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POTENTIOMETRIC STUDY OF THE COPPER(II) IONS COMPLEXATION PROCESS WITH THIOUREA IN ACIDIC MEDIUM

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Abstract

Potentiometric titration method was used to study the copper(II) ions complexation process with thiourea in medium containing 1 mol/l of hydrochloric acid at a temperature of 298 K. It was found out that mononuclear ($CuTM_n$) and binuclear (Cu_2TM_n) complexes were observed in the copper(II) — thiourea system depending on the copper ions concentration. It was determined that in acid medium with copper(II) ions concentration less than $5 \cdot 10^{-4}$ mol/l and mononuclear complexes of the $CuTM_3^{2+}$ composition are generated in the system, which constant is equal to lg β_3 = 11.9. With an increase in the copper(II) ions concentration ($C_{Cu^{+2}} > 5 \cdot 10^{-4}$ mol/l), binuclear thiourea complex dominates in the system. Stability constant logarithm of the Cu_2TM_6 composition binuclear complex is equal to 27.5 and was calculated using the modified Leden's method. Based on the constants, complexes existence regions were determined depending on the ratio $C_{TM}/C_{Cu^{2+}}$. With the $C_{TM}/C_{Cu^{2+}} \geq 5$ relations, existence of a dominant complex significantly depends on the copper(II) ions concentration. It turned out that fractions of all complex particles were growing with an increase in the copper(II) ions concentration in the system. It was found that stability of thiourea complexes in the CuL_i^{2+}, AgL_i^{+}, AuL_i^{+} rows was increasing

Keywords

Thiourea, copper(II) ions, complexation, Leden's method, stability constants

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Introduction. Thiourea (TM) is a complexing agent also in the acidic medium [1], since sulfur atoms are participating in formation of the metal — ligand bonds [2]. Thiourea is being coordinated with metal ions through the sulfur atom and creates strong complex compositions [3–5]. Interaction reactions between copper(II) ions and thiourea were studied in [6–8]. The method based on studying the redox properties of complex systems is of particular interest [9]. Redox reactions and complexation reactions occur simultaneously in the aqueous solution between copper(II) and thiourea at high concentrations. Results of studying the processes of copper(II) ions with the *N* substituted thiourea molecules and thiopyrine in the 1–6 mol/l hydrochloric acid medium were presented in [10–12]. Processes of copper(II) complexation with thiourea in acidic media were not sufficiently studied.

Research objective is to study the process of copper(II) ions with thiourea complexation in the system of copper(II) ions–thiourea–H_2O. To calculate the stability constants, Leden's methods were used with the *Mathcad 15* software.

Materials and methods. Copper dichloride of the chemically pure grade and thiourea of the special purity grade were used as the initial materials, copper electrode (99.999 % purity) — as the indicator electrode, and silver chloride electrode served for reference purposes. The system EMF was measured using a pH-meter-millivoltmeter (pH-150 MA).

Our experiment was carried out at the temperature of 298 K; temperature measurement accuracy was ±0.1 °C. In order to check the copper electrode reversibility, the following dependence was constructed $\Delta E_i\left(\lg C_{\mathrm{CuCl_2}}\right)$. Dependence slope was 28±1 mV, which corresponds to the theoretical value. $CuCl_2$ concentrations varied within the range of $1\cdot10^{-4}$–$5\cdot10^{-3}$ mol/l. Titration was carried out at the nitrogen purge and at least 2 times in the hydrochloric acid (1 mol/l). Complexation constant values were calculated using mathematical models by the Leden's method with the *Mathcad 15* software.

Research results and consideration thereof. Stability constants of the CuTM_n^{2+} mononuclear complexes were calculated using the *F*(TM) function by the Leden's method [13–15]:

$$F(\mathrm{TM}) = \sum \beta_i \left[\mathrm{TM}\right]^{i-1} = \frac{C_{\mathrm{Cu^{2+}}} - [\mathrm{Cu^{2+}}]}{[\mathrm{Cu^{2+}}][\mathrm{TM}]}, \quad (1)$$

where $C_{\mathrm{Cu^{2+}}}$ is the Cu^{2+} ions total concentration; [Cu^{2+}], [TM] are the copper(II) and thiourea(L) ions equilibrium concentrations.

Copper(II) ions equilibrium concentration was calculated using the following equation:

$$\lg[\mathrm{Cu^{2+}}] = \lg C_{\mathrm{Cu^{2+}}} - \frac{E_1 - E_i}{1.985\cdot10^{-4}(T/n)}.$$

Here E_1 is the equilibrium potential in the thiourea absence; E_i is the system equilibrium potential upon adding a certain portion of thiourea; $1.985 \cdot 10^{-4}$ is the stoichiometric coefficient value,

$$\mathrm{SC} = \frac{2.303RT / F}{T / n}.$$

Thiourea equilibrium concentration was determined as:

$$[\mathrm{TM}] = C_{\mathrm{TM}} - N\left(C_{\mathrm{Cu}^{2+}} - [\mathrm{Cu}^{2+}]\right), \qquad (2)$$

where C_{TM} is the thiourea total concentration; N is the ligand average number,

$$N = \frac{E_1 - E_2}{RT / \left(F[\ln(C_{\mathrm{TM}})_1 - \ln(C_{\mathrm{TM}})_2]\right)}.$$

F(TM) function dependences on the thiourea equilibrium concentration. ([TM] = 0) extrapolation gives the β_1 value. The β_2 second stability constant was calculated on the basis of (F(TM) – β_1)/[TM] from [TM] and by extrapolation to the [TM] = 0 value. Subsequently, stability constants were calculated in the similar way.

The N value was determined in subsequent calculations using stability constants by the following formula:

$$N = \frac{\sum i \beta_i [\mathrm{TM}]^{i-1}}{\sum \beta_i [\mathrm{TM}]^{i-1}}.$$

Stability constants for binuclear complexes were calculated using the modified Leden's method [14]. In this case, equations (1) and (2) are transformed into the following equations:

$$F(\mathrm{TM}) = \sum \beta_i \left[\mathrm{TM}\right]^{i-1} = \frac{C_{\mathrm{Cu}^{2+}} - [\mathrm{Cu}^{2+}]}{2[\mathrm{Cu}^{2+}]^2[\mathrm{TM}]};$$

$$[\mathrm{TM}] = C_{\mathrm{TM}} - \frac{N}{2}\left(C_{\mathrm{Cu}^{2+}} - [\mathrm{Cu}^{2+}]\right).$$

Potentiometric titration results are shown in Fig. 1.

Mononuclear complexes are generated in the copper(II)–thiourea system at low concentrations (less than 0.0005 M). At high concentration values, redox reactions are taking place between copper(II) and thiourea ions with the formation of formamidine disulfide and copper(II) ions [6]. With an increase in the medium acidity, copper(II) thiourea complexes are generated. Binuclear complexes are formed at higher concentrations of copper(II) ions in the acidic

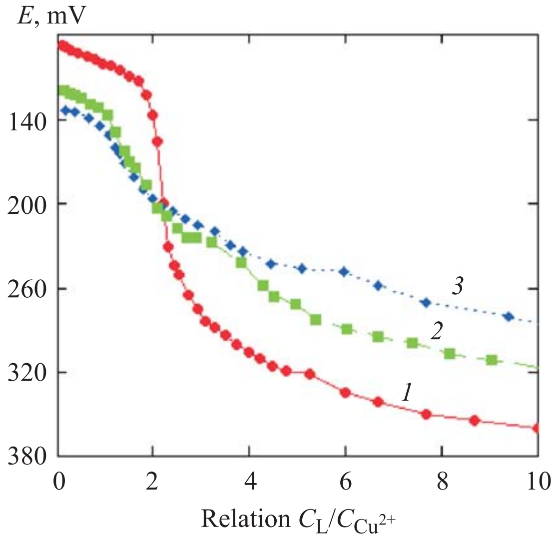

Fig. 1. Cu^{2+} and thiourea potentiometric titration in the 1 M HCl medium: Cu^{2+} ions concentration: *1*) $5{\cdot}10^{-3}$ M; *2*) $1{\cdot}10^{-3}$ M; *3*) $0.5{\cdot}10^{-3}$ M

medium. Therefore, the experiment was carried out in the medium containing hydrochloric acid and copper(II) ions concentration ranging from 10^{-4} to $5 \cdot 10^{-3}$ mol/l. Stability constants of the copper(II) thiourea complexes are provided in Table 1.

Table 1

Stability constants of binuclear copper(II) complexes (Cu_2L_n) with thiourea

$C(Cu^{2+})$	lg β_{21}	lg β_{22}	lg β_{23}	lg β_{24}	lg β_{25}	lg β_{26}
0.0005	7.2	13.5	17.4	20.9	24.2	27.5
0.001	7.2	13.2	17.3	20.8	24.5	28.1
0.005	6.6	13.9	19.2	22.6	25.4	28.0

Concentration stability constants found were used to determine thermodynamic constants of copper(II) complexes with thiourea according to the Vasiliev equation [16]:

$$\lg\beta_0 = \lg\beta - \frac{\Delta\nu z^2 0.509\sqrt{I}}{1+1.6\sqrt{I}} - bI,$$

where $\Delta\nu z^2 = \sum \nu z^2_{derivative} - \sum \nu z^2_{initial}$; I is the ionic strength; b is the empirical coefficient depending on the complex composition (for ML 0.05, ML_2 0.10, for the rest 0.4).

Isocharge reaction equilibrium constants reactions ($\Delta\nu z^2 = 0$) depend on the ionic strength to a much lesser extent. These reactions include the studied reaction $qCu^{2+} + n\text{TM} = Cu_q\text{TM}_n^{2+}$. Calculated values of the complexes thermodynamic stability constants are as follows: lg β_{21} = 6.9; lg β_{22} = 13.4; lg β_{23} = 17.5; lg β_{24} = 21.0; lg β_{25} = 24.3; lg β_{26} = 27.1.

Calculated complexes distributions indicate that at $C_{\text{TM}}/C_{Cu^{2+}} \le 1$ everal complexes are simultaneously observed in the solution (Table 2). At $C_{\text{TM}}/C_{Cu^{2+}} \ge 5$ dominant complex presence significantly depends on the copper(II) ions concentration. According to distribution diagrams (see Fig. 2), proportion of complexes is growing with an increase in the copper(II) ions concentration. With the further increase in the copper(II) ions concentration from 0.001 M, complexes of the Cu_2L_6 composition are dominating in the system.

Table 2

Composition and stability constants of Cu(II), Ag(I) and Au(I) thiourea complexes

Composition	lg β_i, CuL_i^{2+} [6]	lg β_i, CuL_i^{2+}, obtained data	lg β_i, AgL_i^{+} [17]	lg β_i, AuL_i^{+} [18]
ML_1^{n+}	5.7	4.7	8.3	–
ML_2^{n+}	8.5	8.5	11.0	13.3
ML_3^{n+}	11.3	11.9	13.1	–

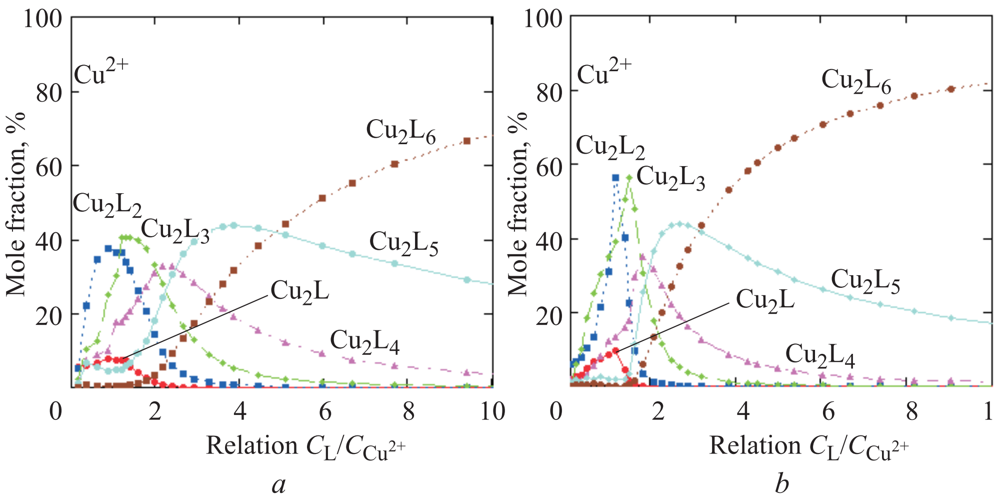

Fig. 2. Diagrams of copper(II) complexes distribution with thiourea:

a) $C_{Cu^{2+}} = 5 \cdot 10^{-4}$ M; *b*) $C_{Cu^{2+}} = 1 \cdot 10^{-3}$ M

It is of interest to compare stability of the Cu(II), Ag(I), and Au(I) thiourea complexes. Silver (I) ion complexes with thiourea were studied in [14, 19]. Thiourea with silver(I) ions provides complexes of the Ag_2L_6 ($\lg\beta_{26}$ = 29,9) composition [14]. Thus, it turned out that stability of the binuclear copper(II) complexes with thiourea is lower than that of the silver(I) binuclear complex with the Ag_2L_n composition. Dependence of the Cu^{2+} and Ag^{+} thiourea complexes stability constants on the number of ligands is presented in Fig. 3.

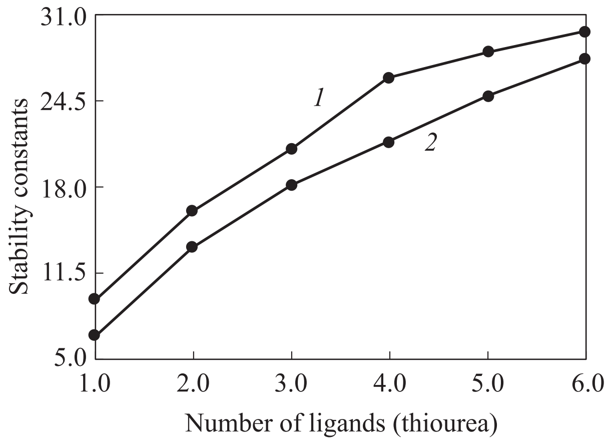

Fig. 3. Dependence of Cu^{2+} and Ag^{+} (M_2L_n, n = 1, 2, ..., 6) thiourea complexes stability constants on the number of ligands:
1) silver(I) thiourea complexes; *2*) copper(II) thiourea complexes

Conclusion. Several complexes are simultaneously present in solution at $C_{TM}/C_{Cu^{2+}} \leq 1$. With $C_{TM}/C_{Cu^{2+}} \geq 5$ dominant complex presence significantly depends on the copper(II) ions concentration. The logarithm of copper(II) complex compounds stability constant with thiourea in case of the binuclear complex (Cu_2TM_6) generation is 27.5. Binuclear copper(II) complexes stability with thiourea is lower than that of the binuclear silver(I) complex of the Ag_2L_n composition.

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