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COMPLEXATION PROCESSES OF Cu^{II} WITH IMIDAZOLE

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Abstract. *The purpose of the study is to investigate the complexation process in the heterogeneous Cu(0)-Cu(II)-imidazole-water system by the classical Clark-Nikolsky oxidation potential method at a temperature of 288.15 K and a solution ionic strength of 1.0 mol/L. The authors found the formation of the following coordination compounds in this system:* $[Cu(HL)_2]^{3+}$, $[CuHL(OH)]^{2+}$, $[Cu(HL)_2(OH)]^{2+}$, $[Cu_2(HL)_2(OH)_2]^{4+}$, $[Cu_2(HL)_2(OH)_3]^{3+}$. *The complexation process proceeds in a rather wide pH range from 1.0 to 10.5.*

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Introduction

Recently biocoordination chemistry began to develop rapidly. It studies the interaction between biologically active ‘metals of life’ and equally active ligands, such as amino acids and peptides. They play a significant biochemical role in systems containing the imidazole ring and are able to give stable complex compounds with metal ions [1-3]. Therefore, the purpose of the research was to investigate the formation of coordination compounds of Cu(II) with imidazole.

According to the analysis of the literature, there is no information on polynuclear, mixed valence, heterovalent copper complexes including Cu^+ and Cu^{2+} in aqueous solutions of various polydentate ligand. The formation of such compounds, apparently, is possible at high pH values, as well as in the presence of $Cu^{2+}$and Cu^+ ions in the reaction medium. Moreover, there is no information about the study of Cu^{2+} complexation in aqueous solutions of imidazole by the oxidation potential method.

Conforming to [4], Cu(I) compounds are insoluble or sparingly soluble in water, while Cu(II) compounds are generally stable. Cu(I) are easily oxidised and decomposed when derivatives undergo slight heating or light exposure of Cu(II) derivatives. Eventually, an equilibrium in solutions between all possible states of copper is established. For example, when metallic copper contact to solution, the following equilibrium is formed:

$$Cu^0_{(s)} + Cu^{2+}_{(l)} \leftrightarrow 2Cu^+_{(st).} \quad (1)$$

Hereinafter: *s* is the solid state, *l* is the liquid state, a *st* is the solution.

The equilibrium constant of the reaction proceeding according to equation (1) should be equal to:

$$K = \frac{a^2_{Cu^+}}{a^2_{Cu^{2+}}} = 6.04 \cdot 10^{-7}\ mol/l \quad (2)$$

Cu^+ ions have d^{10} configuration, and Cu^{2+} – d^9. Therefore, according to the ideas [5] in aqueous solutions these ions exist as aquacomplexes $[Cu(H_2O)_4]^+$ and $[Cu(H_2O)_6]^{2+}$. Cu^+ is characterised by coordination numbers of 2 and 4; $Cu2^+$ is characterised by 4 and 6. Cu(II) can form both cationic and anionic coordination compounds.

The formation of complex particles in solutions usually proceeds in a stepwise manner. Indeed, the water molecules in the aquacomplexes are replaced by the ligand gradually [6]. For instance, a rapid intramolecular transformation of the tetragonal structure occurs in the $[Cu(H_2O)_6]^2+$ aquacomplex. All positions become equivalent; a rapid exchange of ligands takes place.

Main body

We have studied the redox system Cu(0)/Cu(II) by the oxidation potential method [7, 8]. In this case, the following equilibrium is formed at the electrode:

$$Cu^{2+} + 2e^- \rightarrow Cu(Hg). \quad (3)$$

In coordination compounds, heterocyclic structures containing an imidazole core act as ligand. We consider the imidazole molecule (Figure 1).

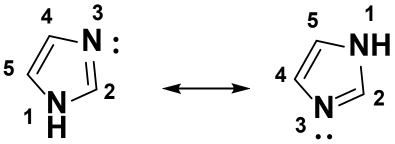

Fig. 1. Tautomerism of imidazoles

Its general formula suggests the presence of two double bonds in the molecule and, as a consequence, two possible structures. Two conjugated double bonds with four π-electrons are combined with an unshared pair of electrons of the first nitrogen atom. A single six π-electron aromatic system is formed. Imidazole can participate in reactions as a neutral molecule or as a cation (anion). It is possible to form complexes either due to the unshared nitrogen pair (3) or due to π-dative interaction of the imidazole ring.

The acid-base equilibrium (Figure 2) of neutral imidazole (II) depends on the nature of the solvent and medium pH; it shifts towards conjugated base (I), towards conjugated acid (III) or the molecule remains neutral (II). Therefore, imidazole is a very strong base but a very weak acid.

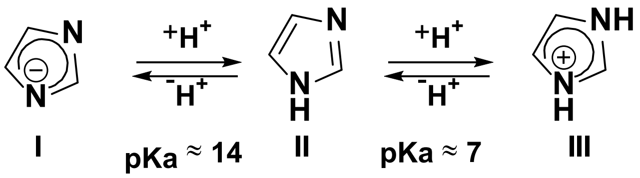

Fig. 2. Acid-base equilibrium of imidazole

The non-equal distribution of electron density in the imidazole ring makes it possible to represent a large number of resonance structures with different charge distributions in it.

In the Cu(0)/Cu(II) system, the heterogeneous interaction of the redox components is represented by the following equation:

$$Cu^{2+} + 2e^- \leftrightarrow Cu^0_{(s)}. \qquad (4)$$

The copper electrode is pre-amalgamated for the experiment. The solubility of copper in mercury at 288.15 K is $7.9 \cdot 10^{-3}$ atomic %. The Cu-Cu bonding energy is close to the Cu-Hg bonding energy; copper does not form strong compounds with mercury. Since the bond energies of copper-mercury and copper-copper bonds have close values; the potential of the amalgamated copper electrode does not differ much from that of the pure metal [7]. The reaction of the amalgamated copper electrode can be represented as follows:

$$Cu^{2+} + 2e^- + Hg \leftrightarrow Cu^0(Hg). \qquad (5)$$

The oxidation potential equation has the following form:

$$\varphi_{Cu(II)/Cu(Hg)} = \varphi^0_{Cu(II)/Cu(Hg)} + \nu/2\lg\,(a_{Cu^{2+}}/a_{Cu(Hg)}). \qquad (6)$$

This expression has the form of the following in dilute solutions:

$$\varphi_{Cu(II)/Cu(Hg)} = \varphi^0_{Cu(II)/Cu(Hg)} + \nu/2\lg\,[Cu^{2+}]/[Cu(Hg)]. \qquad (7)$$

In the most general case, the oxidation potential depends on the concentration of the complexes and ligand, the activity of hydroxyl ions, water, and the initial concentration of copper (II) ions in solution and copper atoms on the amalgam surface. The oxidative potential under these conditions depends only on three variables, i.e.

$$pH = -lga_{H^+}; \qquad pC_{H_2L} = lgC_{H_2L}; \qquad pC_{Cu(II)} = lgC_{Cu^{2+}}. \qquad (8)$$

The dependence of the oxidation potential on each of these parameters, with all others constant, will be represented by a curve consisting of linear sections connected by smooth bends. The dominance condition of the corresponding complex compound should be fulfilled at each linear section of the corresponding curves. The total number of coordinated ligands (L and OH^-), the nuclearity of the complexes, and the number of coordinated ligands L can be determined using the slopes of the experimental curves.

Therefore, such processes may occur as:

$$Cu(Hg + e) \leftrightarrow Cu^+ + e^- + Hg, \qquad (9)$$

$$Cu^+ \leftrightarrow Cu^{2+} + e^-, \qquad (10)$$

$$Cu(Hg) + Cu^{2+} \leftrightarrow 2Cu^+ + Hg. \qquad (11)$$

Meanwhile, reactions (9) and (10) proceed only in the acidic area of solutions. The equilibrium constant of reaction (10) is $6.04 \cdot 10^{-7}$ only in the ideal case.

Hence, when using the Cu(II)/Cu(0) half-element for potentiometric study of complexation in aqueous solutions in a wide range of pH and concentrations of components, some amounts of Cu(I) ions may occur in the system along with Cu(II) ions. This will probably impact the course of the complexation processes and the results of oxredmetric measurements. For example, when introducing a copper amalgamated electrode into the medium under study, new redox couples of the type are possible (depends on the experimental conditions):

Cu(II)/Cu(I): $Cu^{2+} + e^{-} \leftrightarrow Cu^{+}$, $E^0 = 0{,}153$ B (12)
Cu(I)/Cu(0): $Cu^{+} + e^{-} \leftrightarrow Cu^{0}$, $E^0 = 0{,}520$ B (13)

The occurence of redox equilibrium (12) can be proved by measuring the potential at the platinum electrode. As a result of the possible electrode reaction (13), the measured value of the oxidation potential at the copper amalgamated electrode will be significantly different from the value of the equilibrium electrode potential of the corresponding electrochemical reaction:

Cu(II)/Cu(0): $Cu^{2+} + 2e^{-} \leftrightarrow Cu^{0}$, $E^0 = 0{,}337$ B (14)

According to the theory of the oxidation potential method, the experimental curves of dependence indicated above were obtained. Comparison of slopes of experimental curves (mathematical model or matrix) (Table 1) with partial derivatives of the oxidation potential equation (Equation 15) allowed us to calculate numerical values of basis particles (*g, s, l* and *k*, respectively, the number of copper atoms, hydrogen ions, ligand, and hydroxyl groups in the complex*)*, make a table of the chemical model of Cu(II) complexes formation (Table 2).

The general equation of the oxidation potential φ for the system studied is as follows:

$$\varphi = \varphi^0 + \frac{1}{2}\vartheta lg C_0 + \frac{1}{2}\vartheta lg \sum_{1}^{q}\sum_{0}^{s}\sum_{0}^{l}\sum_{0}^{k} q\beta_{qslk}^{\frac{1}{q}} G_{qslk}^{\frac{q-1}{q}} [\mathrm{H}_{b-n}\mathrm{L}^{n-}]^{\frac{1}{q}} h^{-\frac{k}{q}} [\mathrm{Cu}^{(2)+}]^{q}, \quad (15)$$

where: φ^0 is the standard oxidation potential, C_0 is the concentration of Cu(II); $\upsilon = 2.303RT/F$; q is number of Cu(II) atoms in the coordination compound (nuclearity of the complex compound), k is number of protonated ligand groups, x is number of L^{b-} groups, y is number of coordinated hydroxyl groups, r is number of coordinated water molecules, m is the charge of the Cu(II) coordination compound, l is the number of ligands in the complex, u is the number of coordinated ligands A, v is the number of coordinated hydroxyl groups, w is the number of coordinated water molecules, n is the charge of the coordination compound of metal reduced form. Water activity for the dilute solutions studied is a constant value and is assumed to be equal to one.

The values of r, m, u, n with other parameters are related by the following relations:

$$r = 6q - 2x - y; \quad m = (n +)q - x - y; \quad w = 6p - u - v; \quad n = 2p - u - v. \quad (16)$$

Hence, only five complexes are formed in the studied system (Table 1); four contain hydroxyl groups in the inner sphere: $[Cu(HL)_2]^{3+}$, $[CuHL(OH)]^{2+}$, $[Cu(HL)_2(OH)]^{2+}$, $[Cu_2(HL)_2(OH)_2]^{4+}$, $[Cu_2(HL)_2(OH)_3]^{3+}$. They are formed in the *pH* range of 1.0 to 10.0. The specific feature of this system is characterised by the existence of all formed coordination compounds in a rather narrow interval of (0.6 - 2.4 *pH units).* The complexation process proceeds up to $pH = 10.5$.

Table 1. Experimental values of slopes of the oxidation potential curve dependence on concentration variables (stoichiometric matrix) for Cu(0)Hg-Cu(II)-imidazole-water system at temperature 288.15 K, I = 1.0; $C_{Cu(II)} = 1 \cdot 10^{-3}$ and $C_L = 1 \cdot 10^{-2}$ mol/l

Item n/a	Interval of finding slopes on the *pH* scale	Presumed composition of the complexes				Complex formation constant β_{gslk}
		pH	$pC_{Cu(II)}$	pC_L		
1	1.2 - 3.2	-2*v*	- *v*	2*v*	$[Cu(HL)_2]^{2+}$	β_{10220}
2	3.2 - 4.8	-2*v*	- *v*	*v*	$[CuHL(OH)]^{+}$	β_{10111}
3	4.5 - 6.9	-3*v*	- *v*	2*v*	$[Cu(HL)_2(OH)]^{+}$	β_{10221}
4	6.6 - 7.4	-2*v*	- *v*/2	*v*	$[Cu_2(HL)_2(OH)_2]^{2+}$	β_{20222}
5	7.4 - 10.0	-2*v*	- *v*/2	*v*	$[Cu_2(HL)_2(OH)_3]^{+}$	β_{20223}

Analyses of the slopes of the experimental dependences on each of the concentration variables allowed us to construct a chemical model of the equilibria existing in the studied system (Table 2).

Table 2. Chemical model of the equilibria of the Cu(0),Hg-Cu(II)-imidazole-water system at 288.15 K, I = 1.0; $C_{Cu(II)} = 1 \cdot 10^{-3}$ and $C_L = 1 \cdot 10^{-2}$ mol/l

Item n/a	*Cu(II)*	*H*	*L*	*OH*	Composition of the complex
	g	*s*	*l*	*k*	
1	*1*	*2*	*2*	*0*	$[Cu(HL)_2]^{2+}$
2	*1*	*1*	*1*	*1*	$[Cu\ HL(OH)]^{+}$
3	*1*	*2*	*2*	*1*	$[Cu\ (HL)_2(OH)]^{+}$
4	*2*	*2*	*2*	*2*	$[Cu_2(HL)_2(OH)_2]^{2+}$
5	*2*	*2*	*2*	*3*	$[Cu_2(HL)_2(OH)_3]^{+}$

Before calculating the equilibrium constants or other ionic equilibria in the system under study, it is necessary to calculate the values of the experimental oxidation function [9]. The experimental oxidation function f^0_E is calculated in terms of the experimentally measured values of the oxidation potential, according to the following equation:

$$f_E^0 = {}^{C_r}/_{C_o}\, exp^{(\varphi-\varphi^0)n/\vartheta}, \tag{17}$$

where exp is the base of natural logarithms, φ is the experimentally measured value of the oxidising potential, φ^0 is the apparent value of the normal or standard oxidising potential, and $v = 2.303RT/F$.

The application of the oxidation function is based on approximating the theoretical oxidation function f_t^0 by iteration until it coincides with the experimental f_e^0 oxidation function. The theoretical oxidation function is expressed by equation (18):

$$f_T^0 = {}^{1}/_{C_o} \left\{ \sum_{1}^{q} \sum_{0}^{s} \sum_{0}^{l} \sum_{0}^{k} q\beta_{qslk}^{\frac{1}{q}}\, G_{qslk}^{\frac{q-1}{q}} [\mathrm{H}_{b-n}\mathrm{L}^{n-}]^{\frac{1}{q}} h^{-\frac{k}{q}} \left[\mathrm{Me}^{(z-e)+}\right]^{q} \right\} \tag{18}$$

The following terms are used in equation (18): f^0_T is theoretical oxidation function: C_o is the concentration of Cu(II); q is the number of atoms of the oxidised form, s is the number of hydrogen ions, l is the number of ligand atoms, k is the number of hydroxyl groups, β_{qslk} is the total complex formation constant, G_{qslk} is the concentration of polynuclear forms, H is the designation of the hydrogen atom, L is the designation of the ligand, n is the ionisation steps of the polycarboxylic acid, Me is the designation of the metal of the complexing agent, z is the charge of the metal or redox ligand, *e* is the number of electrons involved in the electrode reaction.

Figure 3 shows the dependences of the experimental and theoretical oxidation functions on pH.

It is possible to find the closest values of the formation constants of the coordination compounds established in the investigated system after 8-10 iterations, i.e. successive approximations (Table 3).

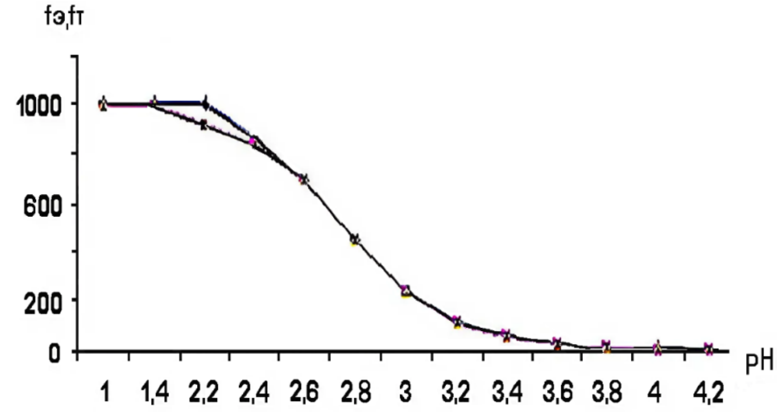

Fig. 3. Dependences of theoretical and experimental oxidation functions on pH for Cu(0)Hg-Cu(II)-imidazole-water system at $I = 1.0$; $C_{Cu(II)} = 1 \cdot 10^{-3}$ and $C_L = 1 \cdot 10^{-2}$ mol/l

Table 3. Calculated values of model parameters of coordination compounds formed in the Cu(0)Hg-Cu(II)-imidazole-water system at a temperature of 288.15 K, $I = 1.0$; $C_{Cu(II)} = 1 \cdot 10^{-3}$ and $C_L = 1 \cdot 10^{-2}$ mol/l.

Item n/a	Composition of the complex	Constant of formation $lg\beta_{qpslk}$	α_{max}, %	*pH*
1	$[Cu(HL)_2]^{2+}$	4.99±0.02	24.2	2.2
2	$[CuHL(OH)]^{+}$	11.38 ±0.02	22.4	3.8
3	$[Cu(HL)_2(OH)]^{+}$	2.19±0.02	32.4	5.5
4	$[Cu_2(HL)_2(OH)_2]^{2+}$	6.50±0.02	72.4	7.6
5	$[Cu_2(HL)_2(OH)_3]^{+}$	20.69±0.02	100.0	9.2

The studies of complexation processes in various redox systems show a significant simplification and acceleration of calculations by the introduction of the oxidation function, a more accurate determination of coordination compounds composition in solutions, and, in the case of heteronuclear and heterovalent complexation, an approximation of equilibrium metal concentrations.

It allows us to determine the composition of coordination compounds in solutions more precisely, and, in the case of heteronuclear and heterovalent complexation – to approximate metals equilibrium concentrations. Calculations are considered complete when the theoretical and experimental pH dependences of the oxidation function are in good agreement with each other. Moreover, the use of the oxidation function is not only convenient for calculations. However, it also allows us to determine complex formation initiation of the oxidised or reduced form of the metal more clearly. At the same time, the oxidation function decreases with increasing pH when the oxidised form of the metal participates in the reaction. Indeed, the numerical value of f^0 does not change or increases when complexes of the reduced form are formed [9].

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