

CHEMISTRY AND TECHNOLOGY OF INORGANIC MATERIALS AND SUBSTANCES

УДК 541.49:546.723:546.562

A. E. Sokolovskiy, PhD (Chemistry), assistant professor (BSTU);
E. V. Radion, PhD (Chemistry), assistant professor, head of department (BSTU).

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

The hydrolysis processes in the system $\text{Fe}^{3+} - \text{Cu}^{2+} - \text{NO}_3^- - \text{H}_2\text{O}$ have been investigated by potentiometric titration and dialysis methods. The experiment data have been obtained under the following conditions: metal ions concentration – 0,01 mol/l, molar ratio $\text{Fe}^{3+} : \text{Cu}^{2+} = 1 : 1$, ionic strength – 0.3 mol/l (NaNO_3), temperature – $(25 \pm 0.1)^\circ\text{C}$, pH-range – 1.5–2.4. The distribution of different Fe (III) and Cu (II) forms upon pH value has been calculated upon experimental data. It has been established that Fe (III) and Cu (II) form heteropolynuclear hydroxocomplexes.

Introduction. When the hydrolysis of Fe^{3+} ions leads to the formation of polynuclear hydroxocomplexes, and, in $\text{Al}^{3+} - \text{Fe}^{3+} - \text{NO}_3^- - \text{H}_2\text{O}$, and $\text{Fe}^{3+} - \text{Al}^{3+} - \text{NO}_3^- - \text{H}_2\text{O}$ heteropolymer complexes are formed [1–3]. The formation of heteropolymer hydroxocomplexes of iron (III) – mercury (II) [3], iron (III) – cadmium (II) was established [4]. On the contrary, the ions of zinc (II), manganese (II) [5], cobalt (II) [6], lead (II) [7], and the iron (III) ions do not manifest the interaction. The study of the hydrolytic interaction between Fe^{3+} ions and Cu^{2+} ions was carried out only by potentiometric titration [8], therefore, the aim of the present work is to investigate the hydrolysis of cations in the system $\text{Fe}^{3+} - \text{Cu}^{2+} - \text{NO}_3^- - \text{H}_2\text{O}$. The methods of potentiometric titration and dialysis were selected for research. The latter allows us to determine the percentage of mononuclear and polynuclear hydroxocomplexes of metals in solution. The contents of aquacomplexes and mononuclear forms can be calculated using the published data on the constants of hydrolysis.

Main part. The solutions of the iron (III) nitrates and copper (II) nitrates obtained by dissolving metal carbonyl iron and copper in nitric acid were used in the work. All reagents were designated “C. P.”.

During the hydrolysis the pH measurement was carried out with the ionomer I-150 with thermostating pH-metric cell. The dialysis and the processing of the results were performed according to the method described in the source [3]. The solutions were exposed in the dialyzer for 7 days. The estimation of the ion contents of iron (III) and copper (II) in sections of dialyzer was performed in the following way: at first the ions amount was defined by the method of reverse chelatometric

titration by salt of copper (II) in the presence of the PAN indicator. Then the crystalline sodium fluoride was added to the same aliquot of the solution to mask the ion Fe^{3+} and carry out the reverse titration by the salt of copper (II) in the presence of the same indicator [9]. The results of the titration determined the concentration of Cu^{2+} . The ion concentration of Fe^{3+} was calculated by the difference between the results of the titration.

The solutions for research with different molar ratio $\text{OH} / \Sigma\text{Me}$ were prepared from initial solutions of the nitrates of iron (III) and copper (II), where the metal ions concentration was determined. On the basis of the obtained results it was calculated the amount of KOH needed to neutralize the free acid and establish certain ratio $\text{OH} / \Sigma\text{Me}$, and the amount of NaNO_3 to maintain a constant ionic strength. Then the calculated amounts of the initial solutions of metal nitrates, 0.2 M KOH solution and 1 M NaNO_3 solution were mixed. When the free acid was partially neutralized the molar ratio $\text{OH} / \Sigma\text{Me}$ was signified by “–” sign, if the base amount exceeded the total metal amount, the “+” sign was used. At temperature control 25°C distilled water was added to the solution to the required volume. The prepared solution was kept in a thermostat at temperature 25°C for 7 days. This is the time to attain equilibrium [1–2].

The following test conditions for carrying out the experiment in the temperature controlled air bath were maintained: metal ion concentration – 0.01 mol/l; molar ratio $\text{Fe}^{3+} : \text{Cu}^{2+} = 1 : 1$; ionic strength 0.3 mol/l (NaNO_3); temperature – $(25 \pm 0,1)^\circ\text{C}$. Determination of the solutions pH was performed 7 days later after preparation. When $\text{OH} / \Sigma\text{Me} > 1.25$, opalescence was observed in the solutions, and at higher values precipitation was formed.

The titration curve of $\text{Fe}^{3+} - \text{Cu}^{2+}$ solution (Fig. 1) contains two areas. The first area in the range of $\text{pH} = 1.0-2.5$ covers the titration of nitric acid. Due to the fact that it is not of interest, this part of the curve is not considered. The second area of titration curve corresponds to the titration of the acid forms of iron (III) and copper (II) and is characterized by two jumps. When the $\text{OH} / \Sigma\text{Me} = 1.5$, the former corresponds to neutralization of iron (III). The latter occurs when the $\text{OH} / \Sigma\text{Me} = 2.5$. Considering the pH value, it can be attributed to the neutralization of copper (II). Jumps determining the neutralization of any other hydroxyforms were not detected.

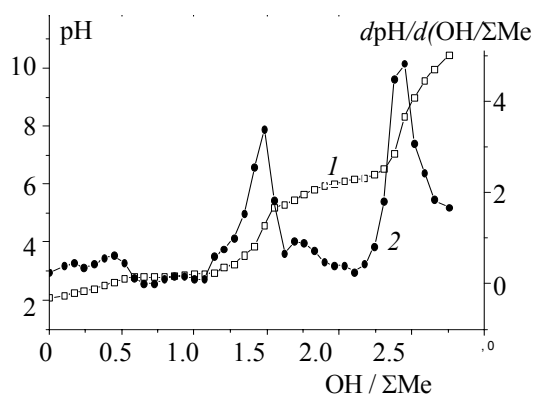


Fig. 1. Curves of potentiometric titration in the system $\text{Fe}^{3+} - \text{Cu}^{2+} - \text{NO}_3^- - \text{H}_2\text{O}$:
1 – integral; 2 – differential

Thus, the results of potentiometric titration does not allow one to establish the possibility of heteropolymeric hydroxocomplexes formation.

The results of studies conducted using the method of dialysis, are presented in the table.

Dialysis coefficients of Fe (III) and Cu (II) in the system $\text{Fe}^{3+} - \text{Cu}^{2+} - \text{NO}_3^- - \text{H}_2\text{O}$

$\text{OH} / \Sigma\text{Me}$	pH	$d(\text{Fe}^{3+})$	$d(\text{Cu}^{2+})$
-1.0	1.56	1.00	1.0
-0.5	1.70	1.00	1.0
0	2.09	0.95	1.0
0.25	2.13	0.81	1.0
0.5	2.14	0.66	1.0
0.75	2.20	0.47	1.0
1.0	2.30	0.34	0.86
1.25	2.34	0.32	0.76

The equilibrium pH values of solutions and factors of dialysis (d) were calculated by the formula

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

where c_b and c_w is the metal ion concentration in the background and working cells, respectively. As shown, the coefficients of iron (III) dialysis

when $\text{OH} / \Sigma\text{Me} \geq 0$ begin to decrease, which indicates the presence in the solution polynuclear complexes of iron (III).

Dialysis coefficients of copper (II) when $\text{OH} / \Sigma\text{Me} > 0.75$ equal to 1. According to the results obtained in the present work, polynuclear complexes of iron (III) in the system $\text{Fe}^{3+} - \text{Cu}^{2+} - \text{NO}_3^- - \text{H}_2\text{O}$ are formed when the pH is 2.0. Copper (II) forms a polynuclear hydroxocomplexes when the $\text{OH} / \Sigma\text{Me} > 1$ and $\text{pH} > 2.3$. Thus, it is possible to draw a conclusion about heteropolymer hydroxocomplexes formation in the system $\text{Fe}^{3+} - \text{Cu}^{2+} - \text{NO}_3^- - \text{H}_2\text{O}$. The precipitation was not formed in the prepared solutions. The molar concentrations of mononuclear (c_m) and polynuclear (c_p) forms were calculated by equation [3]

$$d = \frac{0.5c_m}{c_p + 0.5c_m},$$

where d is the dialysis coefficient; $c_m + c_p = 0.01$ mol/l.

Dividing the numerator and the denominator in the formula for the total concentration of metal in the system, you can find the molar proportion of this form in the solution ω . Because $\omega_m + \omega_p = 1$, then the proportion of polynuclear forms in the solution is

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

On the basis of the obtained data the molar proportion of polynuclear iron (III) and copper (II) hydroxocomplexes (ω_p) was calculated with this equation.

On the basis of the equations of material balance the contents of mononuclear iron (III) and copper (II) complexes were calculated using hydrolysis constants [9, 10]: $\text{p}K_1 = 4.0$; $\text{p}K_2 = 5.7$ for iron (III) и $\text{p}K_1 = 9.4$; $\text{p}K_2 = 9.6$ for copper (II). The calculations showed that in the experimental conditions, the share of mononuclear complexes of copper (II) is negligible if compared with the share of aquacomplexes, so Fig. 2 shows only the results of calculations for iron (III) forms.

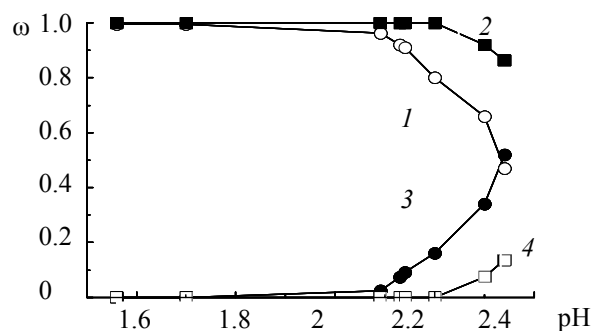


Fig. 2. The distribution of complex forms in the system $\text{Fe}^{3+} - \text{Cu}^{2+} - \text{NO}_3^- - \text{H}_2\text{O}$:
1 – $\text{Fe}(\text{H}_2\text{O})_6^{3+}$; 2 – $\text{Cu}(\text{H}_2\text{O})_6^{2+}$; 3 – polynuclear complexes of Fe^{3+} ; 4 – polynuclear complexes of Cu^{2+}

With increase of the ratio $\text{OH}^- / \Sigma\text{Me}$ there is a gradual decrease in the share of iron (III) aqua-complexes. The percentage of polynuclear forms increases rapidly and reaches 70%, which coincides with the results of works [4, 5]. The percentage of polynuclear forms of copper (II) starts to increase later and reaches 25%.

On the basis of the obtained data we can conclude that in the system $\text{Fe}^{3+} - \text{Cu}^{2+} - \text{NO}_3^- - \text{H}_2\text{O}$ the polynuclear iron (III) and copper (II) complexes are formed during the hydrolysis, which allows us to draw a conclusion on formation of heteropolymeric hydroxocomplexes. Thus, we studied seven systems containing ions of iron (III) with double-cations simultaneously.

These are systems $\text{Fe}^{3+} - \text{Pb}^{2+} - \text{NO}_3^- - \text{H}_2\text{O}$ [8], $\text{Fe}^{3+} - \text{Hg}^{2+} - \text{NO}_3^- - \text{H}_2\text{O}$, $\text{Fe}^{3+} - \text{Cd}^{2+} - \text{NO}_3^- - \text{H}_2\text{O}$ [4, 5], $\text{Fe}^{3+} - \text{Zn}^{2+} - \text{NO}_3^- - \text{H}_2\text{O}$, $\text{Fe}^{3+} - \text{Mn}^{2+} - \text{NO}_3^- - \text{H}_2\text{O}$ [6], $\text{Fe}^{3+} - \text{Co}^{2+} - \text{NO}_3^- - \text{H}_2\text{O}$ [7], and the system $\text{Fe}^{3+} - \text{Cu}^{2+} - \text{NO}_3^- - \text{H}_2\text{O}$, described in this work. In three of them: $\text{Fe}^{3+} - \text{Hg}^{2+} - \text{NO}_3^- - \text{H}_2\text{O}$, $\text{Fe}^{3+} - \text{Co}^{2+} - \text{NO}_3^- - \text{H}_2\text{O}$ и $\text{Fe}^{3+} - \text{Cu}^{2+} - \text{NO}_3^- - \text{H}_2\text{O}$ the formation of heteropolymeric hydroxocomplexes was observed. In four others, on the contrary, in the process of hydrolysis only polynuclear forms of iron (III) were formed.

Conclusion. Methods of dialysis and potentiometric titration ascertained that heteropolymer hydroxocomplexes are formed in the system $\text{Fe}^{3+} - \text{Cu}^{2+} - \text{NO}_3^- - \text{H}_2\text{O}$.

References

1. Радион Е. В., Залевская Т. Л., Баев А. К. Гетероядерное гидроксильное комплексообразование алюминия (III) с железом (III) // *Весті акад. навук Беларусі. Сер. хім. навук.* 1994. № 3. С. 9–14.
2. Радион Е. В., Залевская Т. Л., Баев А. К. Гетероядерное гидроксильное комплексообразование в системе $\text{Fe}(\text{III}) - \text{Cr}(\text{III}) - \text{NO}_3^- - \text{H}_2\text{O}$ //

Весті акад. навук Беларусі. Сер. хім. навук. 1994. № 4. С. 5–8.

3. Капылович М. Н., Радион Е. В., Баев А. К. Схема процесса гетероядерного гидроксокомплексообразования в системах $\text{Fe}(\text{III}) - \text{Cr}(\text{III}) - \text{NO}_3^- - \text{H}_2\text{O}$ и $\text{Fe}(\text{III}) - \text{Al}(\text{III}) - \text{NO}_3^- - \text{H}_2\text{O}$ // *ЖНХ.* 1995. Т. 40, вып. 6. С. 1037–1041.

4. Соколовский А. Е., Радион Е. В., Рудаков Д. А. Гидроксокомплексообразование в системе $\text{Fe}^{3+} - \text{Hg}^{2+} - \text{NO}_3^- - \text{H}_2\text{O}$ // *ЖПХ.* 2006. Вып. XIV. С. 10–12.

5. Соколовский А. Е., Радион Е. В. Гидроксокомплексообразование в системе $\text{Fe}^{3+} - \text{Cd}^{2+} - \text{NO}_3^- - \text{H}_2\text{O}$ // *ЖПХ.* 2003. Т. 76, вып. 3. С. 379–382.

6. Соколовский А. Е., Радион Е. В. Гидроксокомплексообразование в системах $\text{Fe}^{3+} - \text{Mn}^{2+} - \text{NO}_3^- - \text{H}_2\text{O}$ и $\text{Fe}^{3+} - \text{Zn}^{2+} - \text{NO}_3^- - \text{H}_2\text{O}$ // *Труды БГТУ. Сер. III, Химия и технология неорганич. в-в.* 2010. Вып. XVIII. С. 115–117.

7. Соколовский А. Е., Радион Е. В. Гидроксокомплексообразование в системе $\text{Fe}^{3+} - \text{Co}^{2+} - \text{NO}_3^- - \text{H}_2\text{O}$ // *Труды БГТУ.* 2011. № 3: *Химия и технология неорганич. в-в.* С. 34–36.

8. Соколовский А. Е., Радион Е. В. Гидроксокомплексообразование в системах $\text{Fe}^{3+} - \text{Pb}^{2+} - \text{NO}_3^- - \text{H}_2\text{O}$ и $\text{Al}^{3+} - \text{Pb}^{2+} - \text{NO}_3^- - \text{H}_2\text{O}$ // *Труды БГТУ. Сер. III, Химия и технология неорганич. в-в.* 2008. Вып. XVI. С. 14–16.

9. Радион Е. В. Гетероядерные гидроксокомплексы железа (III) и 3d-металлов: автореф. дис. ... канд. хим. наук / Институт химии неорганич. растворов. Иваново, 1990. 20 с.

10. Шварценбах Г., Флашка Г. Комплексонометрическое титрование. М.: Химия, 1970. 264 с.

11. Давыдов Ю. П. Состояние радионуклидов в растворах. Минск: Наука і тэхніка, 1978. 223 с.

12. Лурье Ю. Ю. Справочник по аналитической химии. М.: Химия, 1989. 448 с.

Received 03.03.2014