aqueous solutions of cysteine, using the corresponding equations [7], the experimentally obtained partial dependences of the EMF of the system, measured on a copper amalgam electrode, were analyzed (Figs. 1–3).

The nuclearity (q) of the coordination compounds was established based on an examination of the curves of the dependence of EMF on the negative logarithm of the concentration of Cu^{2+} ions ($pC_{Cu^{2+}} = -lgC_{Cu^{2+}}$) (Fig. 1).

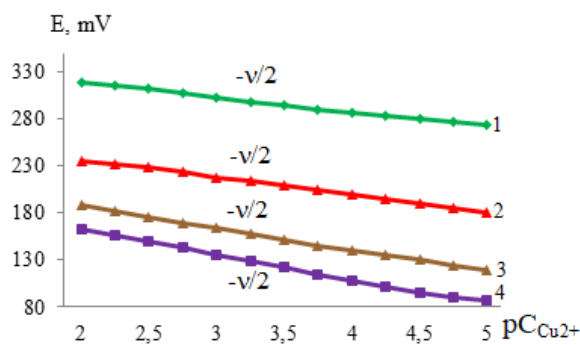


Fig. 1. Dependence of EMF (E , mV) on $pC_{Cu^{2+}}$ for the Cu(Hg)–Cu(II)–Cys–H₂O system; $C_{Cys} = 1 \cdot 10^{-3}$ mol/L. The curves correspond to pH: 1 – 2.0; 2 – 3.5; 3 – 6.5; 4 – 7.6.

By Figure 1, on the curves of the $E - pC_{Cu^{2+}}$ dependence, linear sections with slopes equal to $-v/2$ can be distinguished. According to the theory of redox-metry [5, 6], it indicates the formation of mononuclear copper(II) complexes in solution over the entire studied pH range.

$$\left(\frac{\partial E}{\partial pC_{Cu^{2+}}} \right)_{pC_{Cys}, pH} = -\frac{v}{2q}. \quad (2)$$

Analysis of the curves of the partial dependence of the oxidative potential of the system on the negative logarithm of the amino acid concentration ($pC_{Cys} = -\lg C_{Cys}$), presented in Fig. 2, establishes the number of ligands incorporated in the composition of the copper(II) complexes.

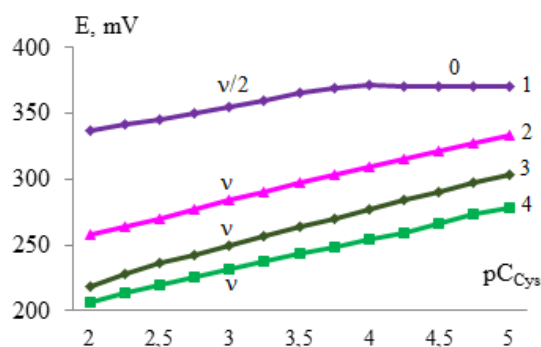


Fig. 2. Dependence of EMF (E , mV) on pC_{Cys} for the Cu(Hg)–Cu(II)–Cys–H₂O system. The curves correspond to pH: 1 – 2.5; 2 – 3.5; 3 – 6.0; 4 – 7.5.

$$\left(\frac{\partial E}{\partial pC_{Cys}} \right)_{pC_{Cu^{2+}}, pH} = \frac{vl}{2q}. \quad (3)$$

At pH 2.5, on the curves of the $E - pC_{Cys}$ dependence, linear sections with a slope of $v/2$ are formed. According to [7], it indicates the incorporation of one ligand into the coordination sphere of the Cu^{2+} ion. At pH 6.5 and 9.5, the slope of the linear sections of the considered $E - pC_{Cys}$ dependence is equal to v . By the equation (3) and the established nuclearity, the coordination compounds of copper(II) formed under these conditions include two ligands ($l = 2$). To find the regions of dominance of the formed copper(II) coordination compounds and determine the total number and type of ligands in them, a graphical analysis of the experimental E –pH dependences was conducted (Fig. 3).

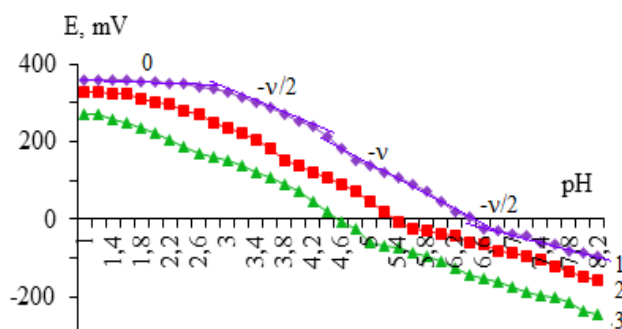


Fig. 3. Dependence of EMF (E , mV) of the Cu(Hg)–Cu(II)–Cys–H₂O system on pH at a temperature of 298 K and an ionic strength of the solution (NaNO₃) of $I = 1.0$; Curves correspond to: 1 – $C_{Cu^{2+}} = 0.001$; 2 – $C_{Cu^{2+}} = 0.02$; 3 – $C_{Cu^{2+}} = 0.05$; $C_{Cys} = 0.01$ mol/L.

The zero slope of the linear sections of the considered dependence, observed at low pH values, reflects the absence of hydrolysis or complexation processes of Cu(II) in the region of acidic solutions. Thus, copper(II) ions at $pH \leq 2.0$ exist under the studied conditions in the form of aqua complexes.

The subsequent decrease in EMF with a further increase in pH, and the formation on the E–pH dependence curves of linear sections with slopes of 0, $-v/2$, $-v$, and $-v/2$ (Table 1), are associated with the stepwise formation of compounds in which one or two ligands, respectively, account for one complexing ion.

Table 1. Slope on the pH scale of the Cu(Hg)–Cu(II)–Cys–H₂O system at a temperature of 298 K, $I = 1.0$; $C_{Cu^{2+}} = 0.001$ and $C_{Cys} = 0.01$ mol/L.

Item n/a	pH scale	Slope, mV	Slope, v
1	1.0-2.4	0	0
2	2.2-4.2	29.5	$-v/2$
3	4.2-6.6	59	$-v$
4	6.6-8.0	29.5	$-v/2$

According to the theory of the method [7], from the equation for the partial derivative:

$$\left(\frac{\partial E}{\partial pH}\right)_{pC_{Cu^{2+}}, pC_{Cys}} = -\frac{v}{2} \left(\frac{sl + k}{q}\right), \quad (4)$$

where l and k are the numbers of ligands and OH[−] groups coordinated by the oxidized form of the metal with a nuclearity equal to q .

According to the results on establishing the nuclearity and the number of ligands, at pH 1.0–8.2, compounds of the type $Cu^{2+} : Cys^{\pm} = 1:1$ and $1:2$ are formed. An increase in $pH \geq 8.2$ resulted in a mixed hydroxo compound with one or two OH[−] groups in the coordination sphere of Cu^{2+} ions ($k = 1$; $k = 2$).

A similar course of the E–pH dependence curves indicates that an increase in the concentration of Cu^{2+} ions from 0.001 to 0.05 mol/L at $C_{Cys} = 0.01$ mol/L does not change the forms of the copper(II) coordination compounds formed in the system over the entire studied pH range.

Dependences of the EMF (E , mV) of the system on pH were obtained (Fig. 4).

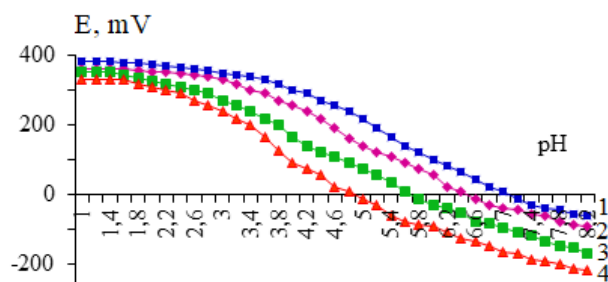


Fig. 4. Dependence of EMF (E , mV) of the Cu(Hg)–Cu(II)–Cys–H₂O system on pH at temperatures of 288.15–318.15 K and an ionic strength of the solution (NaNO₃) of $I = 1.0$; $C_{Cu^{2+}} = 0.001$; $C_{Cys} = 0.01$ mol/L. Curves correspond to: 1 – 288.15; 2 – 298.15; 3 – 308.15; 4 – 318.15 K.

With an increase in temperature from 288.15 to 318.15 K, the length of the linear section with a slope equal to zero decreases and shifts toward the acidic region of the solution.

We consider the analysis of all experimental dependences in the Cu(Hg)–Cu(II)–Cys–H₂O system at a temperature of 298 K and an ionic strength of the solution (NaNO₃) of $I = 1.0$.

A joint consideration of the results of the graphical analysis of the partial derivatives of the oxidative potential (Figs. 1–4), and the protolytic dissociation constants of cysteine ($pK_1 = 1.71$; $pK_2 = 8.27$; $pK_3 = 10.78$), provides formulas for describing the composition of the copper(II) complex compounds formed in the studied system under the selected conditions (Table 2).

Table 2. Experimental values of the slopes of the dependences of EMF on the concentration variables for the Cu(Hg)–Cu(II)–Cys–H₂O system at a temperature of 298 K, $I = 1.0$; $C_{Cu^{2+}} = 0.001$; $C_{Cys} = 0.01$ mol/L.

Item n/a	Dependences of EMF on the concentration variables			Composition of the compounds
	pH	pC_{ox}	pC_L	
1	0	–	–	$[Cu(H_2O)_4]^{2+}$
2	$-v/2$	$-v/2$	$v/2$	$[Cu(Cys)(H_2O)_3]^{2+}$
3	$-v$	$-v/2$	v	$[Cu(Cys)(OH)(H_2O)_2]^+$
4	$-v/2$	$-v/2$	–	$[Cu(OH)_2(H_2O)_2]^0$
5	$-v$	$-v/2$	v	$[Cu(Cys)(L)(H_2O)_2]^+$

Note: Cu(II) is the number of atoms of the oxidized form of copper in the complex; H^+ is the number of protonated groups in the complex; L^- is the number of ligands; OH^- is the number of coordinated hydroxyl groups.

Some ambiguity is observed in the course of the curves of the E – pC_{Cys} dependence at low concentrations of the amino acid, the appearance of yellow spots on the amalgam of the Cu(Hg)/Cu²⁺ electrode, and instability of the potential during the measurement of the E –pH dependence at $pH > 9.0$, $C_{Cu^{2+}} = 5.0 \cdot 10^{-1}$ and $C_{Cys} = 0.01$ mol/L.

The cause of the observed effects during redox-metric measurements is apparently a change in the copper(II) content in cysteine solutions due to the occurrence of the disproportionation reaction of Cu(I) upon contact with the copper amalgam electrode.

A complete analysis of stoichiometric matrix data and the established compositions of the compounds showed the formation of copper(II) coordination compounds in the studied system.

Based on the data of the stoichiometric matrix, a chemical model of the equilibria of the system was compiled with numerical values of the nuclearity of the metal complex compounds, the number of protons, the number of coordinated ligands, and hydroxyl groups – q , s , l , and k , respectively (Table 3). The chemical models can be used for compiling computer programs and calculating ionic equilibria.



Table 3. Chemical model of equilibria of the system Cu(Hg)–Cu(II)–Cys–H₂O system at a temperature of 298 K, I = 1.0; C_{Cu²⁺} = 0.001; C_{Cys} = 0.01 mol/L.

Item n/a	Cu ²⁺ <i>q</i>	H ⁺ <i>s</i>	L ⁻ <i>l</i>	OH ⁻ <i>k</i>	Composition of the compounds	β_{qslk}	Fragments of the equations for the oxidative potential of the system
1	1	1	1	0	[Cu(Cys)(H ₂ O) ₃] ²⁺	β_{1110}	$\text{vlg}(h^3 + \beta_{1110}K_1C_a h^2)$
2	1	1	1	1	[Cu(Cys)(OH)(H ₂ O) ₂] ⁺	β_{1111}	$\text{vlg}(h^3 + \beta_{1111}K_1C_a h^2)$
3	1	0	0	2	[Cu(OH) ₂ (H ₂ O) ₂] ⁰	β_{1002}	$\text{vlg}(h^3 + \beta_{1002}K_1^2C_a^2h)$
4	1	1	2	0	[Cu(Cys)(L)(H ₂ O) ₂] ⁺	β_{1120}	$\text{vlg}(h^3 + \beta_{1120}K_1C_a h)$

Note: The indicated quantities of the oxidized form of copper, protons, ligands, and hydroxyl groups, *q*, *s*, *l*, *k*, respectively, are the main basis particles and are given in the subscript of the designation of the complex formation constants β_{qslk} . *q* is the number of atoms of the oxidized form of copper in the complex; *s* is the number of protonated groups in the complex; *l* is the number of ligands; *k* is the number of coordinated hydroxyl groups.

To calculate the values of the stability constants of the coordination compounds in the studied system, determine the pH intervals of their existence, and confirm the compositions of the particles, the method of minimizing the deviations of the experimental EMF values from the calculated ones was used; β_{qslk} were used as the parameters.

To calculate ionic equilibria in redox systems [14], the concept of the oxidative function was introduced.

The experimental oxidative function f_E is expressed by the following equation:

$$f_E = \frac{1}{C_{\text{Cu}^{2+}}} 10^{\frac{2(E-E^0)}{\nu}}, \quad (5)$$

where *E* is the experimentally measured EMF value, *E*⁰ is the apparent value of the normal or standard EMF; C_{Cu²⁺} is the total concentration of the oxidized form; $\nu = 2.303RT/F$.

The general equations of the oxidative potential can be applied to calculate ionic equilibria in the reactions of formation of coordination compounds, including the formation of hydroxo complexes in solutions of redox systems.

The oxidative function f_E represents the sum of the concentrations of all complex compounds formed in the Cu(Hg)–Cu(II)–Cys–H₂O system. Then, the theoretical value of the oxidative function f_T was calculated in terms of all possible compositions of the coordination compounds.

Based on the data given in Table 3, from equation (5) we find the expressions for the oxidative function of the system under study. Substituting successively the values of *q*, *p*, *s*, *l*, *k*, we expand the sums. It resulted in the following expression:

$$f_T = 1000 \cdot h^3 / (h^3 + \beta_{1110}K_1C_a h^2 + \beta_{1111}K_1C_a h^2 + \beta_{1002}K_1^2C_a^2h + \beta_{1120}K_1C_a h) \quad (6)$$

where *h* is the concentration of hydrogen ions; *K_a* is the dissociation constant of cysteine; *C_a* is the total concentration of cysteine; β is the complex formation constant.

To calculate the constants and regions of dominance of the copper(II) complex, equation (6) is an expression of the oxidative function for the Cu(Hg)–Cu(II)–Cys–H₂O system is used. We can suppose, that this equation is a mathematical model of the studied system.

The values of the experimental oxidative function f_E were calculated, the refinement of the complex constants was proceeded with by the iteration method using equation (6) until the values of the theoretical and experimental oxidative functions coincided (Table 4) within the error of the experiments.



Table 4. Values of the EMF, the experimental f_E and theoretical f_T oxidative functions, and their logarithms as a function of pH for the Cu(Hg)–Cu(II)–Cys–H₂O system at a temperature of 298 K, $I = 1.0$; $C_{Cu^{2+}} = 0.001$; $C_{Cys} = 0.01$ mol/L. The value of the apparent standard EMF (E^0) is 360 mV

pH	E, mV	f_E	f_T	lgf_E	lgf_T	pH	E, mV	f_E	f_T	lgf_E	lgf_T
1.0	360	1000	9.72E+02	3.0	3.0	4.6	215	1.22 E-02	5.81E-02	-1.9	-1.2
1.2	360	1000	9.56E+02	3.0	3.0	4.8	205	5.57E-03	2.18E-02	-2.3	-1.7
1.4	358	8.55+02	9.30E+02	2.9	3.0	5.0	196	2.76 E-03	7.92E-03	-2.6	-2.1
1.6	358	8.55E+02	8.90E+02	2.9	2.9	5.2	178	6.77 E-04	2.77E-03	-3.2	-2.6
1.8	354	6.26E+02	8.26E+02	2.8	2.9	5.4	162	1.94 E-04	9.23E-04	-3.7	-3.0
2.0	352	5.35E+02	7.30E+02	2.7	2.9	5.6	148	6.51E-05	2.92E-04	-4.2	-3.5
2.2	350	4.58E+02	5.97E+02	2.7	2.8	5.8	134	2.18E-05	8.78E-05	-4.7	-4.1
2.4	348	3.92E+02	4.36E+02	2.6	2.6	6.0	120	7.32E-06	2.52E-05	-5.1	-4.6
2.6	340	2.10E+02	2.77E+02	2.3	2.4	6.2	100	1.54E-06	6.94E-06	-5.8	-5.2
2.8	336	1.53E+02	1.53E+02	2.2	2.2	6.4	80	3.22E-07	1.86E-06	-6.5	-5.7
3.0	328	8.23 E+01	7.49E+01	1.9	1.9	6.6	69	1.37E-07	4.87E-07	-6.9	-6.3
3.2	314	2.76 E+01	3.38E+01	1.4	1.5	6.8	48	2.65E-08	1.26E-07	-7.6	-6.9
3.4	300	9.38 E+00	1.45E+01	1.0	1.2	7.0	32	7.61E-09	3.22E-08	-8.1	-7.5
3.6	288	3.68E+00	6.03E+00	0.6	0.8	7.2	14	1.87E-09	8.17E-09	-8.7	-8.1
3.8	270	8.92E+00	2.45E+00	-0.1	0.4	7.4	-2	5.36E-10	2.07E-09	-9.3	-8.7
4.0	254	2.60E-01	9.83E-01	-0.6	0	7.6	-14	2.10E-10	5.22E-10	-9.7	-9.3
4.2	242	1.00 E-01	3.89E-01	-1.0	-0.4	7.8	-38	3.22E-11	1.31E-10	-10.5	-9.9
4.4	229	3.62 E-02	1.52E-01	-1.4	-0.8	8.0	-58	6.77E-12	3.31E-11	-11.2	-10.5

According to Table 4, the values of the theoretical and experimental oxidative functions are in good agreement. Such accuracy in the approximations is necessary for analysis of the average values of the complex constants; the discrepancies are minimal.

The values of the oxidative functions f_E and f_T are numbers with a decimal base. Therefore, these dependences are presented in logarithmic form (Fig. 5), curves 1 and 2. Their coincidence indicates the reliability of the results, i.e., they are identical.

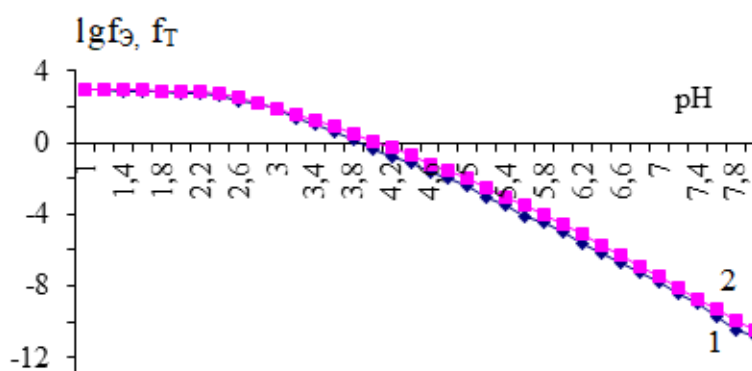


Fig. 5. Values of the logarithmic values of the experimental f_E (1) and theoretical f_T (2) oxidative functions of pH for the Cu(Hg)–Cu(II)–Cys–H₂O system at a temperature of 298 K, $I = 1.0$; $C_{Cu^{2+}} = 0.001$; $C_{Cys} = 0.01$ mol/L.

Summing the equations of the individual linear sections gives the general expression for the theoretical oxidative function of the studied system (7):

$$f_T^0 = 10^4 / \left\{ \sum_{l=1}^q \sum_{s=0}^s \sum_{l=0}^l \sum_{k=0}^k q \beta_{qslk}^{\frac{1}{q}} G_{qslk}^{\frac{q-1}{q}} [H_s L^{n-}]^{\frac{l}{q} h \frac{-k}{q}} \right\}. \quad (7)$$



To calculate f_T , the numerical values of the stability constants determined by solving the equations of the linear sections at the intersection point of the E–pH and E–pC_L dependences were used. At the maximum agreement of the curves of the f_E and f_T dependences on pH, the values of the formation constants are found. They are presented in the table of model parameters (Table 5). All calculations were performed on a computer using Excel programme [15-18].

Table 5. Model parameters of the coordination compounds of the system Cu(Hg)–Cu(II)–Cys–H₂O system at a temperature of 298 K, I = 1.0; C_{Cu}²⁺ = 0.001; C_{Cys} = 0.01 mol/L.

Item n/a	Region of complex existence on the pH scale	Composition of the compounds	Logarithm of the complex formation constant ($\lg \beta_{qslk}$)	Max. degree of accumulation, α , %	pH
1	1.0-4.4	[Cu(Cys)(H ₂ O) ₃] ²⁺	7.52±0.01	31.5	2.4
2	1.8-7.2	[Cu(Cys)(OH)(H ₂ O) ₂] ⁺	4.72±0.09	81.30	4.0
3	2.2-6.4	[Cu(OH) ₂ (H ₂ O) ₂] ⁰	-1.98±0.03	11.80	4.0
4	3.6-8.0	[Cu(Cys)(L)(H ₂ O) ₂] ⁺	12.90±0.09	99.8	8.0

This work is a part of research on the study of copper(II) complexation at various temperatures and ionic forces. Subsequent studies concern with the research on the study of copper(II) complexation at temperatures of 288, 308, and 318 K and ionic forces of 0.1, 0.25, 0.50, 0.75, and 1.00 mol/L.

The equations for the formation reactions of the above-mentioned complex compounds are presented in Table 6.

Table 6. Equations for the formation reactions of complex compounds in the system Cu(Hg)–Cu(II)–Cys–H₂O system at a temperature of 298 K, I = 1.0; C_{Cu}²⁺ = 0.001; C_{Cys} = 0.01 mol/L.

Item n/a	Equations for the complex formation reactions
1	[Cu(H ₂ O) ₄] ²⁺ + Cys [±] ↔ [Cu(Cys)(H ₂ O) ₃] ²⁺ + H ₂ O
2	[Cu(H ₂ O) ₄] ²⁺ + Cys [±] ↔ [Cu(Cys)(OH)(H ₂ O) ₂] ⁺ + H ₃ O ⁺
3	[Cu(H ₂ O) ₄] ²⁺ + H ₂ O ↔ [Cu(OH) ₂ (H ₂ O) ₂] ⁰ + H ₃ O ⁺ + H ⁺
4	[Cu(H ₂ O) ₄] ²⁺ + 2Cys [±] ↔ [Cu(Cys)(L)(H ₂ O) ₂] ⁺ + 2H ₂ O

The mole fractions of complex particles in solutions involving ions of the oxidized form of the metal, α_{qslk}^0 , are calculated using the equation:

$$\alpha_{qslk}^0 = [M_q H_s L_l (OH)_k]^{q+} / \sum_1^q \sum_0^s \sum_0^l \sum_0^k q \beta_{qslk}^{\frac{1}{q}} G_{qslk}^{\frac{q-1}{q}} [H_s L^{n-}]^{\frac{l}{q}} h^{\frac{-k}{q}}. \quad (8)$$

Thus, the values of the mole fractions of ions in equilibrium in the studied system are presented in (Fig. 6) in the form of a distribution diagram.

According to Fig. 6., all the proposed forms in the studied system exist over a fairly wide pH range; their degree of accumulation or formation is greater than 10%. Therefore, they are formed in amounts significantly exceeding the limits of measurement error, which is ±1–3 mV or 3–5%. The calculation and construction of distribution diagrams is the final stage in refining the composition of the formed coordination compounds and calculating their formation constants.

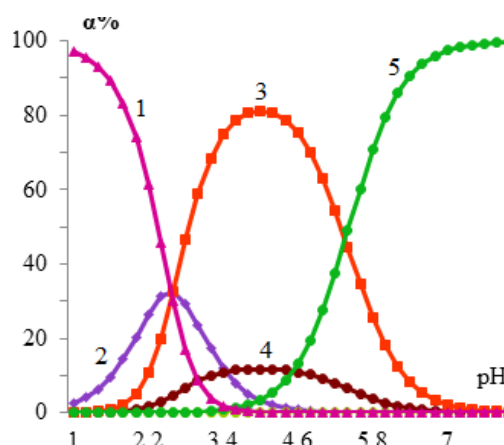


Fig. 6. Dependence of the degree of accumulation of Cu(II) complexes on pH for the Cu(Hg)–Cu(II)–Cys–H₂O system at a temperature of 298 K, $I = 1.0$; $C_{Cu^{2+}} = 0.001$; $C_{Cys} = 0.01$ mol/L. Curves correspond to: 1 – $[Cu(H_2O)_4]^{2+}$; 2 – $[Cu(Cys)(H_2O)_3]^{2+}$; 3 – $[Cu(Cys)(OH)(H_2O)_2]^+$; 4 – $[Cu(OH)_2(H_2O)_2]^0$; 5 – $[Cu(Cys)(L)(H_2O)_2]^+$.

However, expressions can be obtained for calculating the mole fractions of free particles and coordination compounds:

$$\alpha_{Cu(II)} = h^3 / (h^3 + \beta_{1110}K_1C_{a1}h^2 + \beta_{1111}K_1C_{a1}h^2 + \beta_{1002}K_1^2C_{a1}^2h + \beta_{1120}K_1C_{a1}h) \quad (9)$$

$$\alpha_{[Cu(Cys)(H_2O)_3]^{2+}} = \beta_{1110}K_1C_{a1}h^2 / (h^3 + \beta_{1110}K_1C_{a1}h^2 + \beta_{1111}K_1C_{a1}h^2 + \beta_{1002}K_1^2C_{a1}^2h + \beta_{1120}K_1C_{a1}h) \quad (10)$$

$$\alpha_{[Cu(Cys)(OH)(H_2O)_2]^+} = \beta_{1111}K_1C_{a1}h^2 / (h^3 + \beta_{1110}K_1C_{a1}h^2 + \beta_{1111}K_1C_{a1}h^2 + \beta_{1002}K_1^2C_{a1}^2h + \beta_{1120}K_1C_{a1}h) \quad (11)$$

$$\alpha_{[Cu(OH)_2(H_2O)_2]^0} = \beta_{1002}K_1^2C_{a1}^2h / (h^3 + \beta_{1110}K_1C_{a1}h^2 + \beta_{1111}K_1C_{a1}h^2 + \beta_{1002}K_1^2C_{a1}^2h + \beta_{1120}K_1C_{a1}h) \quad (12)$$

$$\alpha_{[Cu(Cys)(L)(H_2O)_2]^+} = \beta_{1120}K_1C_{a1}h / (h^3 + \beta_{1110}K_1C_{a1}h^2 + \beta_{1111}K_1C_{a1}h^2 + \beta_{1002}K_1^2C_{a1}^2h + \beta_{1120}K_1C_{a1}h) \quad (13)$$

To calculate the mole fractions of free and complex-bound copper ions, the equations (9–13) are used.

The calculations are completed by determining the final version of the mole fractions (degrees of accumulation) of the complex forms and constructing their distribution curve (Fig. 6).

According to the presented distribution diagrams, the system under study provides 4 ionic equilibria. They are different in composition, stability, and regions of dominance of the complexes on the pH scale. These data obtained from the final results of the refined formation constants of the coordination compounds, after successive approximation of the theoretical and experimental oxidative functions.

From the obtained calculated data and the distribution diagram, the strongly acidic pH region, a complex of composition $[Cu(Cys)(H_2O)_3]^{2+}$ is formed with a formation constant of 7.52 ± 0.01 . It does not contain a hydroxyl group. Then, a mixed-ligand hydroxo complex of composition $[Cu(Cys)(OH)(H_2O)_2]^+$ is formed with a maximum degree of accumulation – 81.30%. The hydrolysis process competes with complexation with HL. Therefore, the fraction of the hydroxo complex (degree of accumulation) is greater than that with the pure cysteine ion. Moreover, the formation constant of the mononuclear complex is greater than that of the hydroxo complex.



Thus, by the oxidative potential method using the oxidative function and the proposed principle of modeling the equilibria of systems, the composition, stability, regions of existence, and degrees of accumulation of cysteinate coordination compounds of copper were determined: $[\text{Cu}(\text{Cys})(\text{H}_2\text{O})_3]^{2+}$; $[\text{Cu}(\text{Cys})(\text{OH})(\text{H}_2\text{O})_2]^+$; $\text{Cu}(\text{OH})_2(\text{H}_2\text{O})_2^0$; $[\text{Cu}(\text{Cys})(\text{L})(\text{H}_2\text{O})_2]^+$.

The applicability of the modeling principle in redox systems with amino acids has been studied. It significantly accelerates the calculations and improves their accuracy. The calculated model parameters of the complexes delineate the regions of existence and isolation from solution of stable complexes characterized by a high degree of accumulation. The model parameters can be used as reference material for the targeted synthesis of compounds and for thermodynamic calculations.

Conclusions

1. The processes of formation of copper(II) coordination compounds in the Cu(Hg)–Cu(II)–Cys–H₂O system at a temperature of 298 K and an ionic strength of the solution (NaNO₃) of $I = 1.0$ mol/L were studied by the potentiometric method.

2. Experimental curves of the dependences of the EMF on the negative logarithms of the concentrations of hydrogen ions, copper(II), and cysteine were obtained. The formation of complexes of the following composition in the system was demonstrated: $[\text{Cu}(\text{Cys})(\text{H}_2\text{O})_3]^{2+}$; $[\text{Cu}(\text{Cys})(\text{OH})(\text{H}_2\text{O})_2]^+$; $[\text{Cu}(\text{OH})_2(\text{H}_2\text{O})_2]^0$; $[\text{Cu}(\text{Cys})(\text{L})(\text{H}_2\text{O})_2]^+$.

Chemical models of the ionic equilibria of the studied system and possible equations for the formation reactions of the indicated complex compounds have been compiled.

Funding

The study was performed within the framework of a project of the Research Institute of Tajik National University.

Compliance with ethical standards

The article does not contain any studies with animals or humans as subjects.

Conflict of interest

The authors declare no conflict of interest in financial or any other sphere.

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Received 28.05.2026

Approved after reviewing 18.08.2026

Accepted 14.09.2026