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Aluminum Hydroxide's Solubility and the Forms of Dissolved Aluminum's Occurrence in Seawater

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Abstract—The solubility of aluminum hydroxide in seawater of 35‰ salinity at pH = 7.4–8.2 and 25°C was determined experimentally for three samples synthesized in different ways. The solubilities of two phases subjected to ageing and precipitated (a) from a boiling solution of aluminum sulfate and (b) immediately from seawater at room temperature were a little different and showed the minimum within pH = 8.05–8.10. The solubility of aluminum hydroxide precipitated from a solution of sulfate aluminum at room temperature and not subjected to ageing was about twofold at pH~7.9. The analysis of the pH dependence of the concentration of dissolved aluminum allows one to suppose that an $\text{Al}(\text{OH})_2^+$ hydroxo complex is the primary form of the aluminum occurrence in seawater at pH < 8.05, whereas the $\text{Al}(\text{OH})_4^-$ anion is prevailing at pH > 8.10. Electrically neutral $\text{Al}(\text{OH})_3^0$ hydroxocomplexes may be prevailing within the narrow range of pH = 8.05–8.10 and, in general, are of secondary importance.

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INTRODUCTION

The notions of the physicochemical conditions of dissolved aluminum in seawater are based upon the results of thermodynamic calculations. According to them, the primary forms of aluminum's occurrence are hydroxocomplexes with the prevalence of $\text{Al}(\text{OH})_3^0$ and $\text{Al}(\text{OH})_4^-$ [2, 5]. The available experimental data on the seawater solubility of aluminum hydroxide [1, 3] (from which one might draw a conclusion concerning the occurrence forms of dissolved aluminum) are not in good agreement with each other. This is quite often seen for poorly soluble phases synthesized under different conditions.

The present study is aimed to find out the forms of dissolved aluminum's occurrence in seawater using the experimental data on the solubility of aluminum hydroxide phases different in their preparation conditions.

METHODS OF THE EXPERIMENTS

In the course of the experiments, three samples of aluminum hydroxide were used. The first $\text{Al}(\text{OH})_3$ phase was prepared by precipitation at room temperature immediately from seawater. To do this, 1 ml of 0.2 M $\text{Al}_2(\text{SO}_4)_3$ solution was added to 2 l of artificial seawater of 35‰ salinity and increased carbonate alkalinity (Alk = 3.2 mg-equiv/l) at intense mixing;

then, the formed suspension was kept for two months. Before the experiments, the seawater containing the sediment of aluminum hydroxide was intensively stirred and then the suspension aliquots (each of 100 ml) were sampled.

The second phase was obtained as a result of the rapid mixing of equal volumes (1 l) of 0.01 M $\text{Al}_2(\text{SO}_4)_3$ and 0.06 M NaOH solutions at room temperature with the following rinsing with distilled water in a Buchner funnel until a negative reaction for sulfate ions with barium chloride. The synthesis of the third phase was performed by the mixing of equal volumes of $\text{Al}_2(\text{SO}_4)_3$ and NaOH solutions of the same concentrations as those of the above case; however, they were heated up to boiling. The formed sediment was cleansed during two weeks from soluble salts by decantation with distilled water until a negative reaction for sulfate ions with barium chloride with periodic heating to 100°C to accelerate the ageing process. After the purification, distilled water was added to the gel-form sediments of aluminum hydroxide to a volume of 50 ml. In the course of the experiments, 1 ml of $\text{Al}(\text{OH})_3$ gel and 1 ml of artificial seawater of 70‰ salinity were added to 100 ml of ordinary seawater to restore the saline background.

The pH values in the experiments were varied by the addition either of 0–10 ml of 0.2 N borax solution with equal aliquots of 70‰ seawater to keep the constancy of the saline composition or of 0–4 ml of 35‰

Aluminum hydroxide's solubility in seawater of 35‰ salinity at 25°C

[ΣAl], μM	log[ΣAl], M	pH
Phase precipitated from seawater with added Al ₂ (SO ₄) ₃ at room temperature		
2.12	-5.67	8.18
2.06	-5.69	8.19
2.02	-5.69	8.19
2.08	-5.68	8.18
1.86	-5.73	8.11
1.86	-5.73	8.05
2.55	-5.59	7.93
6.57	-5.18	7.49
Phase precipitated from the Al ₂ (SO ₄) ₃ solution at room temperature		
7.48	-5.13	8.18
7.26	-5.14	8.17
7.35	-5.13	8.16
7.03	-5.15	8.17
7.78	-5.11	8.17
7.88	-5.10	8.16
7.55	-5.12	8.15
7.44	-5.13	8.14
6.23	-5.21	8.13
6.41	-5.19	8.08
5.02	-5.30	8.07
5.13	-5.29	8.01
4.47	-5.35	7.97
3.26	-5.49	7.92
6.34	-5.20	7.42
Phase precipitated from the boiling Al ₂ (SO ₄) ₃ solution		
2.40	-5.62	8.20
1.89	-5.72	8.13
1.65	-5.78	8.08
1.96	-5.71	7.95
2.25	-5.65	7.91
6.61	-5.18	7.52

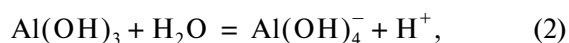
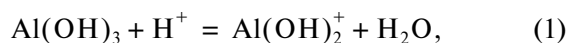
acid seawater in which 0.2 M NaCl was partly substituted for the equivalent amount of HCl.

The experiments were carried out in polypropylene containers of 120 ml volume. During three weeks, the samples were intensively stirred with a shaker for 4–5 h every day to obtain a constant concentration of dissolved aluminum. The temperature of the solutions was equal to 25 ± 1°C. Before analyzing, the samples were filtered with 0.45-μm membrane filters; then, the aluminum concentrations were determined in the filtrates by spectrophotometry using eriochrome cyanine [4] with ±3% accuracy, and the pH values were measured by potentiometry with an accuracy of ±0.005 pH units.

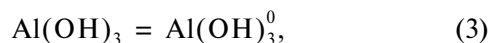
RESULTS AND DISCUSSION

The results of the experiments presented in the table showed that the solubilities of the different phases of aluminum hydroxide are characterized by differences both in the absolute values of the dissolved aluminum concentrations and in the values of the solubility minima falling into the range of pH = 7.9–8.1 (figure).

The least solubility of the close absolute values is characteristic for the aluminum hydroxide phases subjected to ageing (precipitated from seawater and from the boiling solution of aluminum sulfate). For these phases, the solubility minimum was found within the range of pH = 8.05–8.10. At pH < 8.05, the derivative value is $d\log[\Sigma Al]/dpH \approx -1$. From the stoichiometry of reactions



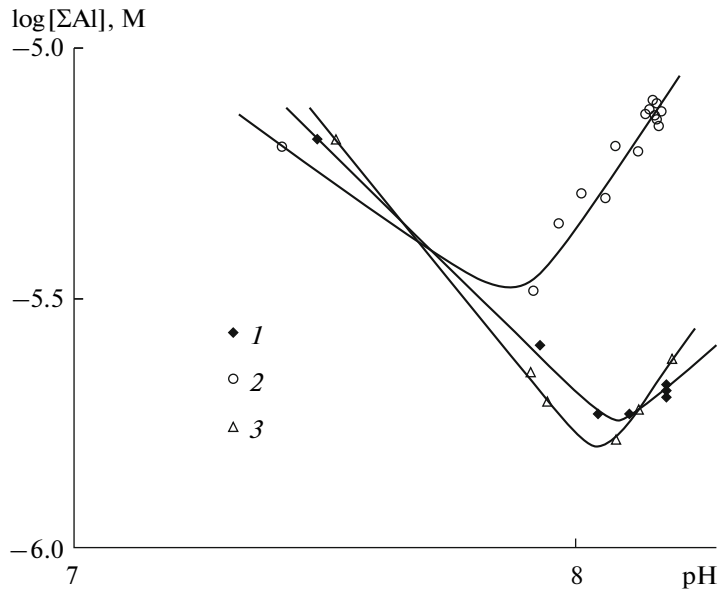
one may draw a conclusion concerning the occurrence of the bulk of the dissolved aluminum as Al(OH)_2^+ at pH < 8.05 and as Al(OH)_4^- at pH > 8.10. Electrically neutral Al(OH)_3^0 hydroxocomplexes with their concentrations being independent of the acidity in equilibrium with the pure phases of aluminum hydroxide,



might prevail only within the narrow range of pH = 8.05–8.10 and, in general, evidently play a secondary role.

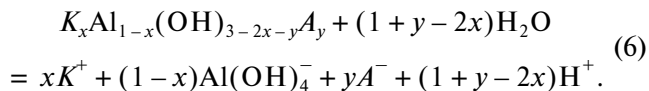
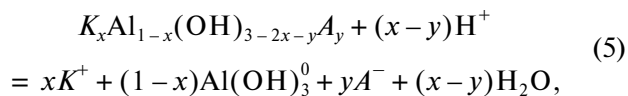
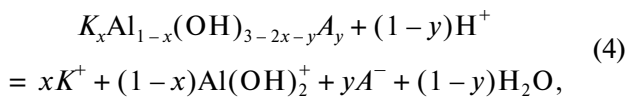
The solubility of the aluminum hydroxide phase precipitated from the aluminum sulfate solution at room temperature and not subjected to preageing was about twofold and showed a slightly displaced minimum of the equilibrium concentration of dissolved aluminum noted at pH ~ 7.9 (figure).

One must note that the derivative $d\log[\Sigma Al]/dpH$ is in the closest agreement with the stoichiometry of reactions (1) and (2) in the case of the phase precipi-



Aluminum hydroxide's solubility in seawater of 35‰ salinity. 1—Phase precipitated from seawater with added $\text{Al}_2(\text{SO}_4)_3$ at room temperature; 2—phase precipitated from the $\text{Al}_2(\text{SO}_4)_3$ solution at room temperature; 3—phase precipitated from the boiling $\text{Al}_2(\text{SO}_4)_3$ solution.

tated from seawater and subjected to ageing. For the phases precipitated from boiling and, especially, from cold solutions of aluminum sulfate, these derivatives are somewhat different from their theoretical values. Most probably, this is caused by the presence of impurities in the aluminum hydroxide. This assumption is illustrated by the stoichiometry of the dissolution of aluminum hydroxide containing an admixture of univalent K^+ cations and A^- anions:



According to (4)–(6), the values of the $d\log[\text{Al}(\text{OH})_2^+]/dp\text{H}$, $d\log[\text{Al}(\text{OH})_3^0]/dp\text{H}$, and $d\log[\text{Al}(\text{OH})_4^-]/dp\text{H}$ derivatives depend on the x and y parameters, i.e., on the quantity of admixed cation and anion components. For the aluminum hydroxide phases subjected to long-time ageing (precipitated from seawater and from the boiling solution of $\text{Al}_2(\text{SO}_4)_3$), the closeness of the inclination angle for the experimental $\text{pH}-\log[\Sigma\text{Al}]$ dependence to theoretical values of the $d\log[\Sigma\text{Al}]/dp\text{H}$ derivatives over the entire pH range considered points to a small content

of impurities. Hence, only data on the solubility of these phases may be used to find out the forms of aluminum's occurrence in seawater.

CONCLUSIONS

(1) In seawater, the solubility of aluminum hydroxide precipitated (a) from a boiling solution of aluminum sulfate and (b) immediately from seawater at room temperature and subjected to ageing is characterized by the minimum within $\text{pH} = 8.05-8.10$. The solubility of aluminum hydroxide precipitated from the aluminum sulfate solution at room temperature and not subjected to preageing is about twofold and reaches the minimum values at $\text{pH} \sim 7.9$.

(2) At $\text{pH} < 8.05$, the primary form of dissolved aluminum's occurrence in seawater is an $\text{Al}(\text{OH})_2^+$ hydroxocomplex; at $\text{pH} > 8.10$, the $\text{Al}(\text{OH})_4^-$ anion is prevailing. Electrically neutral $\text{Al}(\text{OH})_3^0$ hydroxocomplexes may be prevailing only within the narrow range of $\text{pH} = 8.05-8.10$ and, evidently, are in general of secondary importance.

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REFERENCES

1. E. A. Erofeeva, V. S. Savenko, and S. M. Fazlullin, "On the Solubility of Aluminum Hydroxide in Seawater," *Okeanologiya* **29** (3), 421–422 (1989).
2. N. N. Popov, K. N. Fedorov, and V. M. Orlov, *Marine Water* (Nauka, Moscow, 1979) [in Russian].
3. A. V. Savenko, "Alluminum Behavior in Mixing Submarine Hydrothermal and Seawater Solutions: Results of Experimental Modeling," *Okeanologiya* **36** (5), 735–740 (1996) [*Oceanology* **36** (5), 692–697 (1996)].
4. Yu. Yu. Lur'e, *Standardized Methods for Water Analysis* (Khimiya, Moscow, 1971) [in Russian].
5. D. R. Turner, M. Whitfield, and A. G. Dickson, "The Equilibrium Speciation of Dissolved Components in Freshwater and Seawater at 25°C and 1 atm Pressure," *Geochim. Cosmochim. Acta* **45** (6), 855–881 (1981).