A Solvent-Extraction Study of the Hydrolysis of Tracer Concentrations of Bismuth(III) in Chloride Solutions

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The backward solvent extraction with dithizone(H_2dz)-CCl_4 solutions was used to examine the chemical species of bismuth(III) in 1 mol dm^{-3} of a (H,Na)Cl solution. A tracer concentration of bismuth(III) (ca. 10^{-11} mol dm^{-3}) was found to exist mainly in the form of $[BiCl_5]^{2-}$, $[BiCl_5(OH)]^{3-}$, $[BiCl_4(OH)]^{2-}$, and $[BiCl_3(OH)_3]^{3-}$ in the (H,Na)Cl solutions. The constants of the successive hydrolysis, β_1, β_2, and β_3, were calculated by using the distribution data. The resulting $\log\beta_1$, $\log\beta_2$, and $\log\beta_3$ values were 10.9, 17.5, and 30.2 respectively. The chemical composition of the extracted species was most probably $[Bi(Hdz)_3]$.

The hydrolysis of the major concentrations of bismuth(III) in solution has been extensively studied by many investigators. Their works revealed that the chemical species of bismuth(III) exist mainly in polynuclear species in solutions,[1–11] as a result of the hydrolysis of bismuth(III). On the other hand, Bidleman studied the mononuclear species formed in minor concentrations of bismuth(III) (ca. 10^{-5} M; 1 M=1 mol dm^{-3}) in 0.1 M NH_4ClO_4 solutions, based on solvent extraction using dithizone (H_2dz).[12] In his work, the equilibrium constants for the Bi–H_2dz extraction system and the formation constants for the species of $[Bi(OH)]^{2+}$, $[Bi(OH)_3]$, and $[Bi(OH)_4]^-$ have been determined. Furthermore, Hataye et al. studied the mononuclear species formed in more diluted concentrations of bismuth(III) (ca. 10^{-9} M) in 1.0 M (H,Na)ClO_4 and 1.0 M (H,Na)NO_3 solutions, based on the backward solvent extraction with an H_2dz–CCl_4 solution.[13] In their work, they found that chemical species of bismuth exist in the forms of Bi^{3+}, $[Bi(OH)]^{2+}$, $[Bi(OH)_2]^+$, and $[Bi(OH)_3]$ in 1.0 M (H,Na)ClO_4 solutions, and in those of $[Bi(NO_3)_n]^{3-n}$, $[Bi(NO_3)_n(OH)]^{2-n}$, $[Bi(NO_3)_n(OH)_2]^{1-n}$, and $[Bi(NO_3)_n(OH)_3]^{n-}$ in 1.0 M (H,Na)NO_3 solutions, depending on the acidity of the solutions.

In continuation of preceding works on the hydrolysis of tracer concentrations of bismuth(III) in perchlorate and nitrate solutions,[13] we investigated the hydrolysis and chloro complex formation of bismuth(III) in 1.0 M (H,Na)Cl solutions through backward solvent extraction with H_2dz–CCl_4 solutions.

Experimental

Reagents. Water was highly purified with a MILLI-Q reagent-grade water system (MILLIPORE). All the aqueous solutions used were finally purified by extraction with H_2dz-CCl_4 solutions.

Lead (^{210}Pb) containing an equilibrium amount of ^{210}Bi in 3 M HNO_3, imported from the Radiochemical Centre, Amersham, England, was used by diluting it to the appropriate concentration with 3 M HNO_3. A ^{210}Bi tracer solution was prepared by milking with an H_2dz-CCl_4 solution every 4 d from a diluted ^{210}Pb–^{210}Bi solution (pH ≃ca. 1). The ^{210}Bi tracer solution thus prepared was substantially free from any ^{210}Pb and/or ^{210}Po immediately after milking. After the extracted dithizonate (^{210}Bi–H_2dz) has been decomposed with 3 M HNO_3 solution, a portion of the ^{210}Bi tracer solution was transferred into another separatory funnel containing water, and the ^{210}Bi was extracted with an H_2dz–CCl_4 solution of a fixed concentration at $2\leq pH\leq 3$. The stock solution thus prepared in a lower concentration (less than 10^{-5} M H_2dz) showed practically no change for 3 h after preparation.

Measurements of the Distribution of Bismuth. One ml (1 ml=1 cm^3) of the organic phase containing a given concentration of bismuth was mixed with 10 ml of an aqueous solution (1 M (H,Na)Cl) with a given chemical composition, and the mixture was shaken at room temperature until the partition equilibrium was attained. After the completion of the equilibrium, a 0.5-ml portion of the organic phase was pipetted into a stainless steel planchet, evaporated, and subjected to the measurements of the β-activity (A_{org}) using a G.M. counter with aluminum absorbers against α-particles from ^{210}Po. Because it is difficult to count the activity of the aqueous phase in the same geometrical form as the organic phase in the planchet, it was calculated by using this relation: $A_{aq}=A^{\circ}_{org}-A_{org}$, where A_{aq} is the activity of a 5-ml portion of the aqueous phase and where A°_{org} is the initial activity of a 0.5-ml portion of the organic phase before shaking. Hence, the distribution ratio of bismuth, D, is given by:

$$D = 10 \times A_{org}/(A^{\circ}_{org}-A_{org}).$$

In each case of determining D, the multiple-extraction procedures were repeated under conditions of a definite hydrogen-ion concentration and definite amounts of bismuth in the aqueous phase; the data obtained in the first half were all discarded, and only the reproducible data in the other half were taken.

As for acidic media ($-\log[H^+]\leq 1$), the hydrogen-ion concentration was determined by means of titration with NaOH. In other cases, it was measured with a pH meter (TOA Electronics Ltd, Tokyo), which was adjusted by the use of standard solutions of phthalic acid and oxalate or phosphate at room temperature as soon as possible after shaking.

Results and Discussion

Adsorption of Bismuth onto Vessels Used. To examine the adsorption of bismuth onto glass, the inside surfaces of conical beakers were, in advance, repeatedly and sufficiently equilibrated with respect to the adsorption of bismuth(^{210}Bi) with 30 ml of a 1.0 M (H,Na)Cl solution containing bismuth (ca. 10^{-11} M Bi) at $-\log[\mathrm{H}^+]=1.0$. Then, after the conical beaker containing a freshly prepared 1.0 M (H,Na)Cl solution (30 ml, ca. 10^{-11} M Bi), with pH values varying from 0 to 10, has been shaken overnight, the activity of the aqueous phase was measured. The results are shown in Fig. 1. These results indicate that bismuth is leached out from the glass wall in an acidity higher than $-\log[\mathrm{H}^+]=1.0$, while on the contrary, it is adsorbed onto it in a lower acidity. Reproducible results of *D* should, therefore, be obtained in the solvent-extraction study of bismuth only when a distribution equilibrium set up among the aqueous phase, the organic phase, and the glass wall of the vessel used in definite hydrogen-ion and bismuth concentrations.

Dependence of the Distribution Ratio on the Bismuth Concentration. The partition equilibrium of bismuth in a carrier-free state between 1.0 M (H,Na)Cl solutions and the organic phase was reached within 30 min. Accordingly, the partition system involving carrier-free bismuth was shaken for more than 40 min in all the experiments in order to attain a complete equilibrium. On the other hand, in the case of less diluted solutions containing a bismuth carrier, the partition equilibrium of bismuth was not attained within 30 min. Therefore, the shaking time was previously examined in each bismuth concentration. For example, in case of 10^{-7} M Bi, the shaking should be continued for more than 12 h, as is shown in Fig. 2: in addition, it was necessary to take into account the decomposition of the dithizone and dithizonate formed. The higher the carrier concentration, the longer a shaking time was needed. This elongation of the shaking time is thought to be caused by the extreme decrease in the concentration ratio of bismuth to dithizone. However, as far as carrier-free bismuth is concerned, the partition equilibrium of bismuth should be attained within 30 min. Moreover, Fig. 3 shows the variation in the distribution ratios measured as a function of the amounts of the bismuth carrier in minor-to-trace concentrations. No effect of the bismuth concentration was observed for the 1.0 M (H,Na)Cl solutions of $-\log[\mathrm{H}^+]=0.83$ and 3.2. These results suggest that there is no difference in the degree of polymerization of bismuth species between aqueous and organic phases. On the other hand, it is impossible for any polymerized species to remain stable in both phases. We may, therefore, safely assume that the monomers are the main species prevailing in the solvent extraction of tracer concentrations of bismuth.

Dependence of Distribution Ratio on the Dithizone Concentration in the Organic Phase. The distribution ratio, *D*, was plotted as a function of the H_2dz concentration at different hydrogen-ion concentra-

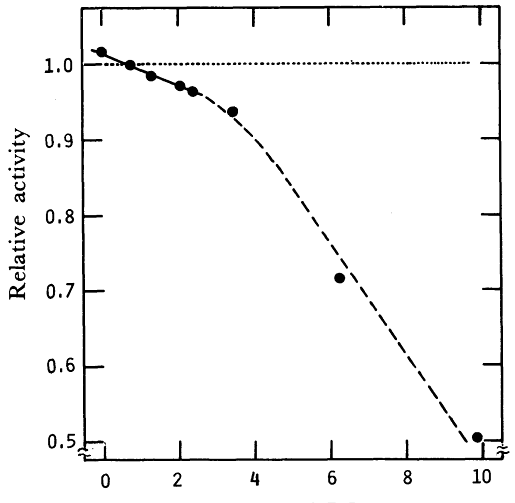

Fig. 1. The adsorption/desorption of bismuth onto/from glass wares (Erlenmeyer flasks). The flasks were in advance equilibrated with 30 ml of ^{210}Bi solution (ca. 10^{-11} M Bi, 1.0 M (H, Na) Cl) at $-\log[\mathrm{H}^+]=1.0$.

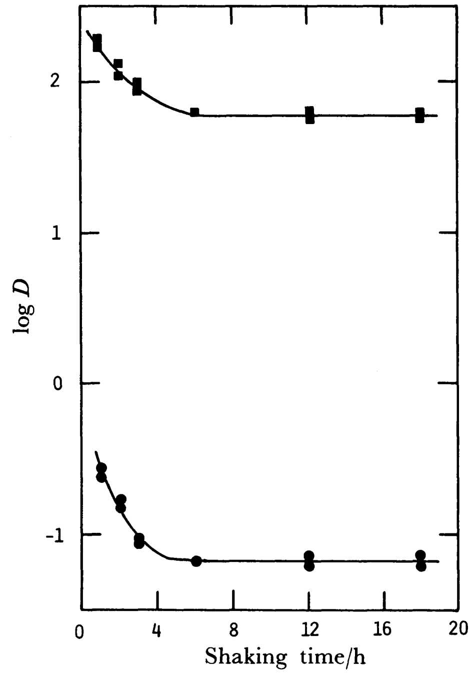

Fig. 2. The effect of shaking time on the distribution ratio in less diluted bismuth concentration (10^{-7} M). ●; $-\log[\mathrm{H}^+]=0.83$, $[\mathrm{H_2dz}]_{\mathrm{org}}=1.9\times10^{-3}$ M. ■; $-\log[\mathrm{H}^+]=3.2$, $[\mathrm{H_2dz}]_{\mathrm{org}}=9.5\times10^{-5}$ M.

tions. Figure 4 shows that the plots of log D vs. log $[H_2dz]_{org}$ have the identical slope of +3, independent of the acidity, where H_2dz denotes a neutral dithizone molecule. The narrow range of dithizone concentrations at $-\log[H^+]=0.5$ is attributable to the limited solubility of dithizone in CCl_4, and at the same time the very low values of the distribution ratio might lead to larger experimental errors. In general, the slope of log D vs. log $[H_2dz]_{org}$, or $\partial \log D/\partial \log [H_2dz]_{org}$, indicates the difference in the average number of univalent (bidentate) dithizonate ligands (Hdz^-) attached to a bismuth atom between the organic and aqueous phases. It is generally accepted that the coordination number of bismuth(III) is six, so the total number of ligands (as univalent) combined to a bismuth atom can be reasonably assumed not to exceed six; at the same time, the extracted species must be electrically neutral. Since the Hdz^- ion is a bidentate ligand, our results, shown in Fig. 4, lead to the conclusion that bismuth exists in the chemical form of the $[Bi(Hdz)_3]$ in the organic phase. It also means that the concentration of the Bi-Hdz^- complex species is negligibly low in the aqueous phase of 1.0 M (H,Na)Cl solutions.

Dependence of the Distribution Ratio on the Hydrogen-Ion Concentration. The distribution ratio for the extraction system of Bi-H_2dz in chloride solutions, D, is expressed as follows:

$$D = [Bi(Hdz)_3]_{org} / \sum_{x=0}^{6-n} \sum_{n=0}^{6-x} [BiCl_x(OH)_n^{3-x-n}] \tag{1}$$

$$= (K_3[H_2dz]^3_{org}[H^+]^{-3}) / \left(\sum_{x=0}^{6-n} \sum_{n=0}^{6-x} \beta_{x,n} Q_w^{\,n} [Cl^-]^x [H^+]^{-n} \right), \tag{2}$$

where:

$$K_3 = [Bi(Hdz)_3]_{org} / ([Bi^{3+}][H_2dz]^3_{org}[H^+]^{-3}), \tag{3}$$

$$\beta_{x,n} = [BiCl_x(OH)_n^{3-x-n}] / ([Bi^{3+}][Cl^-]^x[OH^-]^n), \tag{4}$$

$$Q_w = [H^+][OH^-]. \tag{5}$$

D can be rewritten as follows in terms of the hydrolysis of bismuth in the case of $[Cl^-]=1.0$ M:

$$D/[H_2dz]^3_{org} = K_3 / \left(\sum_{x=0}^{6-n} \sum_{n=0}^{6-x} \beta_{x,n} Q_w^{\,n} [H^+]^{3-n} \right). \tag{6}$$

In the present case, $\sum_{x=0}^{6-n} \sum_{n=0}^{6-x} \beta_{x,n}$ is denoted by $\sum_{n=0}^{6} \beta_n$, because each $\beta_{x,n}$ can not be measured separately, and the $\sum_{x=0}^{6} \beta_{x,0}$ is regarded as unity. Accordingly, Eq. 6 should be rewritten as follows:

$$D/[H_2dz]^3_{org} = K_3 / \left(\sum_{n=0}^{6} \beta_n Q_w^{\,n} [H^+]^{3-n} \right). \tag{7}$$

In Fig. 5, we plot $\log (D/[H_2dz]^3_{org})$ as a function of $-\log[H^+]$ in 1.0 M (H,Na)Cl solutions. Since it is difficult to determine the distribution ratio by using only a single solution of a given dithizone concentration in all regions of the hydrogen-ion concentration, $\log (D/[H_2dz]^3_{org})$ is plotted instead of log D. As is shown in the figure, the slope seems to be nearly +3 at $-\log[H^+]=0$, while it is nearly 0 at $4.5<-\log[H^+]$. Therefore, there exist few chlorohydroxo compounds

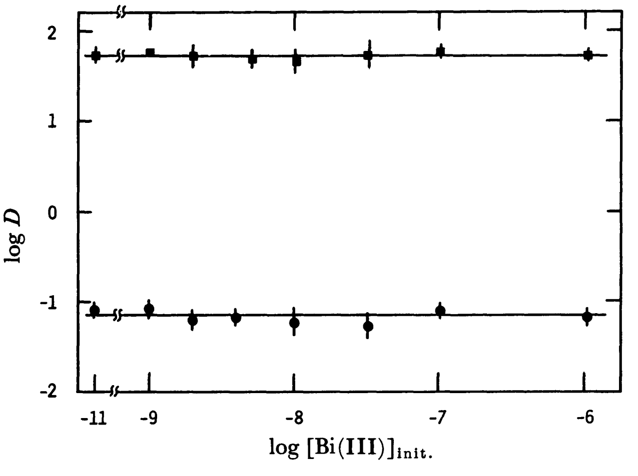

Fig. 3. The dependence of the distribution ratio on the initial concentration of bismuth(III) in 1.0 M (H, Na)Cl solutions.
●; $-\log[H^+]=0.83$, $[H_2dz]_{org}=1.9\times10^{-3}$ M. ■; $-\log[H^+]=3.2$, $[H_2dz]_{org}=9.5\times10^{-5}$ M.

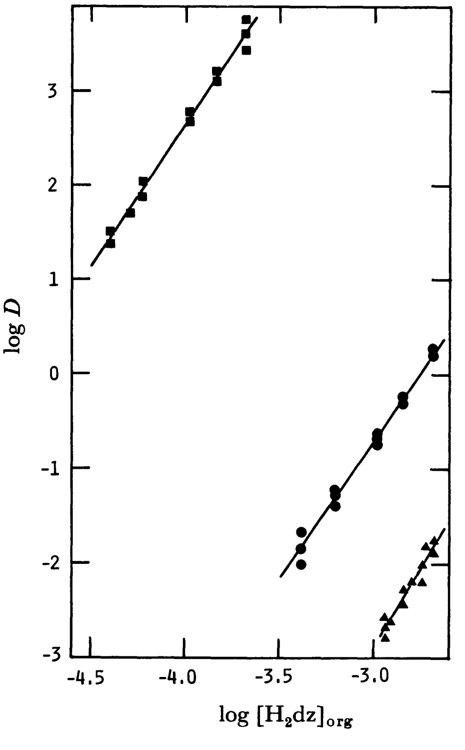

Fig. 4. The dependence of the distribution ratio of bismuth on the dithizone concentration in the organic phase.
▲; $-\log[H^+]=0.5$, ●; $-\log[H^+]=1.38$, ■; $-\log[H^+]=3.7$.

of bismuth in high acidity, while $[BiCl_x(OH)_3]^{x-}$ is predominant in the weakly acidic to neutral solutions. The distribution ratio in Eq. 7 can be expressed in terms of each hydrolysis constant, β_n (n=1, 2, and 3), as follows:

$$D/[H_2dz]^3_{org} = K_3/([H^+]^3 + \beta_1 Q_w[H^+]^2 + \beta_2 Q_w{}^2[H^+] + \beta_3 Q_w{}^3), \tag{8}$$

where:

$$\beta_1 = [BiCl_x(OH)^{2-x}]/([Bi^{3+}][Cl^-]^x[OH^-]), \tag{9}$$

$$\beta_2 = [BiCl_x(OH)_2{}^{1-x}]/([Bi^{3+}][Cl^-]^x[OH^-]^2), \tag{10}$$

$$\beta_3 = [BiCl_x(OH)_3{}^{x-}]/([Bi^{3+}][Cl^-]^x[OH^-]^3). \tag{11}$$

Estimation of K_3, $\beta_3 Q_w{}^3$, $\beta_2 Q_w{}^2$, and $\beta_1 Q_w$. Figure 5 shows that the slope of $\log(D/[H_2dz]^3_{org})$ vs. $-\log[H^+]$ is nearly 3 at $-\log[H^+]=0$, so Eq. 8 can be simplified to $D/[H_2dz]^3_{org} \simeq K_3$. Consequently, the approximate value of K_3 could be obtained as $(4.27\pm0.24)\times10^4$ from the data in Fig. 5 and the vast number of data on the partition equilibrium at $-\log[H^+]=0$, where the uncertainty is designated by σ. This value is much smaller than the K_3 values in 1.0 M (H,Na)ClO$_4$ and 1.0 M (H,Na)NO$_3$, as is shown in Table 1. This fact suggests that the formation of extractable species ($[Bi(Hdz)_3]$) is depressed by forming chloro complexes in trace concentrations of bismuth solutions in the presence of a large amount of chloride ions.

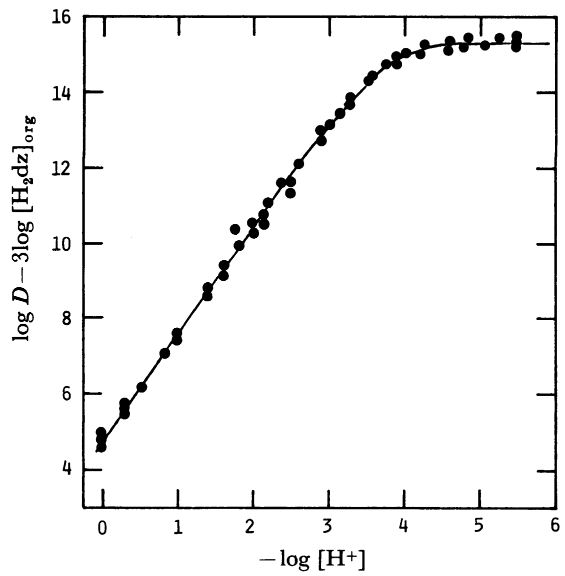

Fig. 5. The dependence of the distribution ratio of bismuth on the hydrogen-ion concentration in 1.0 M (H, Na)Cl solution.

Furthermore, since Fig. 5 shows that the slope of $\log(D/[H_2dz]^3_{org})$ vs. $-\log[H^+]$ ($-\log[H^+]>4.5$) is nearly zero, independent of the acidity, Eq. 8 can be also simplified to $D/[H_2dz]^3_{org} \simeq K_3/(\beta_3 Q_w{}^3)$. Consequently, the approximate value of $\beta_3 Q_w{}^3$ was obtained from Fig. 5 ($-\log[H^+]>4.5$) as $(2.04\pm0.13)\times10^{-11}$ for 1.0 M (H,Na)Cl solutions, where the uncertainty is indicated by σ. By using the set of K_3 and $\beta_3 Q_w{}^3$ values thus obtained, the approximate values of a set of $\beta_1 Q_w$ and $\beta_2 Q_w{}^2$ were obtained by the least-squares fit from the data in Fig. 5; the results were $\beta_1 Q_w=1.91\times10^{-3}$ and $\beta_2 Q_w{}^2=2.00\times10^{-10}$ for 1.0 M (H,Na)Cl solutions. Equation 8 is cubic with respect to the hydrogen-ion concentration; therefore, no meaningful error in $\beta_1 Q_w$ and $\beta_2 Q_w{}^2$ calculations could be obtained. The values obtained for $\log\beta_1$, $\log\beta_2$, and $\log\beta_3$ are 10.9, 17.5, and 30.2 respectively for a 1.0 M (H,Na)Cl solution, when $\log Q_w$ is -13.62.[14] In general, the n-th step-by-step hydrolysis constant gives a lower value than the ($n-1$) th constant. However, our results for bismuth in this solution exhibit an abnormal sequence, compared with those in 1.0 M (H,Na)ClO$_4$ and 1.0 M (H,Na)NO$_3$.[13] For this reason, it is thought that the coordination number of bismuth changes with a variation in the hydrogen-ion concentrations and that, furthermore, the effects of $\Delta H°$ (enthalpy) and/or $\Delta S°$ (entropy) for the formation of the bismuth species in the progressing hydrolysis play an important part. Unfortunately, from the hydrolysis constants alone we can not determine which reason is the dominant factor.

Table 1. Equilibrium Constants on Bismuth Hydrolysis in the Bi-Dithizone Extraction System

Medium	Method[a]	Concentration of Bi [M]	Equilibrium constant[b]					Reference
			$\log\beta_1$	$\log\beta_2$	$\log\beta_3$	$\log\beta_4$	$\log K_3$	
1.0 M (H, Na)Cl	Ex	ca. 10^{-11}	10.9	17.5	30.2	—	4.63	This work
1.0 M (H, Na)ClO$_4$	Ex	$< 10^{-7}$	12.0	22.9	33.9	—	11.38	13
1.0 M (H, Na)NO$_3$	Ex	$< 10^{-7}$	11.9	22.7	33.2	—	11.37	13
0.1 M NH$_4$ClO$_4$	Ex	$> 10^{-5}$	12.4	—	31.9	32.9	10.9	12
3 M NaClO$_4$	P	10^{-4} -0.05	12.4	—	—	—	—	4

a) Ex; extraction, P; potentiometry. b) $\beta_n = \dfrac{[Bi(OH)_nX_x{}^{3-n-x}]}{[Bi^{3+}][OH^-]^n[X^-]^x}$, (X; ClO$_4$, NO$_3$, or Cl), and $K_3 = \dfrac{[Bi(Hdz)_3]_{org}[H^+]^3}{[Bi^{3+}][H_2dz]^3_{org}}$.

The percentage abundances of the chemical species of bismuth calculated from each β_n value at different hydrogen-ion concentrations in 1.0 M (H,Na)Cl solutions are presented in Fig. 6(a), along with those for 1.0 M (H,Na)ClO_4 (b) and 1.0 M (H,Na)NO_3 (c) solutions.[13] As can be seen from Fig. 6, the hydrolysis of bismuth in the 1.0 M (H,Na)Cl solution (a) is greatly depressed compared with the other two solutions (b and c); this is caused by the strong complexing ability of the chloride ion. Furthermore, it is found that $[BiCl_x(OH)_2]^{1-x}$ in the 1.0 M (H,Na)Cl solution is a minor species; its maximum abundance is estimated to be only ca. 0.05%.

Number of Chloride Ions Coordinated to a Bismuth Atom. As no effect of the perchlorate-ion concentration on the distribution ratios of bismuth in the extraction with dithizone from a 1.0 M (H,Na)ClO_4 solution was observed,[13] the 1.0 M (H,Na)ClO_4 solution was employed as the diluent in order to examine the effect of the chloride ion by varying its mole fractions in the aqueous phase.

In general, the slope of log D vs. log $\{[Cl^-]/([Cl^-]+[ClO_4^-])\}$ in 1.0 M (H,Na)(Cl,ClO_4) solutions at a given hydrogen-ion concentration indicates the difference in the average number of univalent chloride ions attached to a bismuth atom between the organic and aqueous phases, so we determined the slope by varying the mole fractions of chloride ions in 1.0 M (H,Na)(Cl,ClO_4) solutions at a given hydrogen-ion concentration; a typical example is shown in Fig. 7 (lower line). The slope of -5.07 ± 0.07 (σ) indicates the average number of chloride ions coordinated to a bismuth atom in a 1.0 M (H,Na)Cl solution at $-\log[H^+]=1.21$; that is, it can be presumed that, in that solution, bismuth exists mainly as such a chemical species as $[BiCl_5]^{2-}$. Furthermore, the average numbers of chloride ions coordinated to a bismuth atom in 1.0 M (H,Na)Cl at $-\log[H^+]=0.29$, 0.83, 1.85, 2.54, and 3.12 were all determined to be close to five (4.67—5.07; they are plotted in Fig. 8) in a manner similar to that above mentioned. However, as the plots seemed not to be a straight line, but to form a concave curve upward at $-\log[H^+]=3.8$, as is shown in Fig. 7 (upper line), the number of chloride ions was determined from the slope of the tangential line (dotted line) of an approximate quadratic equation at $\log\{[Cl^-]/([Cl^-]+[ClO_4^-])\}=0$ obtained by the least-squares fit to the experimental data.

On the other hand, this method can not be applied to the solutions of $-\log[H^+]\geq4$, because it is difficult to adjust the hydrogen-ion concentration without using any buffer solutions. Instead, in this case, the value of $(\log D-3\log[H_2dz]_{org})_{ClO_4}$[13] minus $(\log D-3\log[H_2dz)_{org})_{Cl}$ shown in Fig. 5 was plotted as a function of $-\log[H^+]$ (≥4), as is shown in Fig. 8. Nevertheless, these values are not reasonable because

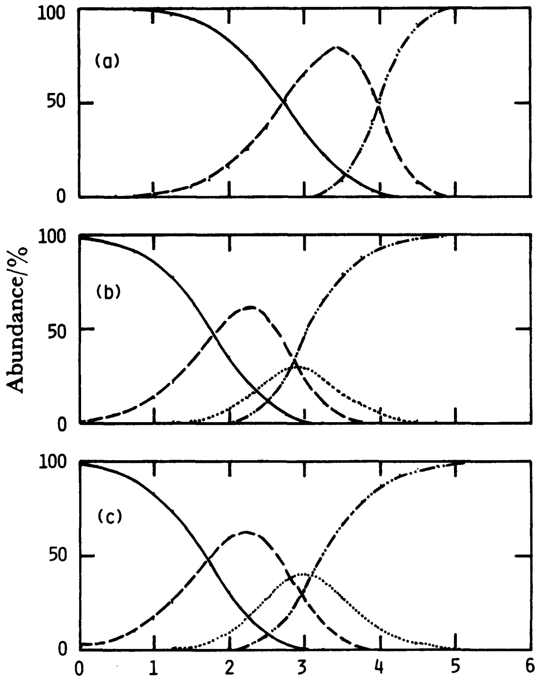

Fig. 6. The abundance of the hydrolyzed chemical species of bismuth(III) in (a) 1.0 M (H, Na)Cl, (b) 1.0 M (H, Na)ClO_4,[13] and (c) 1.0 M (H, Na)NO_3 solutions.[13] (——), (– – – –), (······), and (—·· —) indicate unhydrolyzed, monohydroxide, dihydroxide, and trihydroxide species, respectively.

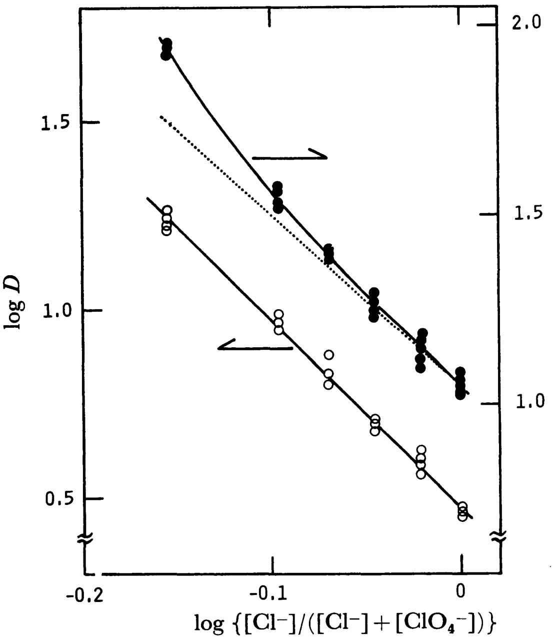

Fig. 7. The dependence of the distribution ratio of bismuth on the chloride ion concentration in 1.0 M (H, Na)(Cl, ClO_4) solutions. ○; $-\log[H^+]=1.21$, $[H_2dz]_{org}=2.6\times10^{-3}$ M, the solid line represents a slope of −5.07. ●; $-\log[H^+]=3.8$, $[H_2dz]_{org}=2.6\times10^{-5}$ M, the dotted line represents a slope of −4.60.

the values were calculated from the inclination of the curve, as is shown in Fig. 9(b), and the total number of ligands (the sum of the chloride and hydroxide ions calculated from the hydrolysis constants) exceeds 6. The reasonable value has to be determined by the method shown in Fig. 9(a) or Fig. 7 (upper line).

The two-dot chain line in Fig. 8 represents a variation in the average number of chloro ligands attached to a bismuth atom, calculated from this relation: (5 minus the average number of hydroxide ligands, as estimated from the hydrolysis constants), by assuming 5 for the coordination number of bismuth (octahedral). In this case, Eqs. 1, 2, 6, and 7 have to be rewritten by using 5 for the coordination number of bismuth, but the original equations remain practically valid to obtain the hydrolysis constants of bismuth. On the other hand, the dash-dotted line was calculated by assuming 6 for the coordination number of bismuth (pentagonal bipyramid), in a way similar to that used for the two-dot chain line. We can assume that the dash-dotted line probably suggests true values at $4 \leq -\log[H^+] < 6$, because the experimental value at $-\log[H^+]=3.8$ is close to the dash-dotted line, while the two-dot chain line is consistent with the experimental results in the region of $-\log[H^+] \leq 1.2$. Moreover, the experimental results in the region of $1.2 < -\log[H^+] < 3.8$ are not consistent with either of the two lines.

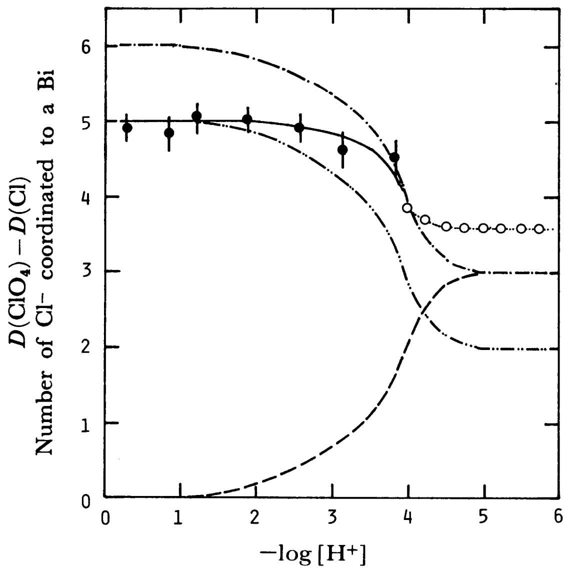

Fig. 8. The number of chloride ions coordinated to a bismuth atom in 1.0 M (H, Na)Cl solutions. ●; experimental values, ○; estimated values from $\{(\log D - 3\log[H_2dz]_{org})_{ClO_4}$[13] $- (\log D - 3\log[H_2dz]_{org})_{Cl}\}$, and (—·—) and (—··—) indicate the values estimated from both formulas; (6 or 5 − average number of hydroxide combined to a bismuth atom in 1.0 M (H, Na)Cl), respectively. (----) represents the variation of average number of hydroxide attached to a bismuth atom in 1.0 M (H, Na)Cl.

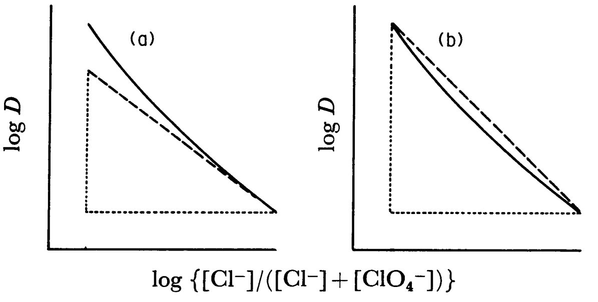

Fig. 9. Estimation of average number of chloride ions attached to a bismuth atom. Tangential broken lines indicate a ture value in (a) and an overestimated value in (b).

We are able to make two assumptions on the basis of the above discussion: that the coordination number of bismuth varies from 5 to 6 with a decrease in the hydrogen-ion concentration in 1.0 M (H,Na)Cl, and that the coordination number holds at 6 in all regions of 1.0 M (H,Na)Cl. Unfortunately, we could not determine directly with any experiments on a trace scale of bismuth which assumption should be adopted. Ahrland et al.,[15] Miranov et al.,[16] and Johansson[17] have obtained formation constants for chloro complexes of bismuth (larger concentrations) in 2, 3, and 4 M chloride solutions respectively. Their results revealed the existence of $[BiCl_6]^{3-}$; that is, those results indicated one of the structures of the pentagonal bipyramid by the sp^3d^3 hybridization with a lone pair of electrons. In our results, moreover, the extracted species of bismuth is $[Bi(Hdz)_3]$, as can be seen from Fig. 4. Therefore, it is reasonable to assume 6 for the coordination number of bismuth throughout the pH region of 1.0 M (H,Na)Cl. Accordingly, in our results at $-\log[H^+] < 3.8$, it is necessary to take into account the coordination of water molecules to a

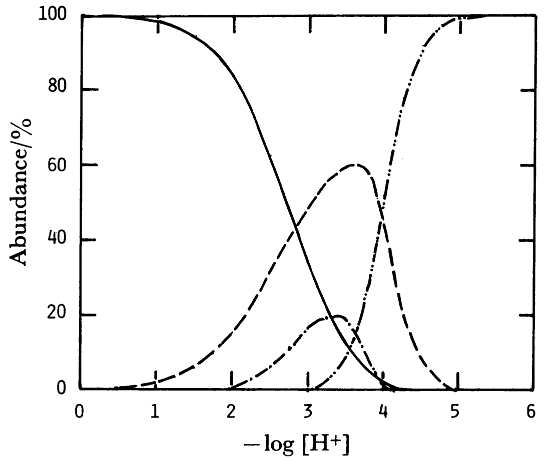

Fig. 10. The abundance of chemical species of Bi(III) in 1.0 M (H, Na)Cl solutions. (——); $[BiCl_5(H_2O)]^{2-}$ (----); $[BiCl_5(OH)]^{3-}$, (—·—); $[BiCl_4(OH)(H_2O)]^{2-}$, (—··—); $[BiCl_3(OH)_3]^{3-}$.

bismuth atom. Hereafter, we will consider the bismuth species in some detail by assuming a pentagonal bipyramid structure.

The average number of chloride ions attached to a bismuth atom in 1.0 M (H,Na)Cl was estimated from a smooth curve combined by the least-squares fit for both the experimental values and the dash-dotted line ($-\log[H^+]\geq 4$) in Fig. 8. In addition, it has been assumed that the only chloride numbers were 3, 4, and 5; that is, 0, 1, 2, and 6 were negligibly low abundances. Consequently, the number of H_2O molecules attached to a bismuth atom was found to be 0 or 1. The average number of hydroxide ions was calculated from the hydrolysis constants, where the second hydrolysis products were neglected because of their very low abundance. Based on the assumptions described above, the following bismuth species can probably be concluded to exist: $[BiCl_5(H_2O)]^{2-}$, $[BiCl_5(OH)]^{3-}$, $[BiCl_4(OH)(H_2O)]^{2-}$, and $[BiCl_3(OH)_3]^{3-}$. In addition, the percentage abundances of the each species were calculated to be as is shown in Fig. 10. The $[BiCl_5(H_2O)]^{2-}$ is present as the main species in a high acidity, while the abundance of $[BiCl_5(OH)]^{3-}$ increases with an increase in $-\log[H^+]$ up to 3.5 and then decreases in the region of further lower acidity. The $[BiCl_4(OH)(H_2O)]^{2-}$ exists in the region of $2\leq -\log[H^+]\leq 4$. Furthermore, the lower the acidity, the higher the abundance of $[BiCl_3(OH)_3]^{3-}$ in an acidity lower than $-\log[H^+]=3$; its abundance may be nearly 100% at $-\log[H^+]>5$ if our assumption is valid. The abundances of $[BiCl_5(OH)]^{3-}$, $[BiCl_4(OH)(H_2O)]^{2-}$, and $[BiCl_3(OH)_3]^{3-}$ contain some uncertainty at $3.5<-\log[H^+]<4.2$, because the average number of chloride ions attached to a bismuth atom can not be determined exactly.

From the above discussion, it is thought that the abnormal variation in hydrolysis constants is mainly dependent on the effects of ΔH° and/or ΔS°, which arise from a competition with the chloro ligand; the hydrolysis constants observed are conditional ones.

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