UDC 541.49:546.492:546.711

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

HYDROXO-COMPLEXES FORMATION IN Al^{3+} – Mn^{2+} – NO_3^- – H_2O SYSTEM

The hydrolysis process in Al^{3+} – Mn^{2+} – NO_3^- – H_2O system has been studied by potentiometric titration and dialysis methods. The experimental data have been obtained under the following conditions: metal ions concentration – 0.01 mol/l, molar ratio Al^{3+} : Mn^{2+} = 1 : 1, ionic strength – 0.3 mol/l ($NaNO_3$), temperature – (25 ± 0.1) °C, pH-range – 1.7–4.0. The distribution of different Al (III) and Mn (II) forms depending upon pH value of the solution in the sphere preceding hydroxidic precipitatin fall out has been calculated. It has been established that ions Al (III) form homopolynuclear hydroxo-complexes. Heteropolynuclear hydroxo-complexes of Al (III) and Mn (II) have not been found.

Introduction. At hydrolysis of ions Al^{3+} polynuclear hydroxo-complexes are formed, but in systems Fe^{3+} – Al^{3+} – NO_3^- – H_2O and Cr^{3+} – Al^{3+} – NO_3^- – H_2O heteropolynuclear hydroxo-complexes are formed [1–3]. The ion of aluminium (III) forms heteropolynuclear hydro-complexes with ions of mercury (II) and zinc (II) [4, 5] and does not interact with ions of cadmium (II) and cobalt (II) [4, 6]. Study of hydrolytic interactions of ions Al^{3+} with ions Mn^{2+} was done only by a method of potentiometric titration [7], therefore the purpose of the present work is hydrolysis research of cations in system Al^{3+} – Mn^{2+} – NO_3^- – H_2O.

For scientific study method of potentiometric titration and a dialysis are chosen. The latter allows to define a share of mononuclear and polynuclear hydroxo-complexes of metals in a solution. The content of aqua-complexes and mononuclear forms can be calculated with use of literary data by hydrolysis constants.

Main part. Solutions of nitrates of aluminium (III) and the manganese (II), received by dissolution of nitrates of aluminium (II) and manganese (II) with nitric acid addition were used in this work. All reactants had qualification «ch.p.».

Measurements of pH in the process of hydrolysis were made by ionometer I-150 with thermostatic pH-metric cell. A dialysis and processing of its results were carried out by a technique mentioned in a reference [3]. Solutions were kept in dialyzer for 7 days.

Test for the ions content of aluminium (III) and manganese (II) in sections of dialyzer was carried out as follows: at first the sum of ions was defined by a method of the back complexo-nometric titration by salt of copper (II) in the presence of the indicator the SIR. Then crystalline sodium fluoride was added to a solution for masking ion Al^{3+} and isolated trilon was titrated by salt of copper (II) in the presence of the same indicator [8]. By results of titration concentration of Al^{3+} was determined. Concentration of Mn^{2+} ion was counted by a difference of results of titration.

For tests solutions with various mole ratio IT / ΣMe were prepared from initial solutions of nitrates of aluminium (III) and manganese (II) in which then concentrations of ions of metals were defined. The received results helped to count KOH quantity necessary for neutralization of free acid and determination of the certain relation IT / ΣMe, as well as quantity of $NaNO_3$ required for keeping a constant ionic force. Then the counted quantities of initial solutions of nitrates of metals, 0.2 M of KOH solution and 1 M of $NaNO_3$ solution were mixed. At partial neutralization of free acid mole ratio IT / ΣMe was designated by a sign "–" if the quantity of the basis(base) exceeded total quantity of metals, it was denoted by a sign "+". After thermostatting at temperature of 25°C the distilled water was added to solutions to the required volume. The prepared solutions were stored in the thermostat at temperature 25°C during 7 days. This period of time is enough for reaching balance [1, 2].

By means of the air thermostat the following conditions for carrying out the experiment were supported: concentration of metals ions – 0.01 mol/l; mole ratio of Al^{3+} : Mn^{2+} = 1 : 1; ionic force – 0.3 mol/l ($NaNO_3$); temperature – (25 ± 0.1) °C. Solutions pH was determined 7 days later after preparation. At ratio IT / ΣMe > 1.25 opalescence was observed in the solutions and at even greater values a deposit was formed.

The curve of titration of solution Al^{3+} – Mn^{2+} contains two areas (Fig. 1). The first area is in an interval pH = 1.0–3.5 and answers nitric acid titration. Since it is of no interest, this part of a curve is not considered. The second area of a curve of titration answers titration of acid forms of aluminium (III) and manganese (II) and it is characterized by presence of two jumps. The first of them is at relation OH / ΣMe = 1.5 and corresponds to neutralization of aluminium (III). The second occurs at relation OH / ΣMe = 2.5. Judging by value of pH, it can correspond to neutralization of ions of manganese (II). The jumps answering neutralization any other hydroxoforms, were not revealed.

Thus, results of potentiometric titration do not allow to establish unequivocally possibility of heteropolynuclear hydroxo-complexes formation.
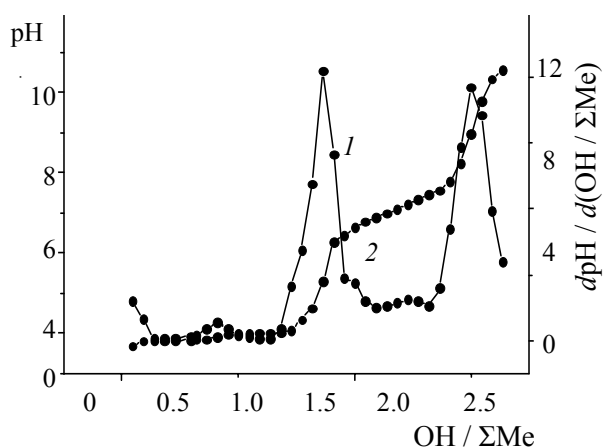
Fig. 1. Curve of potentiometric titration
of system $Al^{3+} - Mn^{2+} - NO_3^- - H_2O$:
1 – integral; *2* – differential

Results of the researches carried out with use of a dialysis method are presented in the table which gives equilibrium values of pH solutions and dialysis factors (d) calculated by the formula

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

where c_b and c_w – concentration of an ion of metal in background and working cells accordingly.

As follows from the resulted data, factors of a dialysis of aluminium (III) at relation OH / ΣMe ≥ 0 start to decrease, and this indicates to the presence of polynuclear complexes of aluminium (III) in the solution.

**Factors of dialysis Al (III) and Mn (II)
in system $Al^{3+} - Mn^{2+} - NO_3^- - H_2O$**

OH / ΣMe	pH	d (Al^{3+})	d (Mn^{2+})
−1.0	1.72	1.00	1.00
−0.5	2.04	1.00	1.00
0	3.48	0.95	1.00
0.25	3.57	0.79	1.00
0.5	3.64	0.64	1.00
0.75	3.70	0.45	1.00
1.0	3.81	0.30	1.00
1.25	4.00	0.10	1.00

Factors of a dialysis of manganese (II) are equal in these conditions 1. On literary data formation of polynuclear complexes of aluminium (III) begins at pH > 4.2 [9]. By the results received in the present work, polynuclear complexes of alu-

minium (III) in system $Al^{3+} - Mn^{2+} - NO_3^- - H_2O$ are formed already at pH $\geq$ 3.5. Manganese (II) at the given value of pH does not form polynuclear hydroxo-complexes. Thus, it is possible to draw a conclusion that there is no heteropolynuclear hydroxo-complexes formation in system $Al^{3+} - Mn^{2+} - NO_3^- - H_2O$. At the same time it is necessary to pay attention to strengthening of hydrolysis of an ion of aluminium (III). Deposit formation in the prepared solutions did not occur.

Molar concentration of mononuclear (c_m) and polynuclear (c_p) forms were counted by the equation [3]:

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

where d – dialysis factor; $c_m + c_p = 0.01$ mol/l.

Having divided numerator and a denominator in this formula by the general concentration of metal in system, it is possible to find molar share of the given form in a solution ω. As $\omega_m + \omega_p = 1$ the share of polynuclear forms in the solution is equal to

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

The molar share of polynuclear hydoxo-complexes (ω_p) of aluminium (III) and manganese (II) has been calculated by means of the given equation on the basis of the received data.

On the basis of the equations of material balance calculation of the content of mononuclear complexes of aluminium (III) and manganese (II) has been carried out. For the calculation hydrolysis constants [9, 10]: $pK_1 = 4.0$; $pK_2 = 5.7$ for aluminium (III) and $pK_1 = 9.4$; $pK_2 = 9.6$ for manganese (II) were used. Calculations have shown, that in the conditions of experiment the share of mononuclear complexes of manganese (II) is too small in comparison with a share of aquacomplexes, therefore only the results of calculations for forms of aluminium (III) are given in Fig. 2. With increase of relation OH / ΣMe there occurs a gradual decrease of a share of aluminium (III) aquacomplexes. At first the share of mononuclear hydroxoforms increases and then decreases. The share of polynuclear forms quickly increases and reaches 70% that coincides with results of works [4, 5].

On the basis of the received data it is possible to draw a conclusion that in system $Al^{3+} - Mn^{2+} - NO_3^- - H_2O$ at hydrolysis only polynuclear complexes of aluminium (III) are formed, and ions of Mn^{2+} don't react with polynuclear complexes of aluminium (III) and don't form heteropolynuclear hydroxo-complexes.
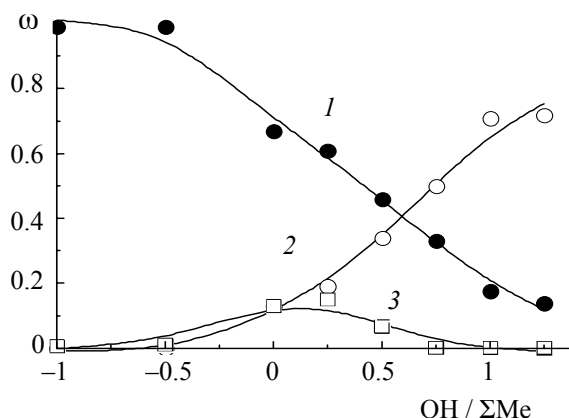
Fig. 2. Distribution of complex forms
in system $Al^{3+} - Mn^{2+} - NO_3^- - H_2O$:
$1 - Al(H_2O)_6^{3+}$; 2 – polynuclear complexes Al^{3+};
$3 - AlOH(H_2O)_5^{2+}$

Thus, with the help of one technique six systems, including ions of aluminium (III) with two charge cations were studied. These are systems $Al^{3+} - Pb^{2+} - NO_3^- - H_2O$ [11], $Al^{3+} - Hg^{2+} - NO_3^- - H_2O$, $Al^{3+} - Cd^{2+} - NO_3^- - H_2O$ [4], $Al^{3+} - Zn^{2+} - NO_3^- - H_2O$ [5], $Al^{3+} - Co^{2+} - NO_3^- - H_2O$ [6] and system $Al^{3+} - Mn^{2+} - NO_3^- - H_2O$, described in the given work. In two of them i.e: $Al^{3+} - Hg^{2+} - NO_3^- - H_2O$ and $Al^{3+} - Zn^{2+} - NO_3^- - H_2O$ formation of heteropolynuclear hydroxocomplexes is established. In four others, on the contrary, in the process of hydrolysis only polynuclear forms of aluminium (III) were formed.

Conclusion. Methods of a dialysis and potentiometric titration have established that in system $Al^{3+} - Mn^{2+} - NO_3^- - H_2O$ only polynuclear hydroxocomplexes of aluminium (III) are formed, and heteropolynuclear hydroxo-complexes are not formed.

References

1. Радион, Е. В. Гетероядерное гидроксильное комплексообразование алюминия (III) с железом (III) / Е. В. Радион, Т. Л. Залевская, А. К. Баев // Вес. акад. навук Беларусі. Сер. хім. навук. – 1994. – № 3. – С. 9–14.

2. Радион, Е. В. Гетероядерное гидроксильное комплексообразование в системе Al (III) – Cr (III) – NO₃⁻ – H₂O / Е. В. Радион, Т. Л. Залевская, А. К. Баев // Вес. акад. навук Беларусі. Сер. хім. навук. – 1994. – № 4. – С. 5–8.

3. Копылович, М. Н. Схема процесса гетероядерного гидроксокомплексообразования в системах Al (III) – Cr (III) – NO₃⁻ – H₂O и Al (III) – Fe (III) – NO₃⁻ – H₂O / М. Н. Копылович, Е. В. Радион, А. К. Баев // ЖНХ. – 1995. – Т. 40, вып. 6. – С. 1037–1041.

4. Соколовский, А. Е. Исследование процесса гидроксокомплексообразования в системах Al³⁺ – Hg²⁺ – NO₃⁻ – H₂O и Al³⁺ – Cd²⁺ – NO₃⁻ – H₂O / А. Е. Соколовский, Е. В. Радион // ЖПХ. – 2009. – Т. 82, вып. 1. – С. 165–167.

5. Соколовский, А. Е. Гидроксокомплексообразование в системе Al³⁺ – Zn²⁺ – NO₃⁻ – H₂O / А. Е. Соколовский, Е. В. Радион // Труды БГТУ. Сер. III, Химия и технология неорган. в-в. – 2010. – Вып. XVIII. – С. 115–117.

6. Соколовский, А. Е. Гидроксокомплексообразование в системе Al³⁺ – Co²⁺ – NO₃⁻ – H₂O / А. Е. Соколовский, Е. В. Радион // Труды БГТУ. – 2011. – № 3: Химия и технология неорган. в-в. – С. 34–36.

7. Радион, Е. В. Гетероядерные гидроксокомплексы алюминия (III) и 3d-металлов: автореф. дис. ... канд. хим. наук / Е. В. Радион; Институт химии неодных растворов. – Иваново, 1990. – 20 с.

8. Шварценбах, Г. Комплексонометрическое титрование / Г. Шварценбах, Г. Флашка. – М.: Химия, 1970. – 264 с.

9. Давыдов, Ю. П. Состояние радионуклидов в растворах / Ю. П. Давыдов. – Минск: Навука і тэхніка, 1978. – 223 с.

10. Лурье, Ю. Ю. Справочник по аналитической химии / Ю. Ю. Лурье. – М.: Химия, 1989. – 448 с.

11. Соколовский, А. Е. Гидроксокомплексообразование в системах Al³⁺ – Pb²⁺ – NO₃⁻ – H₂O и Fe³⁺ – Pb²⁺ – NO₃⁻ – H₂O / А. Е. Соколовский, Е. В. Радион // Труды БГТУ. Сер. III, Химия и технология неорган. в-в. – 2008. – Вып. XVI. – С. 14–16.