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THE HYDROCOMPLEXATION IN THE SYSTEM $\text{Cr}^{3+} - \text{Cu}^{2+} - \text{NO}_3^- - \text{H}_2\text{O}$

The hydrolysis processes in the system $\text{Cr}^{3+} - \text{Cu}^{2+} - \text{NO}_3^- - \text{H}_2\text{O}$ have been investigated by potentiometric titration and dialysis methods. The solutions of the chromium (III) nitrates and copper (II) nitrates obtained by dissolving chromium (III) nitrate and copper in nitric acid were used in the work. The experimental data have been obtained under following conditions: metal ions concentration – 0.01 mol/l, molar ratio $\text{Cr}^{3+}:\text{Cu}^{2+} = 1:1$, ionic strength – 0.3 mol/l (NaNO_3), temperature – $(25 \pm 0.1)^\circ\text{C}$, pH-range – 1.5–3.6. The results of potentiometric titration do not allow one to establish the possibility of heteropolymeric hydroxocomplexes formation. According to the results obtained by dialysis, polynuclear complexes of chromium (III) in the system $\text{Cr}^{3+} - \text{Cu}^{2+} - \text{NO}_3^- - \text{H}_2\text{O}$ are formed when the pH is 2.0. Copper (II) does not form a polynuclear hydroxocomplexes. The distribution of different Cr (III) and Cu (II) forms upon pH value in the region before formation of hydroxides sediments has been calculated upon experimental data. It was established that Cr (III) and Cu (II) do not form heteronuclear hydroxocomplexes.

Key words: hydroxocomplexes, chromium, copper, potentiometric, dialysis.

Introduction. Systems like $\text{Cr}^{3+} - \text{Me}^{3+} - \text{NO}_3^- - \text{H}_2\text{O}$ have been studied in details by methods of spectrophotometry, dialysis, isomolar series, potentiometry and sorption. According to the conducted experiments during hydrolysis polynuclear hydroxocomplexes are formed in solutions. [1]. Formation of heteronuclear chrome (III) hydroxocomplexes with ions Fe^{3+} [1, 2], Al^{3+} [3], Sc^{3+} [4], Co^{2+} , Ni^{2+} , Zn^{2+} and other 3d-metals [5–8] has been established. However, with ions Hg^{2+} , Cd^{2+} [9] and Pb^{2+} [10] Cr^{3+} ions does not interact during the hydrolysis. The aim of this article is studies of cation hydrolysis in the system of $\text{Cr}^{3+} - \text{Cu}^{2+} - \text{NO}_3^- - \text{H}_2\text{O}$.

Potentiometric titration and dialysis methods have been chosen for the research. The latter allows to determine a part of mononuclear and polynuclear hydroxocomplexes of metals in solution. Content of aquacomplexes and mononuclear forms can be calculated with the help of literature data on hydrolysis constant.

Main part. Solution of chrome (III) has been used in this experiment, obtained by dissolution of chromic nitrate (III) and cuprum solution obtained by dissolution of cuprum in nitrogen acid. All reactives had a qualification of chemical pure.

pH measurements have been conducted with the help of ionomer I-150 with thermostate pH-metric unit. Dialysis and processing of its results have been carried out according to method [2]. Holdup time of solutions in a dialyzer was 7 days.

Chrome (III) and cuprum (II) content determination in dialyzer sections and initial solutions has been carried out by the following way. Chrome (III) content has been determined photometrically with the help of photocolormeter CFK-3 as a complex with EDTA [10], herewith Cu^{2+} ions did not influence on light absorbance. Determination

of cuprum (II) content in dialyzer sections and initial solutions has been carried out by the direct complexometric titration with murexide [11]. At this, chrome (III) did not have an effect, as according to the conditions of determination did not react with EDTA.

Solutions for the research with different mole ratio of OH / Me have been prepared from initial solutions of chrome (III) nitrates and cuprum (II). Concentration of metal ions has been determined in initial solutions. In accordance with obtained results amount of KOH, necessary for neutralization of free acid and establishment of certain ratio of OH / Me and amount of NaNO_3 necessary for constant ion power, has been determined. Then mixing of different amounts of initial solutions of metal nitrates has been carried out, 0.2 M of KOH solution and 1 M of NaNO_3 solution. At partial neutralization of free acid mole ratio OH / ΣMe has been marked as sign “–”; if amount of the base exceeded total number of metal ions sign “+” has been used. After thermostating at the temperature of 25°C , distilled water has been added into the solutions to the necessary volume. Prepared solutions have been kept in thermostate at the temperature of 25°C during 7 days. This is enough for equilibration [1–2].

Conditions of the experiment have been maintained by the following: concentration of metal ions – 0.01 mole/l; mole ratio $\text{Cr}^{3+}:\text{Cu}^{2+} = 1:1$; ion power – 0.3 mole/l (NaNO_3); temperature $(25 \pm 0.1)^\circ\text{C}$ has been maintained with the help of air thermostate. pH calculation has been carried out with the help of ionomer I-150 7 days after preparation. Sedimentation has not been observed within the experimental conditions.

Solution titration curve $\text{Cr}^{3+} - \text{Cu}^{2+}$ (Fig. 1) has two areas. First area in range pH = 1.0–2.5 corre-

sponds nitric acid titrated. Because it is not important this part of curve is not considered.

Titration curve of the solution $\text{Cr}^{3+} - \text{Cu}^{2+}$ has one sudden change. Judging by pH size, the sudden change can be related to simultaneous neutralization of cuprum (II) and chrome (III). There is the following reaction during the titration:

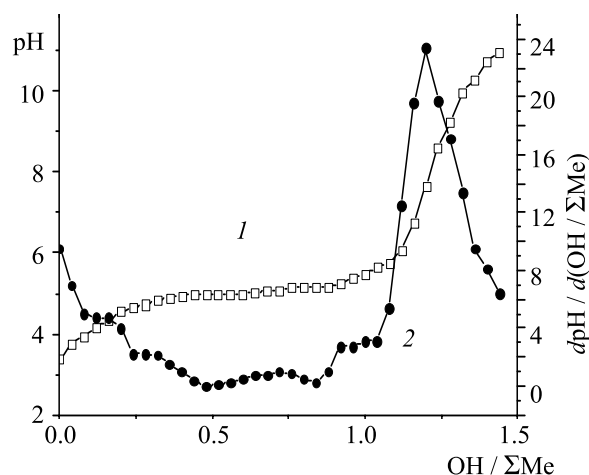


Fig. 1. Potentiometry curves of the system $\text{Cr}^{3+} - \text{Cu}^{2+} - \text{NO}_3^- - \text{H}_2\text{O}$: 1 – integral; 2 – differential

Sudden changes, responsible for formation of other forms, have not been revealed, that gives some grounds to assume that in the present system heteropolynuclear complexes are not being formed or not revealed at potentiometry.

Results of the research carried out with the help of dialysis are presented in the Table where equilibrium pH value and dialysis coefficient (d) calculated by the formula

$$d = \frac{c_p}{c_w},$$

can be found. c_p and c_w – metal ion concentration in phone and working cells correspondingly.

In the system $\text{Cr}^{3+} - \text{Cu}^{2+} - \text{NO}_3^- - \text{H}_2\text{O}$ at the increase of ratio $\text{OH} / \Sigma\text{Me}$ coefficients of cuprum (II) dialysis practically do not change and equal to 1, coefficients of chrome (III) dialysis at ratio of $\text{OH} / \Sigma\text{Me} > -0.5$ decrease.

This indicates the appearance of polynuclear chrome (III) hydroxocomplexes and absence of cuprum (II) polynuclear hydroxocomplexes.

Mole concentrations of mononuclear (c_m) and polynuclear (c_p) forms have been calculated with the help of equation [3]

$$\omega_p = \frac{1-d}{1+d}.$$

Coefficients of chrome (III) dialysis and cuprum (II) in the system $\text{Cr}^{3+} - \text{Cu}^{2+} - \text{NO}_3^- - \text{H}_2\text{O}$

$\text{OH} / \Sigma\text{Me}$	pH	d chrome	d cuprum
-1.0	1.41	1.0	1.0
-0.5	2.19	0.94	1.0
0	2.65	0.92	1.0
0.25	3.01	0.86	1.0
0.5	3.13	0.82	1.0
0.75	3.16	0.80	1.0
1.0	3.39	0.78	1.0
1.25	3.64	0.72	1.0

According to the equations of material balance calculation of mononuclear chrome (III) and cuprum (II) complexes content in the solution has been carried out. Hydrolysis constants $\text{pK}_1 = 4.0$, $\text{pK}_2 = 5.7$ for chrome (III) [13] and $\text{pK}_1 = 9.4$, $\text{pK}_2 = 9.6$ for cuprum (II) have been used for calculation.

Results of calculation are presented in Fig. 2.

According to the calculation, under the conditions of the experiment amount of mononuclear cuprum (II) complexes is a negligible quantity in comparison with the amount of aquacomplexes, that is Fig. 2 depicts only the results of calculation for chrome (III) forms. At the increase of the ratio $\text{OH} / \Sigma\text{Me}$ steady decrease of the amount of chrome (III) aquacomplexes is observed. The amount of chrome (III) polynuclear forms increases fast and reaches to 30%, polynuclear cuprum (II) forms have not been revealed within the experiment.

Conclusion. Thus, absence of heteronuclear hydroxyl complex formation in the system of $\text{Cr}^{3+} - \text{Cu}^{2+} - \text{NO}_3^- - \text{H}_2\text{O}$ has been revealed.

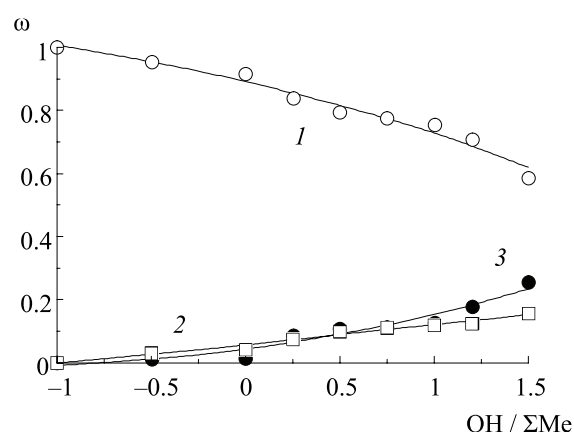


Fig. 2. Distribution of chrome (III) complex forms in the system $\text{Cr}^{3+} - \text{Cu}^{2+} - \text{NO}_3^- - \text{H}_2\text{O}$: 1 – $\text{Cr}(\text{H}_2\text{O})_6^{3+}$; 2 – $\text{CrOH}(\text{H}_2\text{O})_5^{2+}$; 3 – chrome (III) polynuclear complexes

According to our published articles, in solutions containing chrome (III) and ions of such doubly-charged metals as Hg^{2+} , Cd^{2+} [9] and Pb^{2+} [10], only polynuclear forms of chrome (III) are formed and formation of heteropolynuclear hydroxoforms

are not observed. Obtained data and information by the present research, published in [9, 10], contradict the results of the articles [5–8], that indicates the necessity of conducting extra research of the system, containing ion Cr^{3+} .

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