Solvent Extraction Studies of the Hydrolysis of Antimony(III) in Tracer Concentrations

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The hydrolysis of antimony(III) ions was investigated through solvent extraction with dithizone-carbon tetrachloride solutions. In a 3 M (H, Na)ClO$_4$ solution, a tracer concentration of antimony(III) ($<10^{-8}$ M) was found in the form of a monovalent cation, Sb(OH)$_2^+$ or SbO$^+$, and a neutral species, Sb(OH)$_3$ or SbO(OH). The former is predominant in strongly acidic media, while the latter becomes abundant in the weakly acidic-to-neutral region. One of the constants of successive hydrolysis, $K_1=[\mathrm{Sb(OH)_2^+}][\mathrm{Sb(OH)_3}]^{-1}[\mathrm{H^+}]^{-1}$, was calculated from the distribution ratios, giving the result: $\log K_1=1.23_6\pm0.06$. The chemical composition of the extracted species was estimated to be Sb(HDz)$_3$.

Antimony, with its typical amphoteric character, is located on the border between the metal and non-metal regions in the periodic table. Since both antimony(III) and antimony(V) ions easily hydrolyze in an aqueous solution, it is difficult to keep macro amounts of antimony ions stationary in any solution except in highly acidic media. For this reason, relatively little fundamental information is available on the chemical species of antimony in aqueous solutions, especially on their stability constants. In earlier works,[1–12] the solubility measurement was the main tool for studying these problems with some exceptions—for example, spectrophotometry, potentiometry, the measurement of diffusion coefficients, and the chemical analysis of precipitates. Since these techniques necessitated the use of macro amounts of antimony, there was always some ambiguity about the formation of polymerized species whose chemical composition is hard to determine.

We investigated the hydrolysis of antimony(III) through solvent extraction with dithizone, using radioactive tracers. Some reports suggest the reaction of antimony(III) ions with dithizone,[13–15] but no quantitative treatment of this reaction has ever been given. Our preliminary experiment showed that dithizone extracts antimony(III) in the form of dithizonate and that it is very suitable for the present research because of its rather high extractability and good reproducibility.

Experimental

Water. Tap water was deionized with a mono-bed-type ion exchanger and then distilled in an all-glass distilling apparatus.

Perchloric Acid. A G.R.-grade reagent was diluted with distilled water and purified with a dithiozone-carbon tetrachloride solution.

Sodium Perchlorate Solution. The solution was prepared from G.R.-grade sodium carbonate and the purified perchloric acid. After the reagents had been mixed, the resulting solution was purified by filtration, crystallization, and dithizone extraction.

Acetic Acid. G.R.-grade glacial acetic acid was diluted with distilled water. The dilute solution was purified by dithizone extraction.

Ammonia Water. G.R.-grade ammonia water was distilled and absorbed in distilled water.

Carbon Tetrachloride. A G.R.-grade reagent was distilled in an all-glass distilling apparatus, and a fraction with a boiling temperature of 76—78 °C was taken.

Dithizone Solution. The Merck product was purified according to the method by E. B. Sandell.[16] The purity of the dithizone in carbon tetrachloride was checked spectrophotometrically by examining the ratio of the optical density at 620 mμ to that at 450 mμ.[17]

Radioactive Tracers. Two kinds of radioactive antimony(III) tracers were prepared.

a) Sb-125: Carrier-free isotope was purchased from the Oak Ridge National Laboratory, U.S.A. Further purification was carried out to exclude a trace amount of tin, the target element of Sb-125 production, by extraction with isopropyl ether and anion ion-exchange chromatography.[18] The purified Sb(III)-125 was stocked in a carbon tetrachloirde solution of dithizone. The concentration of non-radioactive antimony in this solution was found by neutron-activation analysis to be below 10^{-8} M. This tracer was employed to study the behaviour of the tracer amount of antimony.

b) Mixture of Sb-122 and Sb-124: This mixture was produced through the neutron irradiation of antimony in the JRR-1 reactor at the Japan Atomic Energy Research Institute. The irradiated, highly pure antimony metal was dissolved in *aqua regia*, evaporated to dryness, redissolved in 3 M HCl, and finally purified by dithizone extraction to remove other interfering metal ions. After reduction with SO$_2$, the trivalent antimony was extracted with a dithizone solution. It was then back-extracted and stocked as a perchloric acid solution.

Measurement of the Distribution Ratio. In the case of a tracer amount of antimony, the stocked organic solution of Sb-125 was added to a carbon tetrachloride solution of dithizone. The organic phase thus prepared was mixed with a solution of (H, Na)ClO$_4$ and was then shaken at 25±0.5 °C until the partition equilibrium was attained. In the case of macro amounts of antimony, the purified antimony containing the radio-nuclides was initially in various acidities of perchloric acid. A fresh carbon tetrachloride solution of dithizone was added to the aqueous phase and was shaken in a way similar to that in the case of the tracer amount of antimony.

In both cases, after the equilibrium had been attained, an equal volume of each phase was pipetted into a test tube and subjected to the measurement of the γ-activity. Another portion of the aqueous phase was used for the measurement of the hydrogen ion concentration. The distribution ratio, D, is given by the radioactivity of the organic phase divided by that of the aqueous phase.

Measurement of Hydrogen Ion Concentration. As for acidic media (pH<2), the hydrogen ion concentration was deter-

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mined by the titration method. In other cases it was determined by potentiometry. The emf measurement was carried out using a pH meter (Radiometer PHM-4 type) with a glass electrode at 25±0.5 °C as soon as possible after shaking. As reference solutions, mixtures of 0.01 M $HClO_4$ and $(x-0.01)$ M $NaClO_4$ were prepared for the x M (H, Na)ClO_4 solution series $(-\log[H^+]=2.00)$.

Measurement of Radioactivity. A well-type NaI(Tl) scintillation counter was used. For Sb-125, the sum of γ-rays whose energies are higher than 200 keV was taken in order to eliminate the daughter Te-125m activity. For the mixture of Sb-122 and Sb-124, the total γ-rays were counted.

Results

(1) Time Necessary for the Partition Equilibrium. As is shown in Fig. 1, the partition of antimony(III) between two phases reaches equilibrium within five minutes. This proved to be true under any conditions, independent of the acidity, the concentration of antimony (up to 2×10^{-4} M), the concentration of dithizone, and the phase to which antimony was added initially.

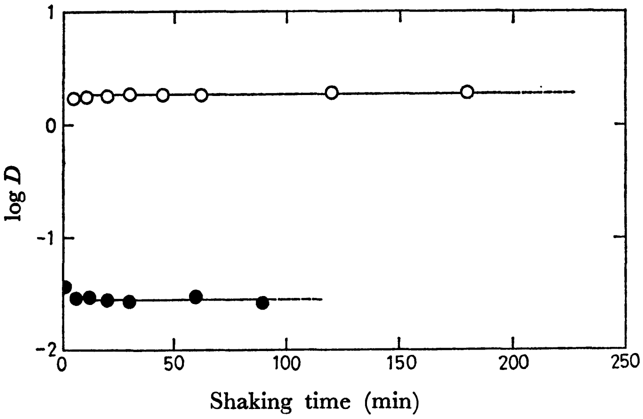

Fig. 1. The effect of shaking time on the distribution ratio in the back-extraction. ●: $[H^+]$ in the aqueous phase of 3.0 M (H, Na)ClO_4=1.5 M, $[H_2Dz]_{org}=2.5\times10^{-4}$ M. ○: $-\log[H^+]$ in the aqueous phase of 3.0 M (H, Na)ClO_4=3.5, $[H_2Dz]_{org}=3.1\times10^{-4}$ M.

(2) Effect of Acetate Buffer Solution. In the weakly acidic region $(-\log[H^+]>2)$, an acetate buffer solution was employed for the adjustment of the hydrogen ion concentration in the aqueous phase. In order to study the effect of the acetate buffer on the distribution ratio, we varied the concentration of the acetate buffer from 3.0 to 0.008 M in the region of $-\log[H^+]=4-5$, where the distribution ratio is practically independent of $-\log[H^+]$. The results in the region are shown in Fig. 2. It may be seen that acetate concentrations less than 0.1 M have no effect on the distribution ratio.

(3) Dependence of the Distribution Ratio on the Antimony Concentration. Figure 3 shows the distribution ratios measured as a function of the antimony concentration in the tracer-amount region ($<10^{-8}$ M). No effect of the antimony concentration was observed for either 3.0 M perchloric acid media or a 3.0 M (H, Na)ClO_4 solution of $-\log[H^+]=4.6$—4.8. This suggests that there is no difference in the polymerization number between the antimony species in the aqueous phase and those in the organic phase. Since it is improbable that any polymerized species are kept stable in both phases over such a wide range of antimony concentrations, we may safely assume that the monomers are the main species involved in the solvent extraction of tracer concentrations of antimony.

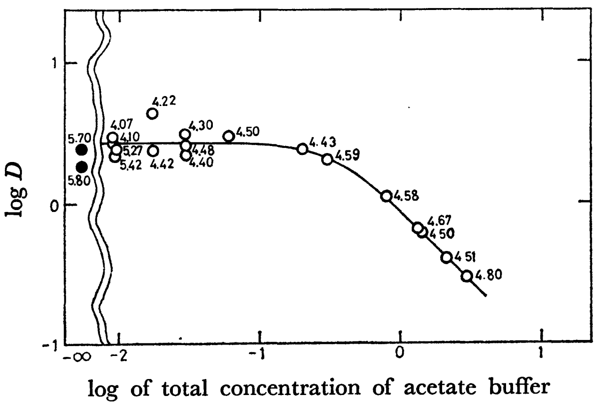

Fig. 2. The dependence of the distribution ratio on the total concentration of acetate buffer added. Each numerical value shows $-\log[H^+]$ in the aqueous phase after the equilibrium. ●: Without any acetate. The concentration of total salts was kept constant (3.0 M) by adding sodium perchlorate. $[H_2Dz]_{org}=3.0\times10^{-4}$ M.

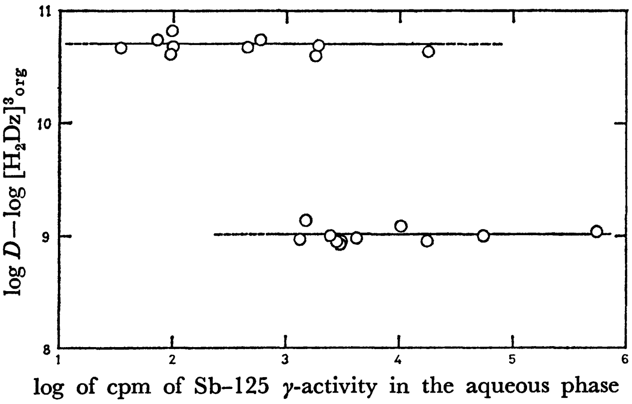

Fig. 3. The dependence of the distribution ratio on the tracer concentration of antimony(III) in the aqueous phase after the equilibrium. Upper group: $-\log[H^+]$ in the aqueous phase of 3.0 M (H, Na)ClO_4=4.6–4.8. Lower group: Aqueous phase --- 3.0 M $HClO_4$.

In the case of the 2×10^{-4} M antimony solution, the distribution ratio for the 0.5 M perchloric acid medium agreed well with that of the tracer amount of antimony, while a slightly higher value was obtained for the 0.06 M perchloric acid medium.

(4) Dependence of the Distribution Ratio on the Dithizone Concentration in the Organic Phase. The distribution ratio, D, was measured as a function of the dithizone concentration under various conditions. The results are shown in Figs. 4 and 5. From the figures we see that the slope of $\log D$ *versus* $\log[H_2Dz]_{org}$ is 3 in all cases, independent of the acid and antimony concentrations, where "H_2Dz" represents a neutral

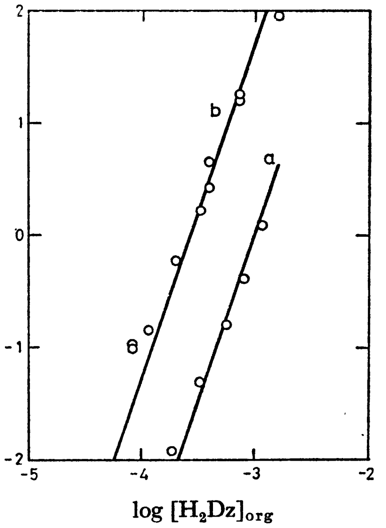

Fig. 4. The dependence of the distribution ratio on the concentration of dithizone in the organic phase. Tracer amount of antimony was used with Sb-125 as the tracer. a: Aqueous phase --- 3.0 M $HClO_4$. b: $-\log[H^+]$ in the aqueous phase of 3.0 M (H, Na)ClO_4=4.2.

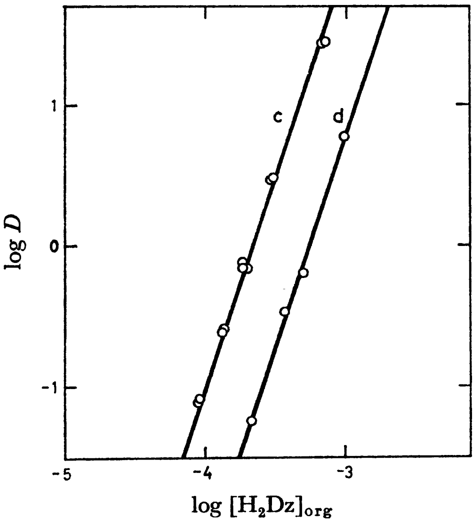

Fig. 5. The dependence of the distribution ratio on the concentration of dithizone in the organic phase. The initial concentration of antimony(III) in the aqueous phase was 2×10^{-4} M. Sb-124 was used as the tracer. c: Aqueous phase --- 0.06 M $HClO_4$. d: Aqueous phase --- 0.5 M $HClO_4$.

dithizone molecule.

The distribution ratio, D, is expressed as follows:

$$D=\frac{\sum\limits_m[Sb(OH)_{3-m}(HDz)_m]_{org}}{\sum\limits_p\sum\limits_q[Sb(OH)_p(HDz)_q^{3-p-q}]}$$

$$=\frac{\sum\limits_m\{\bar{K}_m[Sb(OH)_3][H_2Dz]^m{}_{org}\}}{\sum\limits_p\sum\limits_q\{K_{p,q}[Sb(OH)_p^{3-p}][H^+]^{-q}[H_2Dz]^q{}_{org}\}}\ ,$$

where

$$\bar{K}_m=\frac{[Sb(OH)_{3-m}(HDz)_m]_{org}}{[Sb(OH)_3][H_2Dz]^m{}_{org}}$$

for this reaction:

$$Sb(OH)_3+m\cdot H_2Dz(org)$$
$$=Sb(OH)_{3-m}(HDz)_m(org)+m\cdot H_2O\ ,$$

and where

$$K_{p,q}=\frac{[Sb(OH)_p(HDz)_q^{3-p-q}][H^+]^q}{[Sb(OH)_p^{3-p}][H_2Dz]^q{}_{org}}$$

for this reaction:

$$Sb(OH)_p^{3-p}+q\cdot H_2Dz(org)$$
$$=Sb(OH)_p(HDz)_q^{3-p-q}+q\cdot H^+\ .$$

In general, the slope of log D *versus* log $[H_2Dz]_{org}$, or that of $\partial\log D/\partial\log[H_2Dz]_{org}$, indicates the difference in the average number of monovalent dithizonate ions (HDz^-) attached to an antimony atom between the organic phase and the aqueous phase. The extracted species must be electrically neutral. It is generally accepted that the coordination number of antimony(III) is 4 or 6.[19-29] Therefore, we can reasonably assume that it does not exceed 6. Since HDz^- is a bidentate ligand, our results shown in Figs. 4 and 5 lead to the conclusion that only one kind of antimony species, *i.e.*, $Sb(HDz)_3$, exists in the organic phase without any adduct formation, and that the concentration of the Sb(III)-(HDz^-) complex species is negligibly low in the aqueous phase. Thus, D may be simplified as follows;

$$D=\frac{[Sb(HDz)_3]_{org}}{\sum\limits_{n=0}^{6}[Sb(OH)_n^{3-n}]}=\frac{\bar{K}_3[Sb(OH)_3][H_2Dz]^3{}_{org}}{\sum\limits_{n=0}^{6}[Sb(OH)_n^{3-n}]}$$

where

$$\bar{K}_3=\frac{[Sb(HDz)_3]_{org}}{[Sb(OH)_3][H_2Dz]^3{}_{org}}\ .$$

(5) Dependence of the Distribution Ratio on the Hydrogen Ion Concentration. In Fig. 6, we plot log ($D/[H_2Dz]^3{}_{org}$) for a tracer amount of antiomny as a function of $-\log[H^+]$. The slope is +1 for $-\log[H^+]<1$ and 0 for $-\log[H^+]=3-6$.

The distribution ratio of the previous section is expressed in terms of hydrolysis constants as follows:

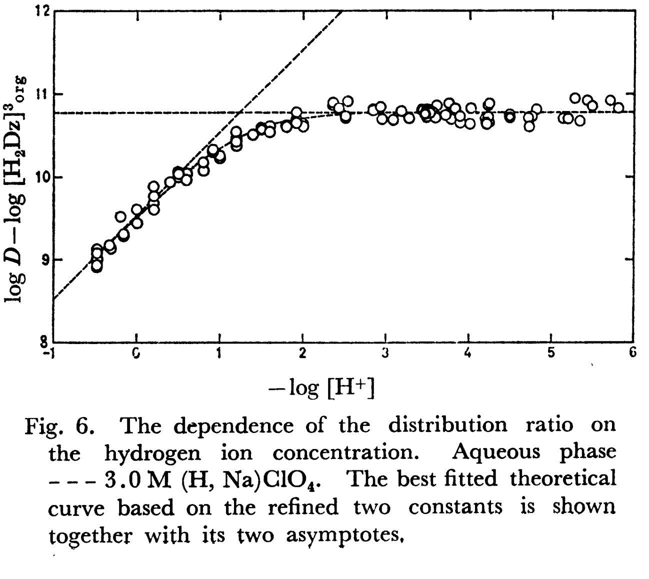

Fig. 6. The dependence of the distribution ratio on the hydrogen ion concentration. Aqueous phase --- 3.0 M (H, Na)ClO_4. The best fitted theoretical curve based on the refined two constants is shown together with its two asymptotes.

$$D=\frac{\bar{K}_3[\mathrm{H_2Dz}]^3{}_{\mathrm{org}}}{\sum_{i=1}^{3}(K_i[\mathrm{H^+}]^i)+1+\sum_{j=1}^{3}(K_j'[\mathrm{H^+}]^{-j})}$$

where

$$K_i=\frac{[\mathrm{Sb(OH)}_{3-i}^{i+}]}{[\mathrm{Sb(OH)_3}][\mathrm{H^+}]^i}$$

and

$$K_j'=\frac{[\mathrm{Sb(OH)}_{3+j}^{j-}][\mathrm{H^+}]^j}{[\mathrm{Sb(OH)_3}]}\ .$$

The plot of log $(D/[\mathrm{H_2Dz}]^3{}_{\mathrm{org}})$ *versus* $-\log[\mathrm{H^+}]$ in Fig. 6 indicates the presence of a neutral species, $\mathrm{Sb(OH)_3}$ (or $\mathrm{SbO(OH)}$), in the region of the long plateau and of a monovalent cation, $\mathrm{Sb(OH)_2^+}$ (or $\mathrm{SbO^+}$), in the acidic region where the slope is +1. Thus, the equation may be written in a simplified form for the present case:

$$\frac{D}{[\mathrm{H_2Dz}]^3{}_{\mathrm{org}}}=\frac{\bar{K}_3}{K_1[\mathrm{H^+}]+1}\ ,$$

where

$$K_1=\frac{[\mathrm{Sb(OH)_2^+}]}{[\mathrm{Sb(OH)_3}][\mathrm{H^+}]}\ .$$

(6) Estimation of the $\bar{K}_3$ and K_1 Constants. The approximate values of a set of $\bar{K}_3$ and K_1 constants were obtained by the graphical curve fitting method.[30,31]

We found:

$$\log \bar{K}_3 = 10.77$$
$$\log K_1 = 1.25\ .$$

These values were refined through computer work using a program based on a modified least-squares method.

The refined values are:

$$\log \bar{K}_3 = 10.77_5 \pm 0.03$$
$$\log K_1 = 1.23_6 \pm 0.06\ ,$$

where the uncertainties mean 3σ.

(7) Effect of Perchlorate and Chloride Ions. From Fig. 7, we can see that the distribution ratios at 0.1 M (H, Na)ClO$_4$ do not differ from those at 3.0 M (H, Na)ClO$_4$ over the range of $-\log[\mathrm{H^+}]=1-4$. It can safely be said that perchlorate ions do not form any complex compounds with antimony(III), as is generally believed.

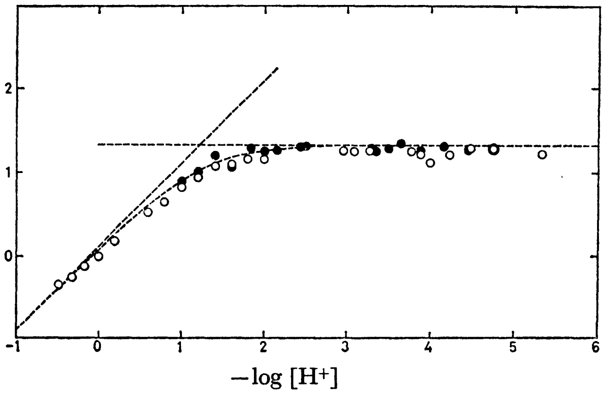

Fig. 7. The influence of the concentration of (H, Na)-ClO$_4$ media on the distribution ratio. ●: 0.1 M (H, Na)ClO$_4$. ○: 3.0 M (H, Na)ClO$_4$. $[\mathrm{H_2Dz}]_{\mathrm{org}}=7.1\times10^{-4}$ M. The best fitted theoretical curve for all the data involving those other than presented here is shown together with its two asymptotes.

As for chloride ions, very little effect is seen in the region where $-\log[\mathrm{H^+}]$ is nearly 4.5 (Fig. 8), while the effect is remarkable in the acidic media, as is shown in Fig. 9. Our preliminary experiment showed that the extraction behavior of the Sb(III)-Cl$^-$-H$_2$Dz system is very complicated and needs to be carefully studied. The details of this kind of investigation will be reported in a separate paper.

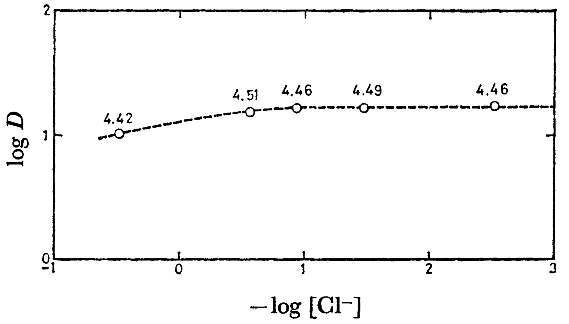

Fig. 8. The dependence of the distribution ratio on the concentration of the chloride ion. $[\mathrm{H_2Dz}]_{\mathrm{org}}=7.1\times10^{-4}$ M. The numerical data show $-\log[\mathrm{H^+}]$ in the aqueous phase of 3.0 M (H, Na)(Cl, ClO$_4$).

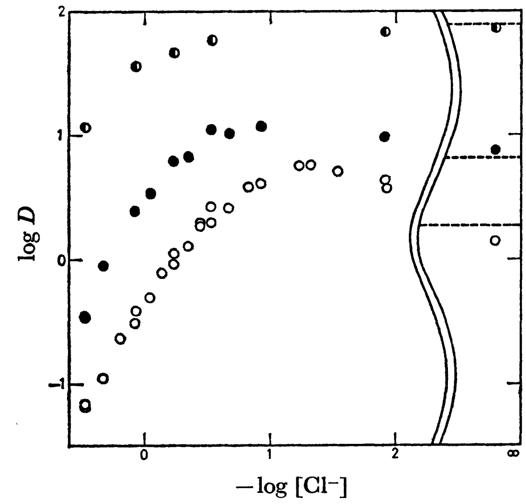

Fig. 9. The dependence of the distribution ratio on the concentration of the chloride ion. $[\mathrm{H_2Dz}]_{\mathrm{org}}=1.16\times10^{-3}$ M. Aqueous phase --- 3.0 M (H, Na) (Cl, ClO$_4$). [H$^+$]: ○ 3.0 M, ● 0.6 M and ◐ 0.012 M. At the right side, the experimental points (as circles) and the calculated values using the refined constants (as broken lines) are also shown on the case without the chloride ion.

Discussion

In acidic and neutral aqueous solutions, a tracer concentration of antimony(III) was found to be present as a monovalent cation and a neutral species of mono-nuclear antimony. The former is predominant in acidic solutions, while the latter is abundant in the weakly acidic and neutral regions. These results agree with the observations by Schuhmann,1) Gayer *et al.*,4) Faucherre,5) Pitman *et al.*,6) and Mishra *et al.*,11) who studied the solubility of macro amounts of antimony(III) oxide, the equilibrium potential of antimony metal–water system, or spectrometry.

The divalent and trivalent cation of antimony(III) could not be detected in the present investigation. The hydrolysis constants given by Kasper from his solubility measurements suggest the existence of the divalent cation in the acidic region.3) Jander and Hartmann describe the possibility of the coexistence of a small amount of the trivalent cation and the predominant monovalent one in the perchloric acid solution judging from the results of their high-voltage ionophoresis and diffusion studies.9) Dawson *et al.* have also reported the existence of the trivalent cation together with the monovalent one in perchloric acid media on the basis of a solvent-extraction study using phenylfluorone.10) Our present results did not confirm these observations.

The value of the hydrolysis constant, K_1, obtained in the present investigation ($\log K_1=1.23_6\pm0.06$) falls in the range of three published data: 1.59,4) 1.42,11) and 0.87.6) Kasper's value ($\log K_1=11.8$) seems to be too large.3)

No evidence of the existence of polymerized species was found in the aqueous media investigated for the concentrations of antimony(III) below 10^{-8} M. According to Jander and Hartmann, no soluble, polymerized species were observed in the solution from 16 M sodium hydroxide to 11 M perchloric acid for the antimony concentrations of 10^{-6}—10^{-5} M in the acidic, 0.4×10^{-6} M in the neutral, and 10^{-6}—10^{-3} M in the alkaline region.9) Dawson *et al.* report that the polymerization of antimony(III) ions occurs in 0.4—4 M perchloric acid solutions with antimony concentrations greater than 1×10^{-4} M.10) For the alkaline solution of antimony(III), Jander and Hartmann report the existence of only one species, very likely a hydrated monomer SbO_2^-, in a sodium hydroxide solution with a 10^{-6}—10^{-3} M antimony concentration (up to 9 M sodium hydroxide),9) while Scholder and Merbeth describe a polymerized species, $Sb_6O_{10}^{2-}$, in a 2.5—8.3 M sodium hydroxide solution with a 10^{-2}—10^{-1} M antimony concentration, $Sb_4O_7^{2-}$ in a 8.3—16.1 M sodium hydroxide solution with a 10^{-1} M order of antimony, and SbO_2^- in a strongly alkaline solution with a 10^{-1} M order of antimony.8) Meites and Schlossel report that antimony(III) ions exist in the forms of $Sb(OH)_4^-$ and $Sb_2O(OH)_4$ in a $(1-5)\times10^{-1}$ M sodium hydroxide solution of 2×10^{-5}—1×10^{-2} M antimony.12)

Using the data of the present work and the literature,32–40) we can compare the monomeric chemical species in aqueous media in the absence of special complexing anions among the ions with the oxidation number of +3 of nitrogen-group elements. The comparison is shown in Fig. 10. A similar comparison is made, in Fig. 11, between antimony(III) and antimony(V), using the constants from this work and the literature.6,41) From these figures we see a regularity on hydrolysis as a function of the charge density.

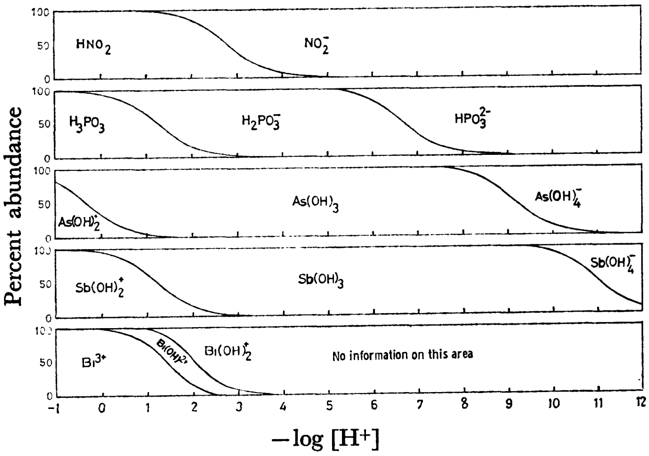

Fig. 10. Variation of the monomeric chemical species of the trivalent ion of the nitrogen group with the change of $-\log[H^+]$ value in the aqueous solution without any special complexing ligands.

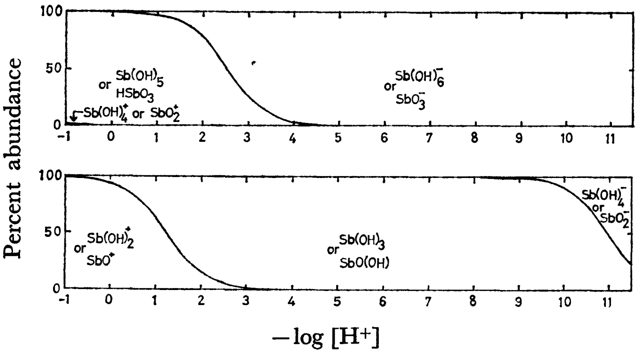

Fig. 11. The chemical species of the antimony(V) and antimony(III) ion in the aqueous solution without any special complexing ligands. Upper: Antimony(V). Lower: Antimony(III).

It may be noted that the distribution ratio for the Sb(III)-H_2Dz system is independent of the total ion concentration, as is shown in Fig. 7. Sekine reports the presence of some effect in the case of the Zn-Amberlite LA-1 system.42) Our results indicate that the number of hydrating water molecules is the same in both phases, or that the change in the water concentration is compensated for by the change in the activity coefficients of the chemical species involved.

In conclusion, it was found that antimony is one of the so-called dithizone metals43) whose dithizonate has a stoichiometric composition of $Sb(HDz)_3$. The formation constant and one of the hydrolysis constants were obtained.

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Calculations were carried out on the HITAC 5020

computer at the Computation Center of the University of Tokyo.

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