© 1980 The Chemical Society of Japan Bull. Chem. Soc. Jpn., 53, 926—929 (1980) [Vol. 53, No. 4

The Coprecipitation of Antimony(III or V) with Iron(III) Hydroxide

Yoshikazu Inoue and Makoto Munemori*

Laboratory of Environmental Chemistry, College of Engineering, University of Osaka Prefecture, Mozu-Umemachi, Sakai 591

(Received August 2, 1979)

The coprecipitation of antimony(III or V) with iron(III) hydroxide as a function of the pH in the range from 4 to 12 was studied in the presence of the chloride ion. Antimony(III) is coprecipitated more easily at any given pH value than antimony(V). The coprecipitation of antimony(III) is quantitative in the pH range from 4 to 10 and is not affected by the chloride ion. On the other hand, the coprecipitation of antimony(V) is affected not only by the pH range, but also by the chloride-ion concentration.

Iron(III) and manganese(IV) oxides(or hydroxide) have been noted as substances which exert a major effect on the concentrations of other heavy metal ions in natural waters,[1-3] because these oxides associate with the heavy metal ions. For example, cadmium(II) and lead(II) are incorporated into the hydrous oxides of iron and manganese.[4,5] Arsenic(III),[6] chromium(III),[7] and mercury(II)[8] are incorporated into iron(III) hydroxide. This incorporation can be ascribable to adsorption, ion-exchange, or coprecipitation. Leckie and James[9] have suggested that the hydrolysis of the heavy metal ion plays an important role in these processes. The hydrolysis reaction differs depending on the oxidation state of the metal ion and is also affected by the presence of complexing agents.

In a previous paper,[10] we studied the coprecipitation of mercury(II) with iron(III) hydroxide in the absence and in the presence of halogenide ions and indicated that the coprecipitation behavior can be explained in terms of the hydrolysis of mercury, *i.e.*, the formation of $Hg(OH)_2$. The present investigation was undertaken in order to evaluate the coprecipitation of antimony(III or V) with iron(III) hydroxide in the presence of the chloride ion. It has been reported that antimony(III) is coprecipitated with iron(III) hydroxide and manganese(IV) oxide.[11,12] Fujinaga *et al.*[11] studied the coprecipitation of antimony(III) with iron(III) hydroxide in natural and artificial seawater and indicated that antimony(III) is quantitatively coprecipitated with iron(III) hydroxide in the vicinity of pH 7. For antimony(V), however, little has been published regarding coprecipitation with heavy metal hydroxides in natural waters.

This paper will describe a coprecipitation study of the antimony(III or V)–iron(III) system and will discuss the effect of the hydrolysis of antimony on its coprecipitation with iron(III) hydroxide and the antimony species which is responsible for coprecipitation from the viewpoint of chemical equilibrium.

Experimental

Reagents. The antimony(III) stock solution, 8.2×10^{-2} mol cm^{-3}, was prepared by dissolving antimony metal (99.999 %) in sulfuric acid with heating and by then diluting the mixture with dilute hydrochloric acid. The antimony(V) stock solution, 8.2×10^{-2} mol dm^{-3}, was prepared by dissolving potassium antimonate(V) in dilute hydrochloric acid(the antimonate is not appreciably soluble in sulfuric acid). The iron(III) stock solution was prepared by dissolving iron(III) sulfate in dilute sulfuric acid and was standardized by titration with potassium permanganate after reduction with zinc. The working solutions were prepared immediately before use by diluting the stock solutions. Sodium chloride was used as the source of the chloride ion. All the chemicals were of an analytical reagent grade.

Procedure. The hydrolysis study was carried out by employing a 500-ml portion of an 8.2×10^{-4} mol dm^{-3} antimony(III or V) solution. The solution was adjusted to pH 4, 10, or 12 with sodium hydroxide and was allowed to stand while it was being stirred at 25 °C. At fixed intervals of time, a 20-ml portion of the solution was filtered through a filter paper(Toyo filter paper No. 2). In the coprecipitation study, a 200-ml portion of a solution containing 8.2×10^{-4} mol dm^{-3} antimony(III or V) and 7×10^{-3} mol dm^{-3} iron(III) was used to obtain the data reported below unless otherwise indicated. The solution was adjusted to an appropriate pH value with sodium hydroxide and then allowed to stand while it was being stirred at 25 °C. After equilibrium had been reached(it required about 20 min), the solution was filtered through a filter paper(Toyo filter paper No. 2). All the pH values reported are equilibrium values. The antimony remaining in the filtrate was colorimetrically determined by the Rhodamine B method. Antimony(V) was reduced to antimony(III) with sodium sulfite by heating[13] and was then subjected to the Rhodamine B method immediately after the reoxidation of antimony(III) to antimony(V) with cerium.

Results and Disccusion

Hydrolysis of Antimony(III). The hydrolysis of antimony(III) was first studied at pH 4, 10, and 12 in

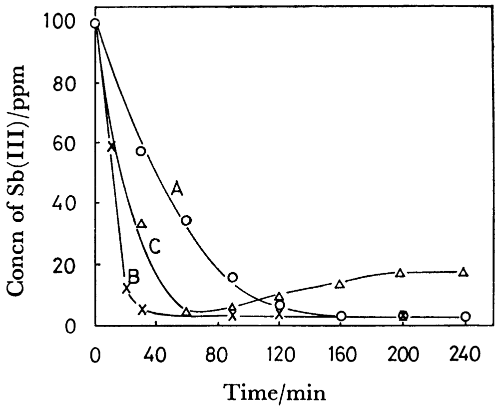
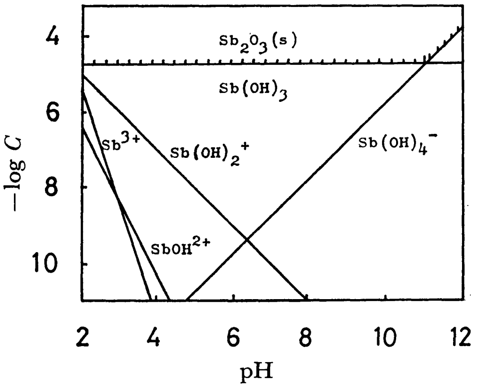


Fig. 1. Effect of pH on the hydrolysis of antimony(III) in the presence of 6×10^{-2} mol dm^{-3} chloride and 1.8×10^{-2} mol dm^{-3} sulfate (A) pH 4, (B) pH 10, and (C) pH 12.



Reactions	Equilibrium constants
$Sb_2O_3(s)+3H_2O=2Sb^{3+}+6OH^-$	$10^{-4.14}$
$Sb_2O_3(s)+2H^++H_2O=2Sb(OH)_2^+$	$10^{-3.11}$
$Sb_2O_3(s)+3H_2O=2Sb(OH)_3$	$10^{-4.7}$
$Sb_2O_3(s)+2OH^-+3H_2O=2Sb(OH)_4^-$	$10^{-2.06}$
$SbOH^{2+}+H_2O=Sb(OH)_2^++H^+$	$10^{-1.4}$
$Sb(OH)_2^++H_2O=Sb(OH)_3+H^+$	$10^{-0.87}$
$Sb(OH)_3+H_2O=Sb(OH)_4^-+H^+$	$10^{-11.0}$

Fig. 2. Log concentration-pH solubility diagram for $Sb_2O_3(s)-H_2O$ system. The diagram was calculated using representative values[14,15] for equilibrium constants for solubility and hydrolysis.

the presence of chloride (6×10^{-2} mol dm^{-3}) and sulfate (1.8×10^{-2} mol dm^{-3}) ions. Figure 1 shows the results as a function of the time. At pH 4 and 10, the concentration of antimony(III) in the solution decreased continuously, depending on the pH, with the lapse of time until equilibrium was established. At pH 12, on the other hand, the concentration of antimony(III) once decreased to minimum and then increased until equilibrium was established. The equilibrium concentration at pH 4 and 10 was about 3 ppm (2.46×10^{-5} mol dm^{-3}), which agrees fairly well with the solubility of $Sb_2O_3(s)$ (2×10^{-5} mol dm^{-3}) as derived from Fig. 2. The equilibrium concentration at pH 12 was about 18 ppm (1.48×10^{-4} mol dm^{-3}), which corresponds with the solubility of $Sb_2O_3(s)$ at pH 12 (1.8×10^{-4} mol dm^{-3}) (Fig. 2). These results indicate that neither chloride nor sulfate ions affect the hydrolysis equilibrium for antimony(III); this is in accordance with the theoretical expectation based on the small formation constants of the antimony(III) chloride and sulfate complexes. Therefore, the hydrolysis of antimony can be expressed by the following chemical equations, even in the presence of chloride and sulfate ions:

$$Sb^{3+} + H_2O = SbOH^{2+} + H^+ \qquad (1)$$

$$SbOH^{2+} + H_2O = Sb(OH)_2^+ + H^+ \qquad (2)$$

$$Sb(OH)_2^+ + H_2O = Sb(OH)_3 + H^+ \qquad (3)$$

$$2Sb(OH)_3 = Sb_2O_3(s) + 3H_2O \qquad (4)$$

At pH 4 and 10, Reactions 1 to 4 take place and antimony(III) is precipitated as Sb_2O_3. Reactions 1 to 3 may be expected to be faster at higher pH values, while Reaction 4 is probably independent of the pH; therefore, the precipitation equilibrium is established faster at pH 10 than at pH 4.

At pH 12, however, Reaction 5 or 6 occurs in addition to the above reactions to produce the $Sb(OH)_4^-$ ion, while the formation of $Sb_2O_3(s)$ is retarded.

$$Sb(OH)_3 + OH^- = Sb(OH)_4^- \qquad (5)$$

$$Sb_2O_3(s) + 2OH^- + 3H_2O = 2Sb(OH)_4^- \qquad (6)$$

The appearance of the minimum solubility during the hydrolysis process clearly indicates that Reaction 6 is predominant.

Coprecipitation of Antimony(III) with Iron(III) Hydroxide. In the antimony(III)–iron(III) system, antimony(III) was precipitated within 20 min over a wide pH range. The concentration of antimony(III) remaining in the aqueous phase at pH 8 was less than 0.05 ppm (4.1×10^{-7} mol dm^{-3}), far less than that expected from the solubility of $Sb_2O_3(s)$ (2×10^{-5} mol dm^{-3}). These results indicate that antimony(III) is coprecipitated with iron(III) hydroxide. The concentration of the chloride ion in the range from 1×10^{-3} to 5.4×10^{-1} mol dm^{-3} did not affect the results, suggesting the absence of any effect of the ionic strength on the coprecipitation.

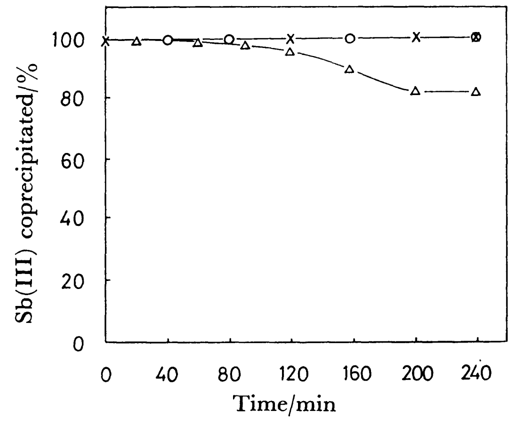


Fig. 3. Effect of hydrolysis of antimony(III) its coprecipitation with iron(III) hydroxide (○) pH 4, (×) pH 10, and (△) pH 12.

Effect of Hydrolysis of Antimony(III) on its Coprecipitation with Iron(III) Hydroxide. Figure 3 shows the effect of the hydrolysis of antimony(III) on its coprecipitation with iron(III) hydroxide. The experiment was performed in the following manner. Prior to the addition of iron(III), the antimony(III) solution was adjusted to pH 4, 10, or 12 with sodium hydroxide and then allowed to stand for a given time while it was being stirred at 25 °C. The time is taken as the abscissa in Fig. 3. The iron(III) solution was adjusted to pH 4, 10, or 12, and antimony and iron solutions with the same pH value were mixed. After the mixture has then been allowed to stand for 5 min while it being stirred at 25 °C, the suspension was filtered through a filter paper (Toyo filter paper No. 2). At pH 4 and 10, as is shown in Fig. 3, antimony(III) was quantitatively coprecipitated with iron(III) hydroxide, irrespective of the time needed for the hydrolysis of antimony. The concentration of antimony(III) remaining in the aqueous phase at both pH values was less than 0.05 ppm. At pH 12, the coprecipitation of antimony(III) was quantitative as long as the antimony(III) solution was allowed to stand for a period of less than 30 min before mixing. After standing for a longer period, however, the extent of the coprecipitation of antimony(III) gradually decreased to a constant value, and then the concentration of antimony(III) remaining in the aqueous phase was 19 ppm (1.6×10^{-4} mol dm^{-3}), approximately equal to the solubility of $Sb_2O_3(s)$ at pH 12. The coprecipitation behavior of antimony(III) described above can be explained by assuming that the $Sb(OH)_4^-$ ion is not coprecipitated with iron(III) hydroxide.

It can be concluded from the results presented above that the antimony(III) species except $Sb_2O_3(s)$ are coprecipitated with iron(III) hydroxide, but there is no evidence to determine what species among Sb^{3+}, $SbOH^{2+}$, $Sb(OH)_2^+$, and $Sb(OH)_3$ is predominantly responsible for the coprecipitation process. Further investigation will be required for a more detailed elucidation of the coprecipitation mechanism.

Coprecipitation of Antimony(V) with Iron(III) Hydroxide. The effect of the pH on the formation of antimony(V) oxide was examined prior to the coprecipitation study of the antimony(V)–iron(III) system. Antimony(V) must be precipitated as Sb_2O_5 in an acid medium when its concentration is higher than 2×10^{-4} mol dm^{-3}.[16] In reality, however, no precipitate appeared when solutions containing 8.2×10^{-4} mol dm^{-3} antimony(V) and 6×10^{-2} mol dm^{-3} chloride were allowed to stand for about 200 min at 25 °C after the pH had been adjusted to 0, 4, 10, and 12. It seems, then, that antimony(V) is present in the solution as chloro complexes, *e.g.*, $Sb(OH)_xCl_{6-x}$ ions (x=2—6).

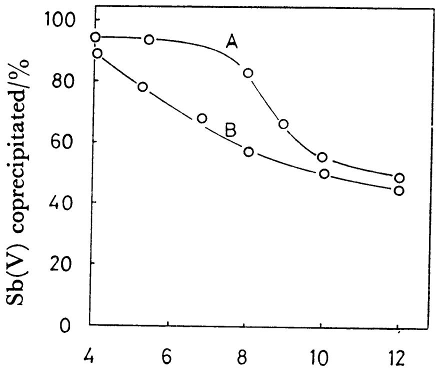


Fig. 4. Coprecipitation of antimony(V) with iron(III) hydroxide in the presence of chloride ion (A) 6×10^{-2} mol dm^{-3} and (B) 5.4×10^{-1} mol dm^{-3}.

In the antimony(V)–iron(III) system, however, antimony(V) was precipitated in the pH range shown in Fig. 4(A). These results indicate that antimony(V) is coprecipitated with iron(III) hydroxide. The coprecipitation of antimony(V) was affected by the concentration of the chloride ion, as is shown in Fig. 4 (A and B). With the increase in the chloride-ion concentration, the coprecipitation is prevented. The effect of the chloride ion may be attributed to the complex formation between antimony(V) and chloride ions, though the speciation of antimony is complicated at the present time[16,17] and further investigation will be required before we can infer the coprecipitation mechanism.

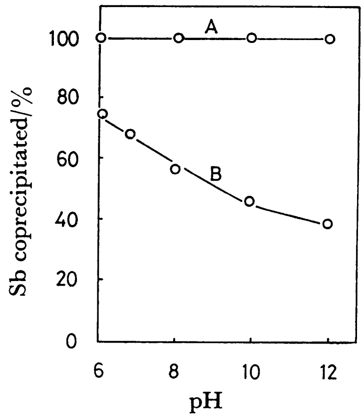


Fig. 5. Coprecipitation of antimony(III or V) with iron(III) hydroxide in artificial seawater (A) antimony(III) (B) antimony(V).

The Coprecipitation of Antimony(III or V) in Artificial Seawater. Coprecipitation behavior was studied in a mixture whose composition was similar to that of seawater with respect to inorganic anions, *i.e.*, 5.4×10^{-1} mol dm^{-3} chloride, 8.1×10^{-4} mol dm^{-3} bromide, 5.3×10^{-5} mol dm^{-3} fluoride, 3.2×10^{-7} mol dm^{-3} iodide, 2.8×10^{-2} mol dm^{-3} sulfate, 2.3×10^{-3} mol dm^{-3} carbonate, and 4.2×10^{-5} mol dm^{-3} borate ions. The results are shown as a function of the pH in Fig. 5. In the artificial seawater, antimony(III) was coprecipitated with iron(III) hydroxide more easily than antimony(V). At pH 8, for example, the concentration of antimony present in the solution was about 43 ppm (3.5×10^{-4} mol dm^{-3}) for antimony(V) and less than 0.05 ppm (4.1×10^{-7} mol dm^{-3}) for antimony(III). From these results, it may be said that, if the coprecipitation of antimony with iron(III) hydroxide occurs in seawater, antimony(III) will be coprecipitated more easily than antimony(V). The fact that antimony is mainly present in seawater as the quinquevalent state[18,19] is possibly ascribable to the difference in hydrolysis behavior between antimony(III) and antimony(V) described above.

Conclusion

The results described above indicate that the hydrolysis of antimony is a crucial step in the coprecipitation of antimony with iron(III) hydroxide. Antimony(III) is not coprecipitated with iron(III) hydroxide in the form of $Sb(OH)_4^-$ ion. The coprecipitation of antimony(V) is somewhat complicated when the chloride ion is present; therefore, further investigation will be required to elucidate the coprecipitation mechanism. The hydrolysis of antimony(III) is independent of the concentration of the chloride ion. The coprecipitation of antimony(III) is not affected by the chloride ion and takes place over a wide range of pH values. On the other hand, the coprecipitation of antimony(V) is affected not only by the pH, but also by the chloride-ion concentration. Accordingly, in seawater which contains a large amount of chloride ion (*ca.* 5.4×10^{-1} mol dm^{-3}), antimony(III) may be coprecipitated with iron(III) hydroxide more easily than antimony(V).

The authors wish to acknowledge the assistance given by Mr. Yoshio Nishioka in the experimental work.

References

1) K. B. Krauskopf, *Geochim. Cosmochim. Acta.* **9**, 1 (1956).

2) E. G. Goldberg, "Oceanography," ACS, Washington, D. C. (1961), No. 67, p. 583.

3) R. C. Harris, *Nature*, **219**, 54 (1968).

4) R. R. Gadde and H. A. Laitinen, *Environ. Lett.*, **5**, 223 (1973).

5) R. R. Gadde and H. A. Laitinen, *Anal. Chem.*, **46**, 2022 (1974).

6) K. Sugawara, M. Tanaka, and S. Kanamori, *Bull. Chem. Soc. Jpn.*, **29**, 670 (1956).

7) R. Fukai and D. Vas, *J. Oceanog. Soc. Jpn.*, **23**, 298 (1967).

8) R. A. Lockwood and K. Y. Chen, *Environ. Lett.*, **6**, 151 (1974).

9) J. O. Leckie and R. O. James, "Aqueous-Environmental Chemistry of Metals," Ann Arbor Science Publishers, Ann Arbor, Mich. (1974), p. 1.

10) Y. Inoue and M. Munemori, *Environ. Sci. Technol.*, **13**, 443 (1979).

11) T. Fujinaga, M. Koyama, K. Izutsu, S. Himeno, and M. Kawashima, *Nippon Kagaku Kaishi*, **1974**, 1489.

12) J. E. Portman and J. P. Riley, *Anal. Chim. Acta*, **35**, 35 (1966).

13) Y. Inoue and M. Munemori, unpublished data.

14) L. G. Sillen and A. E. Martell, "Stability Constants of Metal Ion Complexes," Chem. Soc., London (1964), Spec. Publ. No. 17.

15) G. Charlot, "L'Analyse Qualitative et les Reaction en Solution," Masson et Cie, Paris (1963), p. 297.

16) C. F. Baes and R. E. Mesmer, "Hydrolysis of Cations," Interscience Publishers, New York (1976), p. 370.

17) H. M. Neumann, *J. Am. Chem. Soc.*, **76**, 2611 (1954).

18) S. Gohda, *Bull. Chem. Soc. Jpn.*, **48**, 1213 (1975).

19) P. G. Brewer, "Chemical Oceanography," 2nd ed, Academic Press, New York (1975), Vol. 1, p. 415.