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Solvent Extraction Study on the Hydrolysis of Tracer Concentrations of Bismuth(III) in Perchlorate and Nitrate Solutions

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The backward solvent extraction with dithizone-carbon tetrachloride solutions was used to examine the chemical species of Bi(III). A tracer concentration of Bi(III) ($<10^{-7}$ mol dm^{-3}) was found to exist in the form of Bi^{3+}, $Bi(OH)^{2+}$, $Bi(OH)_2^+$, and $Bi(OH)_3$ in 1.0 mol dm^{-3} (H,Na)ClO$_4$, and $Bi(NO_3)_n^{3-n}$, $Bi(OH)(NO_3)_n^{2-n}$, $Bi(OH)_2(NO_3)_n^{1-n}$, and $Bi(OH)_3(NO_3)_n^{n-}$ in 1.0 mol dm^{-3} (H,Na)NO$_3$ solutions depending on the acidity of the solutions. The constants of successive hydrolysis, β_1, β_2, and β_3, were calculated by using the distribution data. The resulting log β_1, log β_2, and log β_3 values were 12.0, 22.9, and 33.9 for 1.0 mol dm^{-3} (H,Na)ClO$_4$ solution, and 11.9, 22.7, and 33.2 for 1.0 mol dm^{-3} (H,Na)NO$_3$ solution, respectively. The chemical composition of the extracted species was most probably $Bi(HDz)_3$.

The hydrolysis of Bi(III) in solution has been extensively studied. The most significant early work on the identification of the polynuclear species formed as a result of hydrolysis of Bi(III) was the potentiometric study of Graner and Sillén.1) The hydrolysis of Bi(III) was further studied by the absorption spectrophotometry,2) the ultracentrifugation,3) the potentiometry,4) the light scattering measurements,5) the X-ray diffraction,6) the vibration spectrum,7) the relaxation techniques,8) and the spectrophotometric measurements.9) These studies dealt with the polynuclear species of Bi(III) in regions of macro amounts of bismuth (10^{-4}—0.5 M; 1 M = 1 mol dm^{-3}). On the other hand, Bidleman10) studied the mononuclear species formed in minor concentrations of Bi(III) ($<10^{-4}$ M), based on the solvent extraction using dithizone (H_2Dz). In his work, the equilibrium constants for the Bi–H_2Dz system and the formation constants for the species $Bi(OH)^{2+}$, $Bi(OH)_3$, and $Bi(OH)_4^-$ have been determined. However, the hydrolysis of bismuth ion in more dilute aqueous solution and the formation constants of the species $Bi(OH)_2^+$ has not been well studied. Because the Bi–H_2Dz system has been well defined by many authors,11–15) we studied on the hydrolysis of bismuth ion in a tracer concentration of $<10^{-7}$ M by using the backward extraction method,16) by means of which the difficulties due to the anomalous chemical behavior of a tracer scale of substances could be avoided.

Experimental

Reagents. Water and reagents used were all purified to the highest degree, especially to overcome the difficulty due to contaminations. All the aqueous solutions used were finally purified by extraction with H_2Dz–CCl_4 solution. The H_2Dz–CCl_4 solution was prepared according to the method recommended by Sandell.17) The concentration of H_2Dz–CCl_4 solutions purified was determined by the complexometric titration using a standard $AgNO_3$ solution. 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 into the appropriate concentration with 3 M HNO_3. A ^{210}Bi tracer solution was prepared by milking to extract from the diluted ^{210}Pb–^{210}Bi solution (pH<3) with H_2Dz–CCl_4 solution. Bismuth nitrate was employed as a carrier of ^{210}Bi tracer.

Initial Organic Solution of Bismuth Dithizonate. A portion of bismuth stock solution was pipetted into a separatory funnel containing water and the bismuth was extracted with a definite concentration of H_2Dz solution at $2<pH<3$. The stock solution thus prepared in a lower concentration, less than 10^{-5} M of H_2Dz, showed practically no change within 3 h after preparation against any possible decomposition of H_2Dz.

Measurements of Radioactivity. The radioactivity (β-rays) of ^{210}Bi was counted with a G.M. counter (Aloka Co., Ltd.), with an Al foil absorber (1.84 mg/cm^2) put on the sample planchet in which the bismuth extract was evaporated, by which the α-activity due to ^{210}Po contained in the bismuth extracts could be discriminated. The decay of ^{210}Bi activity ($t_{1/2}=5.01$ d) was compensated for by obtaining the activity relative to a standard specimen prepared at the same time.

Measurements of the Distribution Ratio. One ml (1 ml = 1 cm^3) of the organic phase containing a definite amount of bismuth was mixed with 10 ml of 1.0 M (H,Na)ClO$_4$ or 1.0 M (H,Na)NO$_3$ solution; 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}). 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 using $A_{aq}=A^0_{org}-A_{org}$, where A_{aq} is the activity of a 5 ml portion of the aqueous phase and A^0_{org} is the initial activity of a 0.5 ml portion of the organic phase before shaking. The distribution ratio of bismuth, D, is given as follows;

$$D = 10\times A_{org}/(A^0_{org}-A_{org}).$$

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

Measurements of Hydrogen Ion Concentration. As for acidic media (pH<1), the hydrogen ion concentration was calculated from the acidity of the $HClO_4$ or HNO_3 used. In other cases, it was measured with a pH meter (TŌA Electronics Ltd.) at room temperature as soon as possible after shaking.

Results and Discussion

Time Necessary for the Partition Equilibrium. As shown in Fig. 1, the partition of bismuth between

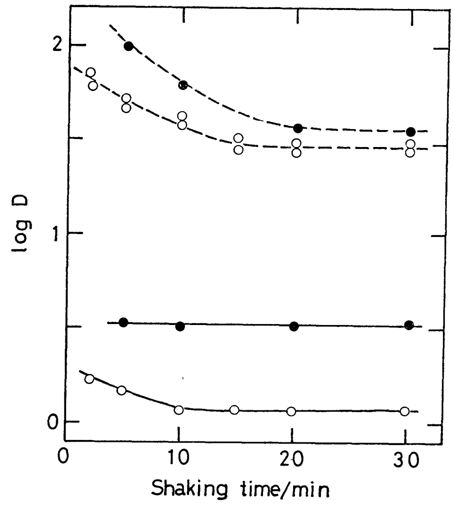

Fig. 1. The effect of shaking time on the distribution ratio in the backward extraction.
—●—: 1.0 M $HClO_4$ solution, $\log[H_2Dz]_{org}=-3.64$, --●--: 1.0 M $(H,Na)ClO_4$ solution ($-\log[H^+]=3.80$), $\log[H_2Dz]_{org}=-5.77$, —○—: 1.0 M HNO_3 solution, $\log[H_2Dz]_{org}=-3.40$, --○--: 1.0 M $(H,Na)NO_3$ solution ($-\log[H^+]=3.46$), $\log[H_2Dz]_{org}=-5.51$.

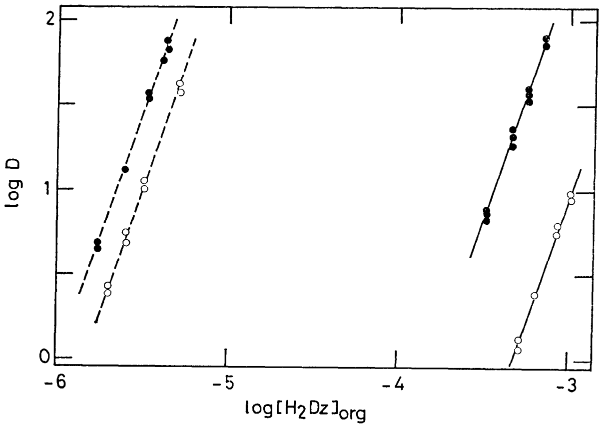

Fig. 2. The dependence of the distribution ratio on the concentration of dithizone in the organic phase.
—●—: 1.0 M $HClO_4$ solution, --●--: 1.0 M $(H,Na)ClO_4$ solution ($-\log[H^+]=2.53$), —○—: 1.0 M HNO_3 solution, --○--: 1.0 M $(H,Na)NO_3$ solution ($-\log[H^+]=3.01$).

two phases reaches equilibrium within 10 minutes for a high acidity (1.0 M $HClO_4$ and 1.0 M HNO_3) and in about 20 min for a weak acidity (1.0 M $(H,Na)ClO_4$, $-\log[H^+]=3.80$; 1.0 M $(H,Na)NO_3$, $-\log[H^+]=3.46$). Accordingly, the partition system was shaken for 25 min in all experiments to attain the equilibrium.

Dependence of the Distribution Ratio on the Bismuth Concentration. Table 1 shows the distribution ratios measured as a function of the amount of bismuth carrier in the tracer concentration ($<10^{-7}$ M). The bismuth concentration of the original tracer solution prepared in a carrier-free state was examined substoichiometrically with dithizone extraction. No effects of the bismuth concentration were observed for either 1.0 M $HClO_4$ media or 1.0 M $(H,Na)ClO_4$ solutions of $-\log[H^+]=3.84$, nor for either 1.0 M HNO_3 or 1.0 M $(H,Na)NO_3$ solutions of $-\log[H^+]=3.46$. 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, since it is improbable that any polymerized species remain stable in both phases, we may safely assume that the monomers are the main species involved in the solvent extraction of tracer concentrations of bismuth.

Dependence of the Distribution Ratio on the Dithizone Concentration in Organic Phase. The distribution ratio, D, was plotted as a function of the H_2Dz concentration at different hydrogen ion concentrations. Figure 2 shows that the plots of $\log D$ *vs.* $\log[H_2Dz]_{org}$ show a slope of +3 independent of the acidity and the media, where H_2Dz denotes a neutral dithizone molecule. 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 dithizone ions (HDz^-) attached to a bismuth atom between the organic and aqueous phases. It is generally accepted that the coordination number of Bi(III) is six, so the total number of ligands (as univalent) combined to a bismuth atom can be reasonably assumed not to exceed six, and the extracted species must be electrically neutral. Since HDz^- ion is a bidentate ligand, our results shown in Fig. 2 lead to the conclusion that bismuth exists in the chemical form of $Bi(HDz)_3$ in the organic phase. It also means that the concentration of $Bi\text{–}HDz^-$ complex species is negligibly low in the aqueous phase of 1.0 M $(H,Na)ClO_4$ and 1.0 M $(H,Na)NO_3$.

The distribution ratio, D, is expressed as follows:

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

$$=\{K_3[H_2Dz]^3{}_{org}[H^+]^{-3}\}/\{\sum_{n=0}^{6-x}\sum_{x=0}^{6-n}\beta_{n,x}Q_w{}^n[H^+]^{-n}\times[X^-]^x\}, \tag{2}$$

where

$$K_3=[Bi(HDz)_3]_{org}/\{[Bi^{3+}][H_2Dz]^3{}_{org}[H^+]^{-3}\}, \tag{3}$$

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

$Q_w=[H^+][OH^-]$, and also X^- denotes ClO_4^- or NO_3^-.

D should be written in terms of the hydrolysis of bismuth in case of $[X^-]=1.0$ M, as follows:

$$D/[H_2Dz]^3{}_{org}=K_3/(\sum_{n=0}^{6-x}\sum_{n=0}^{6-n}\beta_{n,x}Q_w{}^n[H^+]^{3-n}). \tag{5}$$

In the present case, $\sum_{n=0}^{6-x}\sum_{n=0}^{6-n}\beta_{n,x}$ is denoted by $\sum_{n=0}^{6}\beta_n$, because each $\beta_{n,x}$ can not be measured and the $\sum_{x=0}^{6}\beta_{0,x}$ is regarded as unity. Accordingly, Eq. 5 should be rewritten as follows:

$$D/[H_2Dz]^3{}_{org}=K_3/(\sum_{n\ 0}^{6}\beta_nQ_w{}^n[H^+]^{3-n}). \tag{6}$$

Dependence of the Distribution Ratio on the Hydrogen Ion Concentration. In Fig. 3, we plot $\log(D/[H_2Dz]^3{}_{org})$ as a function of $-\log[H^+]$ in 1.0 M

TABLE 1. THE DEPENDENCE OF THE DISTRIBUTION RATIO ON THE BISMUTH CONCENTRATION

Aqueous phase	$-\log[H^+]$	$[H_2Dz]_{org}/M$	$[Bi(III)]_{org}{}^{a)}/M$	$\log D$
1.0 M $(H, Na)ClO_4$	0.0	3.98×10^{-4}	Carrier free($<10^{-9}$)	1.15 ± 0.11
			0.92×10^{-9}	1.18 ± 0.09
			0.92×10^{-7}	1.22 ± 0.15
	3.84	2.06×10^{-6}	Carrier free($<10^{-9}$)	1.75 ± 0.05
			0.84×10^{-9}	1.76 ± 0.15
			0.84×10^{-7}	1.78 ± 0.11
1.0 M $(H, Na)NO_3$	0.0	5.08×10^{-4}	Carrier free($<10^{-9}$)	0.45 ± 0.15
			0.84×10^{-9}	0.44 ± 0.12
			0.84×10^{-7}	0.40 ± 0.12
	3.46	3.40×10^{-6}	Carrier free($<10^{-9}$)	1.60 ± 0.15
			0.84×10^{-9}	1.59 ± 0.09
			0.84×10^{-7}	1.62 ± 0.10

a) Initial concentration of Bi(III) in H_2Dz-CCl_4 solution.

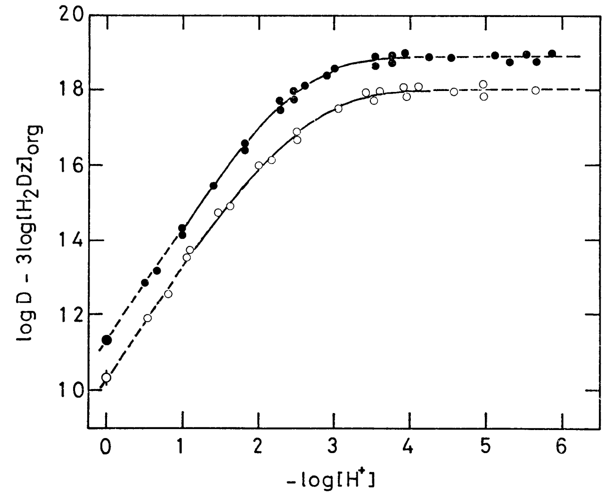

Fig. 3. The dependence of the distribution ratio on the hydrogen ion concentration.
●: 1.0 M (H,Na)ClO_4 solution, ○: 1.0 M (H,Na)NO_3 solution.

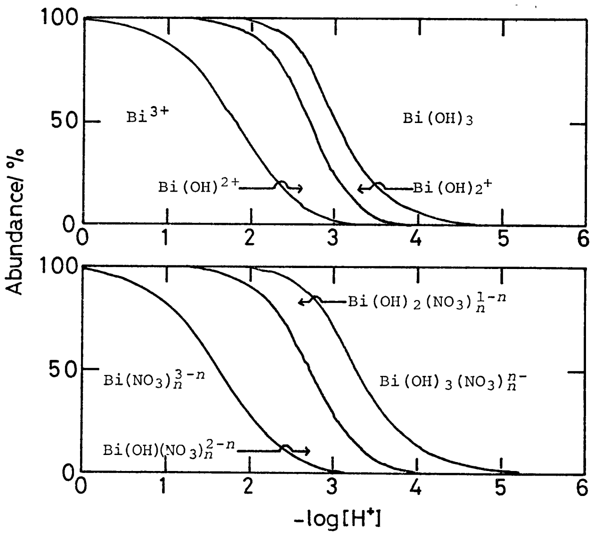

Fig. 4. The chemical species of the bismuth ion in 1.0 M (H,Na)ClO_4 solution (upper) and 1.0 M (H,Na)NO_3 solution (lower).

(H,Na)ClO_4 and 1.0 M (H,Na)NO_3 solutions. Since it is difficult to determine the distribution ratio by using only a single H_2Dz solution with a definite concentration in all regions of hydrogen ion concentration, $\log(D/[H_2Dz]^3_{org})$ is plotted instead of $\log D$. As shown in the figure, the slope seems to be $+3$ for the region of $-\log[H^+]<1.5$ in both 1.0 M (H,Na)ClO_4 and 1.0 M (H,Na)NO_3 solutions, while it is 0 for $-\log[H^+]=4.0$—5.7. Therefore, there exist few hydroxo-compounds of Bi(III) in high acidity, while hydroxo-compounds such as $Bi(OH)_3X_x$ are predominant in the weakly acidic to neutral solutions. The distribution ratio in Eq. 6 can be expressed in terms of hydrolysis constants β_n as follows:

$$D/[H_2Dz]^3_{org} = K_3/([H^+]^3+\beta_1Q_w[H^+]^2 + \beta_2Q_w{}^2[H^+]+\beta_3Q_w{}^3), \quad (7)$$

where

$$\beta_1 = [Bi(OH)X_x{}^{2-x}]/([Bi^{3+}][OH^-][X^-]^x), \quad (8)$$

$$\beta_2 = Bi(OH)_2X_x{}^{1-x}]/([Bi^{3+}][OH^-]^2[X^-]^x), \quad (9)$$

$$\beta_3 = [Bi(OH)_3X_x{}^{x-}]/([Bi^{3+}][OH^-]^3[X^-]^x). \quad (10)$$

Estimation of K_3, $\beta_3Q_w{}^3$, $\beta_2Q_w{}^2$, and β_1Q_w. Figure 3 shows that the slope of $(\log D-3\log[H_2Dz]_{org})$ *vs.* $-\log[H^+]$ at $-\log[H^+]=0$ is nearly 3, so Eq. 7 can be simplified as $D/[H_2Dz]^3{}_{org}\approx K_3$. Consequently, the approximate values of K_3 were obtained from Figs. 1 and 3 and Table 1 to be $K_3=(2.40\pm0.33)\times10^{11}$ for 1.0 M (H,Na)ClO_4 solution and $K_3=(2.34\pm0.60)\times10^{11}$ for 1.0 M (H,Na)NO_3 solution. Furthermore, since Fig. 3 shows that the slope of $(\log D-3\log[H_2Dz]_{org})$ *vs.* $-\log[H^+]$ $(-\log[H^+]>4)$ is zero, independent of the acidity, Eq. 7 can be simplified as $D/[H_2Dz]^3{}_{org}\approx K_3/(\beta_3Q_w{}^3)$. Consequently, the approximate value of $\beta_3Q_w{}^3$ was obtained from Fig. 3 to be $\beta_3Q_w{}^3=(3.02\pm1.01)\times10^{-8}$ for 1.0 M (H,Na)ClO_4 solution and $\beta_3Q_w{}^3=(2.24\pm0.86)\times10^{-8}$ for 1.0 M (H,Na)NO_3 solution. By using the set of K_3 and $\beta_3Q_w{}^3$ obtained, the approximate values of a set of β_1Q_w and $\beta_2Q_w{}^2$ were obtained by least squares fit from the data in the region of $-\log[H^+]=1.5$—4 in Fig. 3; the values are $\beta_1Q_w=1.44\times10^{-2}$ and $\beta_2Q_w{}^2=1.81\times10^{-5}$ for 1.0 M (H,Na)ClO_4 solution, and also $\beta_1Q_w=2.13\times10^{-2}$ and $\beta_2Q_w{}^2=3.09\times10^{-5}$

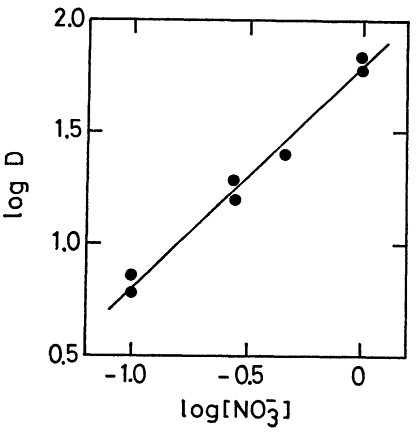

Fig. 5. The influence of the concentration of the nitrate ion on the distribution ratio at $-\log[H^+]=1.0$ ($\log[H_2Dz]_{org}=-3.87$).

for 1.0 M (H,Na)NO_3 solution, respectively. Equation 7 is third order 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 of $\log \beta_1$, $\log \beta_2$, and $\log \beta_3$ are 12.0, 22.9, and 33.9 for 1.0 M (H,Na)ClO_4, when $\log Q_w$ is -13.80,[18] and 11.9, 22.7, and 33.2 for 1.0 M (H,Na)NO_3 solutions, when $\log Q_w$ is -13.61.[19] Per cent abundances of the chemical species of bismuth calculated from each β value at different hydrogen ion concentrations in 1.0 M (H,Na)ClO_4 and 1.0 M (H,Na)NO_3 solutions are represented in Fig. 4. In the latter case, because of possible coordination of nitrate ions to the bismuth atom in 1.0 M (H,Na)NO_3 solution, we have taken into consideration the contribution of nitrate ions to the bismuth species.

The Effect of Nitrate and Perchlorate Ion Concentration on the Distribution Ratio. The extractability of bismuth increased with an increasing nitrate ion concentration; this might be attributed to a salting-out effect of $NaNO_3$ as an electrolyte. Kapantsyan and Nabivanets[20] reported on the nitrate complexes of bismuth in the solution. Bismuth nitrate complexes may be present in 1.0 M (H,Na)NO_3 solution, because the values of $\log(D/[H_2Dz]^3_{org})$ for 1.0 M (H,Na)NO_3 solution are always smaller than those for the corresponding 1.0 M (H,Na)ClO_4 solution in all regions of $0 \leq -\log[H^+] \leq 5.7$, as shown in Fig. 3. This also implies that some effect opposing the bismuth extraction arises from the complexation of bismuth with the nitrate ion. Consequently, each β value obtained for 1.0 M (H,Na)NO_3 solution should be considered as conditional constants obtained under our experimental conditions. The effect of perchlorate ion concentration on the distribution ratio of Bi(III) was examined in the concentration of 0.1—1.0 M at $-\log[H^+]=1.0$, where little effect was observed in the concentration range of ClO_4^- examined. It is difficult to assume the presence of bismuth perchlorate complexes on a tracer scale in 1.0 M (H,Na)ClO_4 solution because of the less-complexing perchlorate ion, but in the macro region the formation of $Bi_6(OH)_{12}(ClO_4)_2^{4+}$ was reported by Johnson *et al.*[21] It can be said, nevertheless, that the effect of perchlorate ion concentration in the present study may be negligibly small, since the ionic concentration in the aqueous phase was kept constant to 1.0 M in all experiments.

Graner and Sillén[1] reported that Bi(III) was unhydrolyzed at acid concentrations greater than 0.5 M, and that the number of hydroxides bound per bismuth atom appeared to approach asymptotically the value 2 in titration experiments on 0.01, 0.025, and 0.05 M Bi(III) in 3 M $NaClO_4$ solutions. They proposed a species of polymeric hydrolysis products with the general formula $Bi_nO_{n-1}^{n+2}$ to account for their observations. Olin[4] extended the measurements to a broader range of Bi(III) concentrations, 10^{-4}—0.05 M Bi(III), and his more precise data from an amalgam electrode were analyzed in terms of two species $Bi(OH)^{2+}$ and $Bi_6(OH)_{12}^{6+}$. The mononuclear species was formed only in minor amounts. The vibration spectrum of $Bi_6(OH)_{12}^{6+}$ in very high concentrations of Bi(III) (up to 8.41 M Bi(III) in 8.85 M ClO_4^- solution) was reported by Maroni and Spiro.[7] Bidleman[10] studied the hydrolysis of bismuth ions in dilute ($<10^{-4}$ M) aqueous solution by the extraction measurements using dithizone, and obtained the equilibrium constants for the bismuth–dithizone system and the formation constants of the $Bi(OH)^{2+}$, $Bi(OH)_3$, and $Bi(OH)_4^-$, where the values of $\log \beta_1$, $\log \beta_3$, and $\log \beta_4$ are 12.4, 31.9, and 32.9 (μ(ionic strength)$=0.1$), respectively. In tracer concentrations of bismuth in 1.0 M (H,Na)ClO_4 and 1.0 M (H,Na)NO_3 solutions in the region of $0 \leq -\log[H^+] \leq 5.7$, our results showed the presence of Bi^{3+}, $Bi(OH)^{2+}$, $Bi(OH)_2^+$, and $Bi(OH)_3$, and/or $Bi(NO_3)_n^{3-n}$, $Bi(OH)(NO_3)_n^{2-n}$, $Bi(OH)_2(NO_3)_n^{1-n}$, and $Bi(OH)_3(NO_3)_n^{n-}$. For this latter group a further study on the mean charge of each species should be made. At the same time, no evidence for the existence of any polymerized species was found in the present conditions of aqueous media. However, in the stored and/or more concentrated bismuth solution, some polymerized species may be formed.

The value of $\log K_3$ (11.4) for 1.0 M (H,Na)ClO_4 found in this work is larger than those reported by Bidleman (10.9 at $\mu=0.1$ and 10.8 at $\mu=1.0$),[10] Busev and Bazhanova (10.0 at $\mu=0.2$),[14] Koroleff (9.7),[12] and Pilipenko (10.6 at $\mu=0.5$).[13] This fact may suggest that the formation of extracted species ($Bi(HDz)_3$) is depressed by forming polynuclear complexes in macro concentrations of bismuth solution. Another reason why the value of $\log K_3$ (10.4) for 1.0 M (H,Na)NO_3 is smaller than that for 1.0 M (H,Na)ClO_4 solution may be complex-formation with nitrate ion.

References

1) F. Graner and L. G. Sillén, *Acta Chem. Scand.*, **1**, 631 (1947).

2) P. Souchay and D. Peschanski, *Bull. Soc. Chim. Fr.*, **1948**, 439.

3) R. W. Holmberg, K. A. Kraus, and J. S. Johnson, *J. Am. Chem. Soc.*, **78**, 5506 (1956).

4) A. Olin, *Acta Chem. Scand.*, **11**, 1445 (1957).

5) R. S. Tobias and S. Y. Tyree, Jr., *J. Am. Chem. Soc.*,

82, 3244 (1960).

6) H. A. Levy, M. D. Danfold, and P. A. Agron, *J. Chem. Phys.*, **31**, 1458 (1959).

7) V. A. Maroni and T. G. Spiro, *J. Am. Chem. Soc.*, **88**, 1410 (1966).

8) V. Frei, G. Mages, and H. Wendt, *Ber. Bunsenges. Phys. Chem.*, **77**(**4**), 243 (1973).

9) C. Dragulescu, A. Nimaro, and I. Julean, *Rev. Roum. Chim.*, **7**, 1181 (1972).

10) T. F. Bidleman, *Anal. Chim. Acta*, **56**, 221 (1971).

11) J. Reith and C. Van Dijk, *Chem. Weekblad*, **36**, 343 (1939).

12) F. Koroleff, Thesis, Univ. of Helsingfors, Helsinki, Finland, 1950.

13) A. Pilipenko, *Zh. Anal, Khim.*, **8**, 256 (1963).

14) A. Busev and L. Bazhanova, *Russ. J. Inorg. Chem.*, **6**, 1128 (1961).

15) T. Ashizawa, K. Nagasawa, and K. Haruyama, *Bunseki Kagaku*, **13**, 1011 (1964).

16) I. Hataye, H. Suganuma, M. Sakata, and Y. Nagame, *J. Inorg. Nucl. Chem.*, **43**, 2101 (1981).

17) E. B. Sandell, "Colorimetric Determination of Traces of Metals," Interscience, New York (1964), p. 170.

18) F. Fischer and J. Byé, *Bull. Soc. Chim. Fr.*, **1964**, 2970.

19) V. P. Vasilév and G. A. Lovanov, *Zh. Fiz. Khim.*, **41**, 838 (1967).

20) E. E. Kapantsyan and B. I. Nabivanets, *Ukr. Khim. Zh.*, **33**, 961 (1967).

21) J. S. Johnson, G. Scatchard, and K. A. Kraus, *J. Phys. Chem.*, **63**, 787 (1959).