ISSN 1070-4272, Russian Journal of Applied Chemistry, 2009, Vol. 82, No. 1, pp. 162−165. © Pleiades Publishing, Ltd., 2009.
Original Russian Text © A.E. Sokolovskii, E.V. Radion, 2009, published in Zhurnal Prikladnoi Khimii, 2009, Vol. 82, No. 1, pp. 165−167.

BRIEF COMMUNICATIONS

Study of the Process of the Hydroxo Complexes Formation in the Al^{3+}–Hg^{2+}–NO_3^-–H_2O and Al^{3+}–Cd^{2+}–NO_3^-–H_2O Systems

A. E. Sokolovskii and E. V. Radion

Mendeleev Russian Chemical Engineering University, Moscow, Russia
Neorganika Ecological Research and Production Company Public Corporation, Electrostal', Moscow region, Russia
Lomonosov State University, Moscow, Russia

Abstract—The process of hydrolysis in the Al^{3+}–Cd^{2+}–NO_3^-–H_2O and Al^{3+}–Hg^{2+}–NO_3^-–H_2O systems is studied by the methods of pH-metric titration and dialysis. Effect of mutual influence of cations on the hydrolytic behavior of the process of heteronuclear complexation is elucidated.

DOI: 10.1134/S1070427209010315

Solutions of aluminum(III) and iron(III) salts are used as collectors at the treatment of water from various contaminants including toxic metal ions. For the iron(III)–mercury(II) and iron(III)–cadmium(II) systems formation of heteronuclear hydroxo complexes [1, 2] was established. Hydrolytic interaction of ions Al^{3+} with the ions Hg^{2+} and Cd^{2+} was not studied so far, therefore the aim of this work was the investigation of the hydrolysis of cations in the Al^{3+}–Hg^{2+}–NO_3^-–H_2O and Al^{3+}–Cd^{2+}–NO_3^-– H_2O systems.

EXPERIMENTAL

For the preparation of aqueous solutions were used aluminum(III) and mercury(II) nitrates of "chemically pure" grade. A solution of cadmium nitrate was prepared by dissolving cadmium carbonate in nitric acid of "chemically pure" grade. The Al^{3+} concentration was measured using reverse complexometric titration in the presence of PAN [3], Hg^{2+} by reverse complexometric titration with Eriochrom black T [3], Cd^{2+} by direct complexometric titration with Eriochrom black T [3]. Determination of aluminum(III) and mercury(II) at their join presence was carried out by the following procedure. Total content of aluminum(III) and mercury(II) was measured by reverse complexometric titration with a copper(II) salt in the presence of PAN. Then by adding KI, mercury(II) was bound and the liberated EDTA was titrated by a copper(II) salt. At the analysis of solutions containing Al^{3+} and Cd^{2+} the total content of aluminum(III) and cadmium(II) by reverse complexometric titration with a zinc salt in the presence of Xylene orange was also initially measured. The content of cadmium(II) was measured by direct complexometric titration in the presence of Eriochrom black T [3]. Aluninum(III) was therewith masked with trietanolamine [4]. For measuring the content of free HNO_3 in the parent solution the potentiometry was used in the presence of EDTA [5].

Solutions of Al^{3+}–Hg^{2+}–NO_3^-–H_2O and Al^{3+}–Cd^{2+}–NO_3^-– H_2O varied by the OH/M mole ratio were prepared from the solutions of aluminum(III), mercury(II) and cadmium(II) nitrates. In each parent solutions were determined concentrations of the respective metal ion and of free nitric acid. From the data obtained was calculated the quantity of KOH required for the neutralization of the free nitric acid and obtaining a given OH/M ratio, and the quantity of $NaNO_3$ required for the supporting constant ionic strength. Then the calculated volumes of the solutions of parent salts, 0.2 M solution of KOH and 1 M solution of $NaNO_3$ were mixed together. At the partial neutralization of free acid the OH/M mole ratio was labeled with "minus". After preparation, the solutions were thermostated for 7 days for attaining equilibrium.

The experiments were carried out under the following conditions: concentration of the metal ions was 0.01 mol l^{-1}, the total concentration of the metal ions in both the studied systems was 0.02 mol l^{-1} at the mole ratio Al^{3+} : M^{2+} = 1 : 1; temperature 25 ± 0.1°C; ionic strength 0.3 mol l^{-1} ($NaNO_3$).

For the study of hydrolysis were applied the methods of pH-metric titration and dialysis. For the measuring pH was applied an I-160 ionometer with the termostated

pH-metric cell. The dialysis and treatment of the obtained results were conducted along the procedure in [6]. Duration of keeping of solution in the dialyser was 7 days.

The titration curve of the solution Al^{3+}–Hg^{2+} (Fig. 1a) contains two maxima. Formation of precipitate begins at pH = 2.0, that corresponds to the beginning of the first maximum. The first maximum occurs at the OH/M ratio ~1, the second one at the ratio OH/ΣM = 2.5. Judging from the pH values, the first maximum can be assigned to the neutralization of mercury(II) ions [1], the second one to the neutralization of aluminum(III) ions. No inflection was detected related to any other hydroxo form.

The integral and differential curves of the potentiometric titration of Al^{3+}–Cd^{2+} solutions is shown in Fig. 1b. The first maximum on the titration curve at the ratio OH/ΣM ~1.5 responds to neutralization of aluminum(III) ions, the second, at the ratio OH/ΣM = 2.5, to the neutralization of cadmium(II) ions. Like the preceding case, there are no inflections on the titration curve that could be assigned to the formation of either a polynuclear or a heteropolynuclear form.

Thus, the method of potentiometric titration was found insufficient for the revealing interaction of ions in the systems of Al^{3+}–Hg^{2+}–NO_3^-–H_2O and Al^{3+}–Cd^{2+}–NO_3^-–H_2O. However, this does not evidence the absence of interaction, because separate titration of different hydroxo forms is possible when their dissociation constants differ considerably.

In Table 1 are listed the coefficients of dialysis of aluminum(III) and mercury(II) in the Al^{3+}–Hg^{2+}–NO_3^-–H_2O system and equilibrium pH values of the solutions.

The aluminum(III) and mercury(II) dialysis coefficients at their joint existence differ from the dialysis coefficients of the same ions in the individual solutions. The dialysis coefficients of aluminum(III) and mercury(II) below the OH/ΣM = 0 are equal to 1, but then in a narrow pH interval they fall sharply to 0.

Proceeding from the data obtained we calculated according to the procedure in [6] the fractions of the polynuclear forms in the solution, and with the material balance equation calculated the content of the mononuclear forms of aluminum(III) and mercury(II). For the calculations were used the hydrolysis constants values $pK_1 = 5.0$, $pK_2 = 5.5$ for aluminum(III) and $pK_1 = 3.4$, $pK_2 = 2.77$ for mercury(II) [7]. The results are shown in Fig. 2, *a*. According to the calculations, increase in OH/ΣM ratio initially leads to increase in the fraction of the mononuclear hydroxo forms of mercury(II). Almost simultaneously begins the precipitation drop and the fraction of the polynuclear complex increases sharply.

Table 1. Coefficients of dialysis of aluminum(III) and mercury(II) in the Al^{3+}–Hg^{2+}–NO_3^-–H_2O system

OH/ΣM	pH	K_d	
		Al^{3+}	Hg^{2+}
–1	1.72	1.0	1.0
–0.75	1.79	1.0	1.0
–0.5	1.97	1.0	1.0
–0.25	2.26	1.0	1.0
0	2.64	0.94	0.95
0.125	2.69	0.65	0.8
0.25	2.73	0	0

According to the published data, the formation of the aluminum(III) polynuclear complexes begins at the pH > 4.2 [6–8]. At the same time, mercury(II) can form

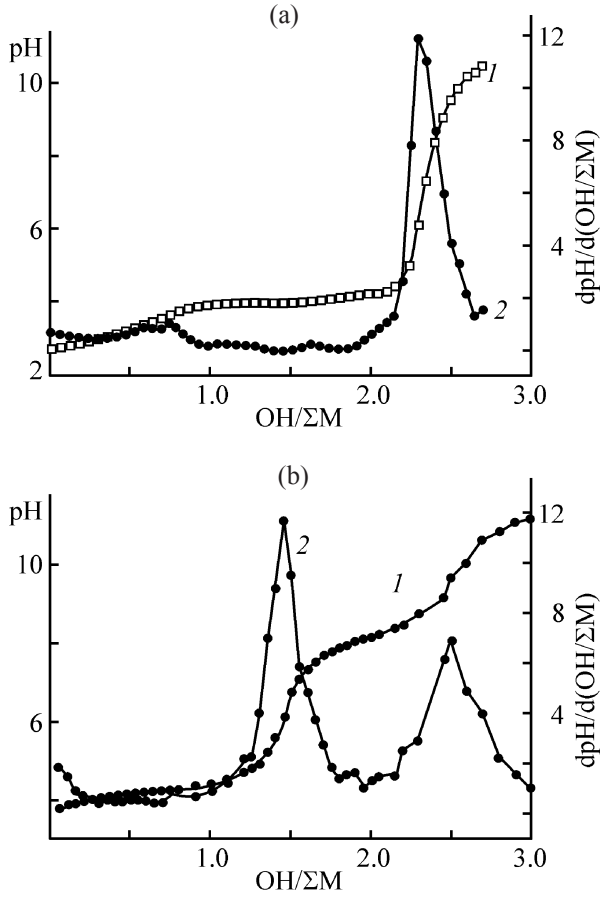

Fig. 1. Integral (*1*) and differential (*2*) curves of potentiometric titration of the Al^{3+}–Hg^{2+}– NO_3^-–H_2O (a) and Al^{3+}–Cd^{2+}–NO_3^-–H_2O (b) solutions.

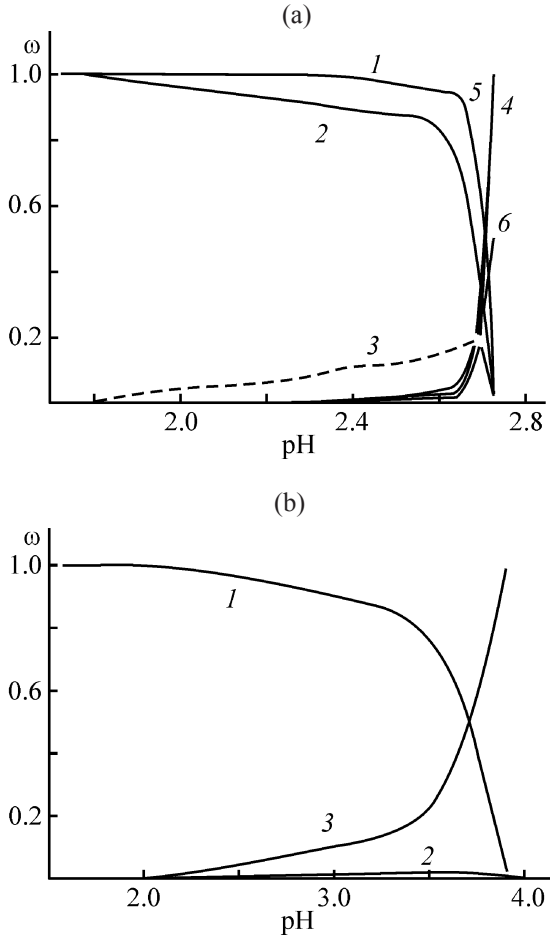

Fig. 2. Distribution of the aluminum(III) complex forms in the Al^{3+}–Hg^{2+}–NOO_3^-–H_2O (a) and Al^{3+}–Cd^{2+}–NO_3^-– H_2O (b) systems. (ω) a fraction of the complex form. (a) (*1*) $Al(H_2O)_6^{3+}$, (*2*) $Hg(H_2O)_6^{2+}$, (*3*) $HgOH(H_2O)_5^+$, (*4*) polynuclear Al^{3+} forms, (*5*) polynuclear Hg^{2+} forms, (*6*) HgO precipitate; (b) (*1*) $Al(H_2O)_6^{3+}$; (*2*) aluminum(III) in the composition of polynuclear hydroxo complexes, (*3*) $AlOH(H_2O)_5^{2+}$.

the polynuclear hydroxo forms at the concentration above 0.01 mol l^{-1} [1, 7, 9]. The results obtained attest a significant mutual influence of the aluminum(III) and mercury(II) ions and "enhanced" hydrolysis in the Al^{3+}–Hg^{2+}–NO_3^-–H_2O system as compared with the solutions of individual ions, with the formation of heteropolynuclear hydroxo complexes.

The dialysis coefficients K_d of aluminum(III) and cadmium(II) in the Al^{3+}–Cd^{2+}–NO_3^-–H_2O system are listed in Table 2 together with the equilibrium pH values of the respective solutions. From these data we calculated the mole fraction ω_p of the aluminum(III) polynuclear hydroxo complexes in the solution, and from the material balance equations [6] calculated the

Table 2. Coefficients of aluminum(III) and cadmium(II) dialysis in the Al^{3+}–Cd^{2+}–NO_3^-–H_2O system

OH/ΣM	pH	K_d	
		Al^{3+}	Cd^{2+}
–1	1.57	1.0	1.0
–0.75	1.77	1.0	1.0
–0.5	1.95	1.0	1.0
–0.25	1.99	1.0	1.0
0	2.89	1.0	1.0
0.25	3.57	0.68	1.0
0.5	3.61	0.55	1.0
0.75	3.67	0.44	1.0
1.0	3.77	0.23	1.0
1.25	3.91	0	1.0

fraction of the aluminum(III) mononuclear hydroxo complexes. Therewith were used the same data on the dissociation constants as in the respective calculations for the Al^{3+}–Hg^{2+}– NO_3^-–H_2O system. The cadmium(II) ions in the studied pH range are mainly in the form of aqua complexes, therefore respective calculations were not performed. The results are shown in Fig. 2b.

From the data obtained follows that in the Al^{3+}–Cd^{2+}–NO_3^-–H_2O system at the increase in the OH/M ratio the coefficients of aluminum(III) dialysis decreases sharply, that is connected with the formation of the polynuclear hydroxo complexes. The dialysis coefficient of cadmium(II) at any OH/M ratio equals to 1, that points to the presence in the solutions of aqua complexes and mononuclear hydroxo complexes of cadmium(II) only. Thus, cadmium(II) does not form the heteropolynuclear compexes with aluminum(III).

CONCLUSIONS

1. By the method of dialysis is found that in the Al(III)–Hg(II) solution occurs mutual influence of the ions affecting their hydrolytic behavior owing to formation of the heteronuclear hydroxo complexes.

2. In the Al^{3+}–Cd^{2+}–NO_3^-–H_2O system the ions do not interact substantially, and only aluminum(III) polynuclear hydroxo complexes are found to form.

REFERENCES

1. Sokolovskii, A.E., Radion, E.V., and Rudakov D.A., *Zh. Prikl. Khim.*, 2002, vol. 75, no. 11, pp. 1780–1783.
2. Sokolovskii, A.E. and Radion, E.V., *Zh. Prikl. Khim.*, 2003,

vol. 76, no. 3, pp. 379–382.
3. Shvartsenbakh, G. and Flashka, G., *Kompleksometricheskoe titrovanie* (Complexpmetric Titration), Moscow: Khimiya, 1970.
4. Lur'e, Yu.Yu., *Spravochnik po analiticheskoi khimii* (Analytical Chemistry Handbook), Moscow: Khimiya, 1989.
5. Bulatov, M.I. and Bulatova, A.A., *Zh. Analyt. Khim.,* 1983, vol. 38, no. 9, pp. 1607–1610.
6. Kapylovich, M.T., Radion, E.V., and Baev, A.K., *Koord. Khim.*, 1995, vol. 21, no. 1, pp. 66–71.
7. Davydov, Yu.P., *Sostoyanie radionuklidov v rastvorakh* (State of Radionuclides in Solutions), Minsk: Nauka & Tekhnika, 1978.
8. Kapylovich, M.T., Radion, E.V., and Baev, A.K., *Zh. Neorg. Khim*., 1995, vol. 40, no. 6, pp. 1037–1041.
9. Radion, E.V., Zalevskaya, T.L., Baev, A.K., and Sheremet, E.N., *Koord. Khim*., 1998, vol. 24, no. 5, pp. 339–342.