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COLLOID CHEMISTRY  
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## Study of Equilibria in the “CuCl<sub>2</sub>–H<sub>2</sub>O–NaOH” System by Potentiometric Titration<sup>1</sup>

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Equilibrium processes in the “CuCl<sub>2</sub>–H<sub>2</sub>O–NaOH” system are studied with the consideration of the formation of low soluble phases of various compositions based on mathematical processing of experimental results from potentiometric titration using EQ-5 software. The values of instability constants of copper complex ions and dynamic equilibrium constants of copper low soluble compounds are calculated along with their stoichiometric compositions and regions of stable existence.

**Keywords:** copper(II) chloride, complexation, potentiometric titration, mathematical processing, equilibrium processes, thin films

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### INTRODUCTION

Recently thin film nanostructures based on transition metal chalcogenides have attracted great attention of scientists due to their unique physical and chemical properties depending not only on shape and size of crystallites forming them but also on the presence of various impurity phases in their composition.

Copper selenide is among desired semiconductors. Its thin films are widely used in electronic and optoelectronic devices as an anode material in lithium-ion batteries, gaseous sensors, Schottky diodes, optical filters, superionic conductors, photodetectors and thermoelectric generators [1–8].

One of the most challenging methods of synthesis of nanostructural films based on copper selenide is a chemical bath deposition. This method is highly competitive along with achieving required electro-physical properties of obtained materials compared to other methods of synthesis. Besides, technology is realized at temperatures below boiling point of aqueous solution without using complex and expensive equipment and initial reagents with high degree of purity.

The features of chemical bath deposition are side reactions which occur along with the primary reaction of metal chalcogenide formation. Side reactions result in formation of not only mononuclear but also a large amount of polynuclear hydroxocomplexes and oxy-

gen-containing compounds with low-solubility in water. In order to obtain copper selenide nanostructural layers of high quality without impurity phases inclusions it is important to study the composition and regions of stable existence in solution of complex hydroxyl forms and low-soluble compounds of corresponding transition metal.

According to numerous literature data copper ions in solution can exist in the form of both basis (mononuclear) and polynuclear [9–11] hydroxocomplexes and compounds. In works [12, 13] possible formation of low-soluble hydroxides and oxides of metal in reasonably concentrated solutions is mentioned. There is a large number of research works [9, 11, 14, 15] which mention the prevailing influence of initial metal salt concentration and its anion on the amount and the composition of forming polynuclear solid-phase compounds of Cu(II). In spite of this fact in most works describing the study of equilibria that are formed in aqueous solutions copper sulfate was used as a metal salt. Data on the study of behavior of metal chloride solution while changing its alkalinity are not found in literature. No doubt that the absence of information about formation and composition of complex hydroxide compounds of copper(II) makes it significantly difficult to choose the conditions for deposition of copper chalcogenide films from aqueous solutions while using chloride salt.

The results from potentiometric titration of metal salt in the presence of complexing agents allow to

<sup>1</sup> The article was translated by the authors.

develop an accurate model of equilibrium processes occurring in the system. It gives an opportunity to reveal different metal complexes in free forms, in forms of low soluble compounds and compounds existing in a small amount in the system. The latter can essentially influence on the results of film deposition [16].

The aim of the present work is to study equilibria in the “CuCl<sub>2</sub>–H<sub>2</sub>O–NaOH” system by mathematical processing of the experimental results from potentiometric titration using EQ-5 software to determine the composition and regions of stable existence of forming polynuclear hydroxocomplexes and low soluble copper(II) compounds.

## EXPERIMENTAL

We used copper chloride dihydrate solution CuCl<sub>2</sub> · 2H<sub>2</sub>O (pure for analysis grade) standardized by iodometric titration as a copper source. Titrant was aqueous solution of sodium hydroxide NaOH (pure for analysis) standardized by the results of acid-base titration.

Experimental data on potentiometric titration in aqueous solutions of copper chloride CuCl<sub>2</sub> · 2H<sub>2</sub>O by sodium hydroxide NaOH were obtained at varying of metal salt concentration in the ranges 0.0001–1.01 M, and titrant concentration from 0.001 to 10.25 M.

Potentiometric measurements were made using pH-meter “Ekspert-pH” with accuracy ±0.01 at temperature 25°C. To stir solutions we used magnet drive with steel rod in a capron cover as a stirrer. The processing of titration results was made by EQ-5 software developed and proposed in work [16].

Potentiometric titration was made according to the standard procedure: a fixed volume (25 mL) of copper salt CuCl<sub>2</sub> · 2H<sub>2</sub>O was poured in a glass beaker, into which NaOH solution was added dropwise from a burette with continuous stirring by a magnetic stirrer. At the end of each interval between the drops (from 30 to 180 s), the added volume of alkali and pH value of the solution were recorded. During pH measurements the solution was not stirred.

While titration we recorded pH values corresponding to the beginning of the precipitation. It was defined visually by observing turbidity in the solution. After the beginning of precipitation in the solution the interval between the drops was increased because the heterogeneous process requires more time for reaching the equilibrium state.

## RESULTS AND DISCUSSION

The experimental data on potentiometric titration were presented as plotted dependences of the function of formation for hydroxide ions  $n_{\text{OH}^-}$  on pH for mathematical processing. It helps clearer and more infor-

mative to determine the composition and regions of existence of forming complex compounds than the classical representation ( $\text{pH} = f(V_{\text{NaOH}_i})$ ).

The function of formation for hydroxide ion  $n_{\text{OH}^-}$  is the experimental dependence of the change in pH upon the addition of the titrant:

$$n_{\text{OH}^-} = \frac{C_{\text{NaOH}}V_{\text{NaOH}}}{C_{\text{Cu}}V_{\text{Cu}}}, \quad (1)$$

where  $C_{\text{Cu(II)}}$  and  $V_{\text{Cu(II)}}$  initial concentration of copper(II) and volume of reaction solution before the addition of titrant, respectively;  $C_{\text{NaOH}}$  and  $V_{\text{NaOH}_i}$  initial concentration of sodium hydroxide (titrant) and its volume, added in titration, respectively.

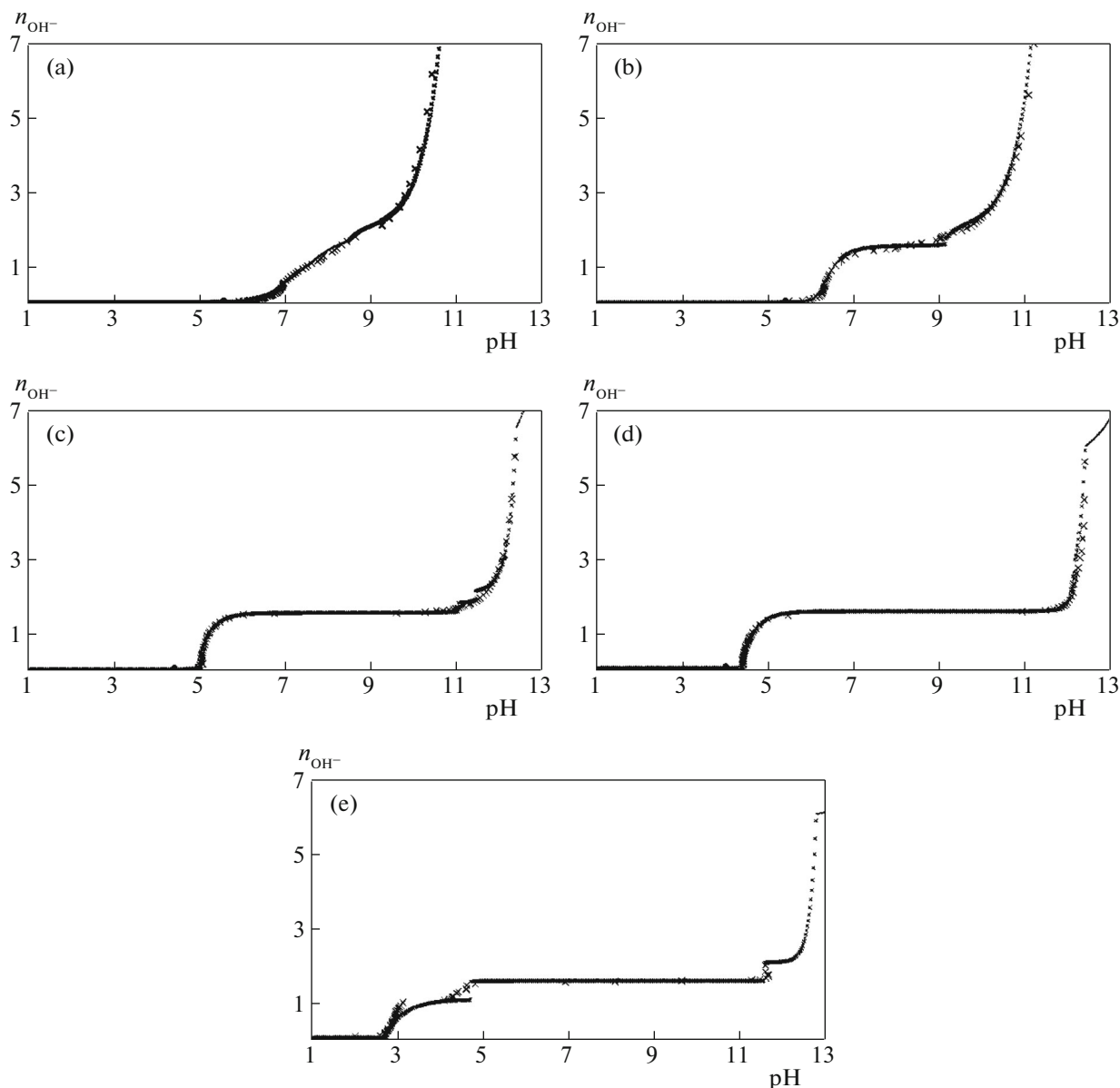
In general potentiometric titration curves presented in  $n_{\text{OH}^-} = f(\text{pH})$  coordinates are qualitatively described by a step with a beginning and a plateau, by the number of steps observed upon transiting from one solid phase into another, and the final part of the curve. Note that we can see thin and thick lines on the calculated (solid) curve. The former characterize pH regions free of precipitates, while the latter characterize precipitation from the solution.

To describe potentiometric titration curves in the “CuCl<sub>2</sub>–H<sub>2</sub>O–NaOH” system in the first approximation we used reference values for instability constants of mononuclear hydroxocomplexes of Cu<sup>2+</sup> [17]. However, as obtained model showed, it is not possible to describe experimental data using only these values of constants. This fact means that we should consider not only mononuclear metal complexes but also polynuclear charged and neutral hydroxoforms and low soluble compounds.

Summary experimental results (crosses) and calculated data using EQ-5 software (solid lines) on potentiometric titration of copper chloride solutions by sodium hydroxide in  $n_{\text{OH}^-} = f(\text{pH})$  coordinates are given in Fig. 1.

Figure 1 shows that the copper(II) salt concentration increasing results in deeper hydrolysis of the solution, and the beginning of the potentiometric titration curve is shifted to lower pH values. Particularly, at 0.0001 M copper(II) chloride concentration (Fig. 1a), hydrolysis begins at pH 5.7, and the maximum content of metal ions in the solution (1.01 M) shifts the beginning of this process toward the more acidic region with pH 2.7 (Fig. 1e).

The attention should also be paid to the change of the angle of incline on potentiometric titration curves (Fig. 1), which gradually decreases with the increasing of copper(II) content in the solution. So, at 0.0001 M CuCl<sub>2</sub> concentration (Fig. 1a) the angle of incline is the largest. It due to the consistent formation of several positively charged and neutral forms of copper(II) compounds at the insignificant increasing of the function of formation for hydroxide ions  $n_{\text{OH}^-}$ .



**Fig. 1.** Dependences of the function of formation for hydroxide ions  $n_{\text{OH}^-}$  on pH of copper(II) chloride solution according to the results from processing experimental (crosses) and calculated (solid lines) potentiometric titration curves at 25°C and the following initial concentrations of copper(II) salt and sodium hydroxide, M:  $C_{\text{Cu(II)}} = 0.0001$ ,  $C_{\text{NaOH}} = 0.001$  (a);  $C_{\text{Cu(II)}} = 0.001$ ,  $C_{\text{NaOH}} = 0.01$  (b);  $C_{\text{Cu(II)}} = 0.01$ ,  $C_{\text{NaOH}} = 0.10$  (c);  $C_{\text{Cu(II)}} = 0.20$ ,  $C_{\text{NaOH}} = 2.00$  (d);  $C_{\text{Cu(II)}} = 1.01$ ,  $C_{\text{NaOH}} = 10.25$  (e).

Further increasing of Cu(II) ions concentration from 0.001 M (Fig. 1b) to 0.20 M (Fig. 1d) results in the decreasing of the angle of incline on the potentiometric titration curve due to the decreasing of the number of formed polynuclear hydroxocomplexes and compounds. However, at the maximum content of metal salt (1.01 M) the increasing of the angle of incline is observed again that indicates the appearance of new polynuclear copper complex forms in the solution (Fig. 1e).

Stoichiometric composition of the formed solid phase can be determined by projection the plateau on

the calculated curve on the ordinate axis. For the “CuCl<sub>2</sub>–H<sub>2</sub>O–NaOH” system the function of formation for hydroxide ions  $n_{\text{OH}^-}$  is 1.5. It indicates that the compound with Cu<sub>x</sub>(OH)<sub>1.5x</sub>Cl<sub>0.5xS</sub> composition is deposited from the solution in the region where “plateau” exists. Thus, at  $x = 1$  the low soluble Cu(OH)<sub>1.5</sub>Cl<sub>0.5S</sub> compound can be formed in the solution that corresponds with the results obtained in work [12] for the “CuCl<sub>2</sub>–NH<sub>4</sub>Cl–NH<sub>3</sub>–H<sub>2</sub>O” system.

It should be noted that the increasing of the initial copper(II) concentration results in significant broad-

**Table 1.** Theoretical values of instability constants for copper(II) hydroxocomplexes and dynamic equilibrium constants for low soluble compounds calculated according to potentiometric titration data. Reference values of instability constants for copper(II) hydroxocomplexes are given to comparison [17]

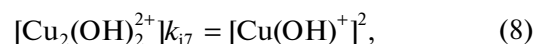
Equilibrium constants	Calculated value	Reference value
$pk_{i1}$	$6.1 \pm 0.1$	6.0
$pk_{i2}$	$10.8 \pm 0.1$	10.7
$pk_{i3}$	$14.3 \pm 0.1$	14.2
$pk_{i4}$	$17.6 \pm 0.1$	16.4
$pk_{i5}$	$20.8 \pm 0.1$	—
$pk_{i6}$	$23.7 \pm 0.1$	—
$pk_{i7}$	$5.1 \pm 0.1$	—
$pk_{i8}$	$23 \pm 1.0$	—
$pk_{i9}$	$22 \pm 0.3$	—
$pk_{i2S}$	$-5.5 \pm 0.1$	—
$pk_{i7S}$	$-4.2 \pm 0.1$	—
$pk_{i8S}$	$-5.3 \pm 0.1$	—
$pk_{i9S}$	$-10.9 \pm 0.2$	—
$pk_{i10S}$	$-9.1 \pm 0.1$	—

ening of the range where  $Cu_x(OH)_{1.5x}Cl_{0.5xS}$  phase exists due to the shift of the initial and final parts of “plateau” in more acidic and more alkaline region, correspondently. For example, at metal salt concentration 0.001 M (Fig. 1b) the range of existence of  $Cu_x(OH)_{1.5x}Cl_{0.5xS}$  is within  $5.8 \leq pH \leq 9.2$ , while at  $[CuCl_2] = 1.01$  M (Fig. 1e) this range broadens to  $pH 4.8-11.6$ . At the minimum copper(II) chloride concentration plateau is not observed on the potentiometric titration curve (Fig. 1a) and just one inflection point is seen. At  $pH > 8.5$  on the calculated curve “thick” line can be observed that characterizes solid phase formation, which has other composition if compared with  $Cu_x(OH)_{1.5x}Cl_{0.5xS}$ . The presence of this compound is also typical for 0.001 M copper(II) content (Fig. 1b), however, its appearance is observed in more alkaline range at  $pH > 9.1$ .

On the calculated potentiometric titration curve when copper(II) chloride concentration is 0.01 M (Fig. 1c) two additional steps in alkaline area at  $n_{OH^-} = 1.75$  and 2 can be observed due to the formation of compounds with compositions  $Cu_x(OH)_{1.75x}Cl_{0.25xS}$  and  $Cu_x(OH)_{2xS}$ , correspondently. Thus, by both experimental and calculated methods it was proved that at higher metal ions content in the initial solution  $Cu_x(OH)_{1.75x}Cl_{0.25xS}$  solid phase is not formed, whereas the area of existence of  $Cu_x(OH)_{2xS}$  broadens.

When copper chloride concentration is 1.01 M (Fig. 1e) at  $pH < 4.8$  the step corresponding to  $n_{OH^-} = 1$  appears, i.e., firstly the compound of stoichiometric composition  $Cu_x(OH)_xCl_{xS}$  is deposited from the solution, and only then  $Cu_x(OH)_{1.5x}Cl_{0.5xS}$  phase is formed.

Mathematical processing the experimental results from potentiometric titration was carried out using EQ-5 software to establish equilibria in aqueous solutions of metal salts. This allowed us to create basic equations for main equilibrium processes, that significantly influence on the ionic composition changes in the “ $CuCl_2-H_2O-NaOH$ ” system during titration



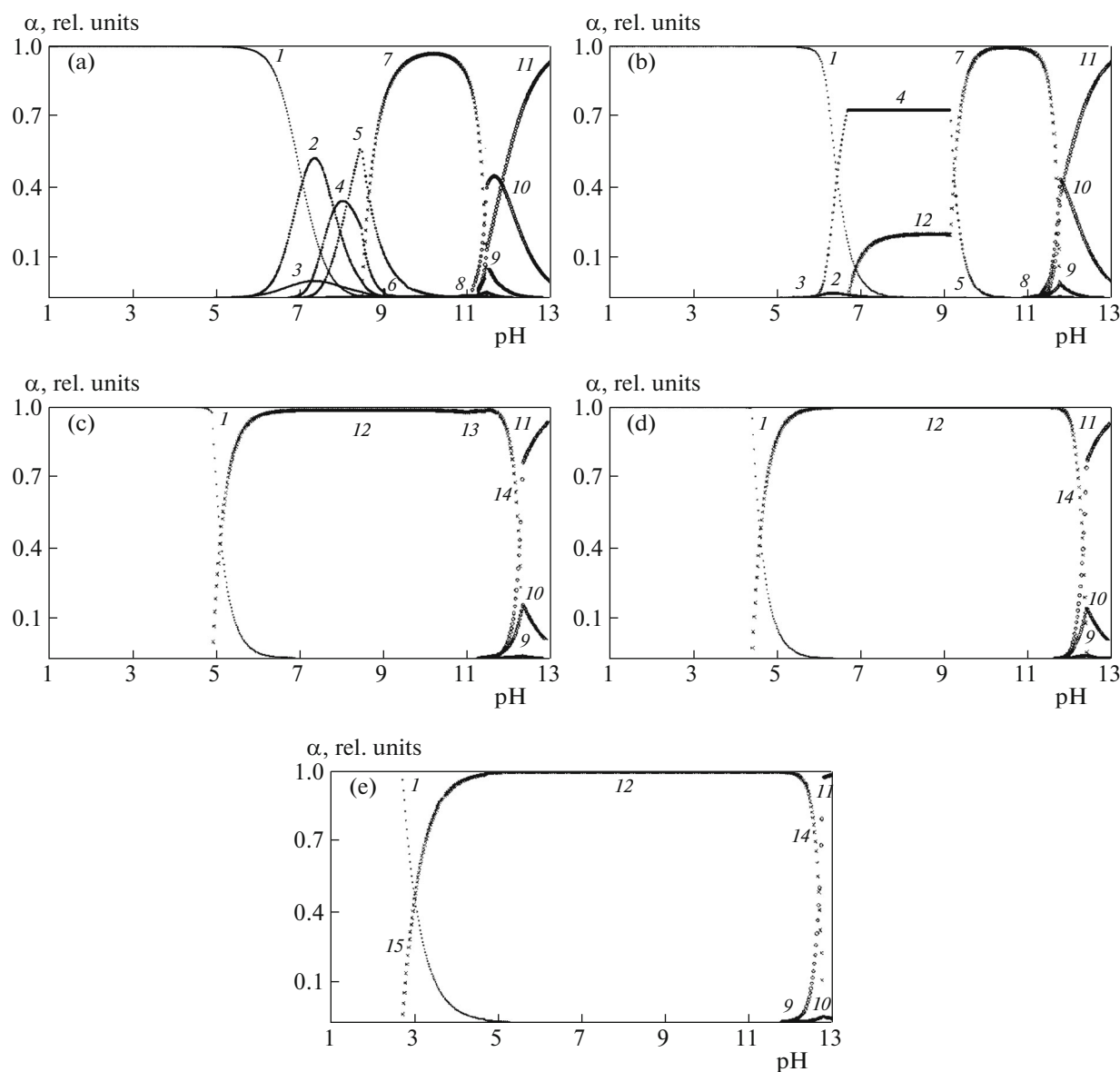
where  $k_{i1}-k_{i9}$  are dynamic equilibrium constants of the corresponding processes that characterize the stability of the inner sphere of a complex ion, i.e., instability constants.

In the considered system the formation of both mono- and polynuclear low soluble compounds:  $Cu(OH)_{2S}$  ( $k_{i2S}$ ),  $Cu_2(OH)_2Cl_{2S}$  ( $k_{i7S}$ ),  $Cu_2(OH)_3Cl_S$  ( $k_{i8S}$ ),  $Cu_4(OH)_7Cl_S$  ( $k_{i9S}$ ),  $CuO_S$  ( $k_{i10S}$ ) is also possible, where  $k_{i2S}$ ,  $k_{i7S}-k_{i10S}$  are equilibrium constants for the formation of corresponding phases.

Table 1 presents calculated by EQ-5 software and reference values for the instability constants of the processes discussed above.

It can be seen from the table that the calculated and reference values of the instability constants of copper hydroxocomplexes ( $pk_{i1}-pk_{i4}$ ) are in good agreement with each other. Comparing the values of instability constants for copper(II) complex ions obtained in this research and in work [14], it should be mentioned that neither metal salt anion nor ligands introducing in the system do not influence on their values, however result in the formation of low soluble metal compounds with various compositions.

The fractional distribution of hydroxocomplexes and low soluble compounds of copper(II) formed in the “ $CuCl_2-H_2O-NaOH$ ” system, depending on  $pH$  at different initial concentrations of the reactants, is shown in Fig. 2. Its analysis allows us to explain more



**Fig. 2.** Calculated overlapping regions of the formation of uncomplexed ions  $\text{Cu}^{2+}$  (1), hydroxocomplexes  $\text{Cu}_2(\text{OH})_2^{2+}$  (2),  $\text{Cu}(\text{OH})^+$  (3),  $\text{Cu}_2(\text{OH})_3^+$  (4),  $\text{Cu}_4(\text{OH})_7^+$  (5),  $\text{Cu}(\text{OH})_2$  (6),  $\text{Cu}(\text{OH})_3^-$  (8),  $\text{Cu}(\text{OH})_4^{2-}$  (9),  $\text{Cu}(\text{OH})_5^{3-}$  (10),  $\text{Cu}(\text{OH})_6^{4-}$  (11) and low soluble compounds  $\text{Cu}(\text{OH})_{2\text{S}}$  (7),  $\text{Cu}_2(\text{OH})_3\text{Cl}_{\text{S}}$  (12),  $\text{Cu}_4(\text{OH})_7\text{Cl}_{\text{S}}$  (13),  $\text{CuO}_{\text{S}}$  (14),  $\text{Cu}_2(\text{OH})_2\text{Cl}_{2\text{S}}$  (15) in the solution at the following initial concentrations of copper(II) salt and sodium nitrate, M:  $C_{\text{Cu(II)}} = 0.0001$ ,  $C_{\text{NaOH}} = 0.001$  (a);  $C_{\text{Cu(II)}} = 0.001$ ,  $C_{\text{NaOH}} = 0.01$  (b);  $C_{\text{Cu(II)}} = 0.01$ ,  $C_{\text{NaOH}} = 0.10$  (c);  $C_{\text{Cu(II)}} = 0.20$ ,  $C_{\text{NaOH}} = 2.00$  (d);  $C_{\text{Cu(II)}} = 1.01$ ,  $C_{\text{NaOH}} = 10.25$  (e);  $t = 25^\circ\text{C}$ .

clearly the features of experimental curves, given in Fig. 1, over the whole investigated range of copper(II) chloride and sodium hydroxide concentrations. Thus, the inflection point observed on the calculated dependence of the function of the formation for hydroxide ions on pH for the system with the minimum metal ion content in the solution that is 0.0001 M at  $\text{pH} > 8.5$  (Fig. 1a), corresponds to the beginning of the formation of the only  $\text{Cu}(\text{OH})_{2\text{S}}$  phase (Fig. 2a). Along with this, basic copper forms are mononuclear hydroxo-

complexes and polynuclear ions  $\text{Cu}_2(\text{OH})_2^{2+}$ ,  $\text{Cu}_2(\text{OH})_3^+$ ,  $\text{Cu}_4(\text{OH})_7^+$ . The review of reference literature [17, 18] showed that copper has basic complex forms with coordinated numbers from 1 to 4, whereas the results of calculations by EQ-5 software indicate the existence of a large number of mononuclear hydroxocomplexes of transition metal.

When initial concentration of copper(II) salt is 0.001 M (Fig. 2b), the decreasing of the mole fractions

of the basic metal complexes occurs. It also narrows the area of the formation of low soluble  $\text{Cu}(\text{OH})_2\text{S}$  phase toward higher pH values. At this copper content in the solution  $\text{Cu}_x(\text{OH})_{1.5x}\text{Cl}_{0.5x}\text{S}$  solid phase begins to form, in particular, low soluble compound with  $x = 2$ , i.e.,  $\text{Cu}_2(\text{OH})_3\text{Cl}_3\text{S}$ , which region of existence broadens with the increasing of copper chloride concentration.

The increasing of  $\text{CuCl}_2$  content to 0.20 M (Figs. 2c–2d) results in the formation of one more chlorine-containing compound  $\text{Cu}_4(\text{OH})_7\text{Cl}_5\text{S}$  and copper oxide  $\text{CuO}_\text{S}$ . Moreover, compound  $\text{Cu}_4(\text{OH})_7\text{Cl}_5\text{S}$  begins to form just when metal concentration in the solution is 0.01 M (Fig. 2c). In Figs. 1c–1d it is clearly seen that formula compositions  $\text{Cu}_x(\text{OH})_{1.75x}\text{Cl}_{0.25x}\text{S}$  and  $\text{Cu}_x(\text{OH})_{2x}\text{S}$  corresponds to mentioned polynuclear compounds ( $\text{Cu}_4(\text{OH})_7\text{Cl}_5\text{S}$  and  $\text{CuO}_\text{S}$ ).

It should be noted that at the maximum copper salt concentration (Fig. 2e) a number of complex forms and low soluble metal compounds decreases in the solution. Thus, the formation of solid phase with the composition  $\text{Cu}_2(\text{OH})_2\text{Cl}_2\text{S}$  occurs at pH 2.7–4.8, the region of the existence of low soluble hydroxide compound  $\text{Cu}_2(\text{OH})_3\text{Cl}_3\text{S}$  covers practically the whole considered range of pH 4.8–11.5, while solid phase oxide  $\text{CuO}_\text{S}$  begins to form at pH > 11.5. It is due to relative stability of these compounds in the considered conditions.

The results of mathematical processing of the data on potentiometric titration of aqueous solutions of copper(II) chloride also shows that the complete hydrolytic decomposition of polynuclear metal compounds, accompanied by the formation of negatively charged hydroxocomplexes  $\text{Cu}(\text{OH})_4^{2-}$ ,  $\text{Cu}(\text{OH})_5^{3-}$ ,  $\text{Cu}(\text{OH})_6^{4-}$  occurs in a strongly alkaline medium.

## CONCLUSIONS

A equilibrium processes in the “ $\text{CuCl}_2\text{—H}_2\text{O—NaOH}$ ” system was studied by mathematical processing with EQ-5 software of the experimental results from potentiometric titration taking into consideration the formation of mononuclear and polynuclear copper(II) hydroxocomplexes and its low soluble compounds of various compositions. The calculated values of instability constants and determined compositions of compounds forming in the system allow to explain the features of ions behavior of investigated

transition metal in aqueous solutions using experimental dependences.

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