

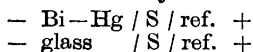
Studies on the Hydrolysis of Metal Ions

23. The Hydrolysis of the Ion $\text{Bi}_6(\text{OH})_{12}^{6+}$ in Perchlorate Medium

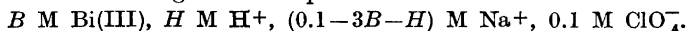
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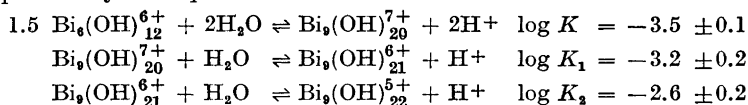
The hydrolysis of the ion $\text{Bi}_6(\text{OH})_{12}^{6+}$ has been studied at 25°C in 0.1 M sodium perchlorate medium by means of the cells



where S had the general composition



The small solubility of the hydrolysis products necessitated the low concentration of the neutral salt. To keep the activity factors constant, the total metal ion concentration had to be diminished accordingly. *B* was varied between 4 and 0.5 mM. The data may be explained by the equilibria



The hydrolysis of Bi(III) in perchlorate medium can, for ease in description, be arbitrarily divided into two parts. The first part may be called the hydrolysis of the bismuth ion (Bi^{3+}) and the second part the hydrolysis of the $\text{Bi}_6(\text{OH})_{12}^{6+}$ ion.

The hydrolysis of the bismuth ion has been studied a number of times^{1,2}. The explanations of the experimental data, though divergent in details, give as main hydrolysis products polynuclear complexes with the ratio Bi:O equal or close to one. Recent studies^{2,2a} strongly indicate $\text{Bi}_6(\text{OH})_{12}^{6+}$ (or $\text{Bi}_6\text{O}_6^{6+}$ etc.) as the predominating species.

Holmqvist³ found that solutions of the analytical composition BiOClO_4 are acid, which shows that the hydrolysis proceeds beyond the "bismuthyl" stage. He suggested the formation of the complex $\text{Bi}_2(\text{OH})_5^+$. In 1954 Faucher⁴ published $\log h$ measurements on bismuth perchlorate solutions which had a composition varying between BiOClO_4 and $\text{Bi}_2(\text{OH})_5\text{ClO}_4$. From the

measurements he concluded that the complex $\text{Bi}_6(\text{OH})_{20}^{4+}$ is formed in this region. Faucherre states, however, that the result is quite uncertain. The present investigation is an extension to lower $\log h$ values of a previous study by the present author² on the hydrolysis of bismuth perchlorate solutions using electrometric methods.

Some of the symbols frequently encountered in the text are defined below:

B	total bismuth(III) concentration
b	concentration of Bi^{3+}
C	total bismuth(III) concentration, calculated as $\text{Bi}_6(\text{OH})_{12}^{6+}$; $C = B/6$
c	concentration of $\text{Bi}_6(\text{OH})_{12}^{6+}$
H	analytical hydrogen ion concentration
h	actual hydrogen ion concentration
Z	average number of hydrogen ions split off by one Bi^{3+}
Z'	average number of hydrogen ions split off by one $\text{Bi}_6(\text{OH})_{12}^{6+}$. $Z' = 6(Z-2)$
$\eta =$	$\log B/b$
$\eta' =$	$\eta +$ (unknown) constant defined by eqn. (7)
$\delta =$	concentration of basic impurity in NaClO_4
$\kappa_{P,Q}$	formation constant for $\text{Bi}_Q(\text{OH})_P$ from $\text{Bi}_6(\text{OH})_{12}^{6+}$ and H_2O
$y(x)_v$	y as a function of x at constant v

Other symbols used are defined when they first appear. All concentrations in the tables and figures are expressed in M (mole/l) and equilibrium constants are given on the M scale. In the text, however, the more convenient unit mM will be used frequently.

Method of investigation and choice of experimental conditions

The hydrogen ion concentration and the variation of free $[\text{Bi}^{3+}]$ with $\log h$ have been measured electrometrically for a large number of bismuth perchlorate solutions at equilibrium. As usual the measurements were carried out as potentiometric titrations keeping the total bismuth concentration constant in each run and varying $\log h$ by adding acid or base.

Because of the fairly low solubility¹¹ (ca. 25 mmoles/l) of the salt described as $\text{Bi}_2(\text{OH})_3\text{OClO}_4$ it was found necessary to use a total ClO_4^- concentration as low as 0.1 M in order to keep the bismuth in solution in the $\log h$ range between -3 and -5 . To minimize variations in the activity factors, the metal ion concentration has to be diminished accordingly. In 3 M $(\text{Na})\text{ClO}_4$ it appears possible to use solutions containing at least 0.1 M of the metal ion investigated without causing serious variations in the activity factors; since little is known about these factors in solutions of low neutral salt concentration, the highest bismuth(III) concentration was now chosen by proportionality as 4 mM. In this way one is likely to be on the safe side⁵.

The solutions measured had the general composition

$$[\text{Bi(III)}] = B \text{ M}; [\text{H}^+] = H \text{ M}; [\text{Na}^+] = (0.1 - 3B - H) \text{ M}; [\text{ClO}_4^-] = 0.1 \text{ M}$$

where B denotes the total bismuth(III) concentration, and H the analytical hydrogen ion concentration defined by

$$H = [\text{ClO}_4^-] - 3B$$

In the present study H is always a negative number.

The following cells were used to measure the hydrogen ion concentration, h , and unhydrolysed Bi^{3+} , b .

$$- \text{glass} / \text{H}^+ / \text{ref} + \quad (\text{I})$$

$$E_g = E_g^\circ - 59.15 \log h - E_j \quad (\text{I})$$

$$- \text{Bi-Hg} / \text{Bi}^{3+} / \text{ref} + \quad (\text{II})$$

$$E_{\text{am}} = E_{\text{am}}^\circ - 19.72 \log b - E_j \quad (\text{2})$$

As reference half-cell

$$0.1 \text{ M NaClO}_4 / 0.1 \text{ M ClO}_4^-, 0.095 \text{ M Na}^+, 0.005 \text{ M Ag}^+ / \text{AgCl}, \text{Ag} \quad (\text{III})$$

was used, and the salt bridge was of the "Wilhelm" type ⁶.

To study the effect of a change in the nature of the neutral salt a few titrations were carried out in 0.1 M (Ba)ClO₄. In addition the direction of titration was reversed and Ba(OH)₂ was added to an acid solution. The use of this base ensures the absence of interfering carbonate. In general, acid was added to a hydrolysed solution. The experiments were carried out at 25°C.

Determination of the liquid junction potential in 0.1 M NaClO₄ and free acid or base in neutral salt solutions

The liquid junction potential in 0.1 M (Na)ClO₄ was determined between 0 and 15 mM $\frac{1}{2}$ H⁺ by means of the cell

$$\text{Ag}, \text{AgCl} / 0.005 \text{ M Ag}^+, H \text{ M H}^+, (0.095 - H) \text{ M Na}^+, 0.1 \text{ ClO}_4^- / \text{ref.} \quad (\text{IV})$$

$$E = E^\circ - 59.15 \log[\text{Ag}^+] - E_j = E^{\circ'} - E_j \quad (\text{3})$$

since $[\text{Ag}^+]$ was kept constant. The liquid junction potential so defined contains any variation in the activity factors. The procedure to obtain E_j from the measurements has been described by Biedermann and Sillén ⁷. The above-mentioned cell has the advantage, over those containing $\log h$ sensitive electrodes, that small errors in the hydrogen ion concentration do not influence the result at low concentrations. Moreover the extrapolation involved in the determination can be carried out with greater confidence since the extrapolated value ($E^{\circ'}$), *i.e.* the potential of the cell with no acid added, can also be measured as a check.

The results fit the simple Henderson equation ⁸ with

$$E_j = -59.15 \log(1 + 26.7 h) \quad 0 < h < 0.015 \text{ M} \quad (\text{4})$$

The formula reproduces the experimental data to better than 0.05 mV.

When using the cell

$$\log h \text{ sensitive electrode} / h \text{ M H}^+, I - h \text{ M Na}^+, I \text{ M ClO}_4^- / \text{ref.} \quad (\text{V})$$

$$E = E^\circ - 59.15 \log h - E_j \quad (\text{5})$$

to determine E_j , it is often found that the points lying close to the origin ($H' < 3$ mM) are off the straight line $E + 59.15 \log H'$ (H'). This is due to small acidic or basic impurities in the neutral salt, which cause the calculated hydrogen ion concentration, H' , and actual hydrogen ion concentration, h , to be different.

The amount of impurity, $\delta = H' - h$, can be found by the following procedure. Let us assume, to be specific, that we want to know the concentration of small amounts of acid or alkali suspected to be present in a 1 M NaClO₄ solution at 25°C. To a known volume of this solution is added gradually a standardized HClO₄ solution, also containing NaClO₄, to make $[\text{ClO}_4^-] = 1$ M, and the emf of the above cell (V) is measured. $E + 59.15 \log H'$ is then plotted as a function of H' , where H' is the hydrogen ion concentration calculated from the volume of acid added. At higher acidities, where the impurity is small compared to H' , the plot is linear and can be extrapolated to $H' = 0$ to give E° . Once E° is known, h can be found for the first few points. The difference between h and H' for each point is then used to find the concentration of the impurity. It seems possible to determine this impurity to ± 0.01 mM.

The liquid junction potentials determined with the quinhydrone electrode agreed within ± 0.1 mV with those obtained with the silver-silverchloride electrode, which is to be expected if the activity factors stay constant (or change in the same manner with $\log h$), since the basicity of quinone⁹ does not show up if $h < 15$ mM.

MATERIALS AND ANALYSIS

Sodium perchlorate was prepared from recrystallized Na₂CO₃ (Merck p.a.) and HClO₄ (Kebo p.a.). The product was recrystallized once from distilled water. The stock solution of NaClO₄ was analysed by evaporating a known volume to dryness and weighing the residue as NaClO₄. The determination of acidic or basic impurities was made as described above. After a preliminary determination of this impurity, a calculated amount of acid or base was added to make the solution neutral. The final product was reanalysed and found to be neutral to within ± 0.01 mM H⁺ or OH⁻.

Barium perchlorate was prepared from Ba(OH)₂ (Merck p.a.) and HClO₄. The product was recrystallized twice to reduce the chloride content to the order of 10⁻⁶ M in a 0.05 M solution. The stock solution was analysed by evaporating a known volume to dryness and weighing the residue as Ba(ClO₄)₂. Ba(ClO₄)₂ is known to be a very hygroscopic substance, therefore the result was checked by passing known volumes through a cation-exchange resin and titrating with standard base. The two methods gave results identical to 0.1 %.

Perchloric acid solutions were prepared by diluting HClO₄ (Kebo p.a. 70–72 %) and were standardized against KHCO₃.

Barium hydroxide solutions were prepared by dilution of a filtered stock solution of Ba(OH)₂. All solutions containing this base were handled under nitrogen.

Bismuth (III) perchlorate solutions were prepared from Bi₂O₃ and HClO₄. Two stock solutions were made. The first solution, which had the analytical composition BiOClO₄, was prepared from known amounts of the oxide and the acid. As a check it was analysed for bismuth according to Winkler¹⁰ and for perchlorate by cation exchange. Calculated and found values agreed to 0.1 %. The second solution was prepared by dissolving the oxide in hot acid but now choosing the molar proportion Bi₂O₃ : HClO₄ = 1:1.2. On cooling the solution crystals separated. These crystals gave the same X-ray powder photographs as crystals prepared by adding a concentrated NaClO₄ solution to BiOClO₄, or NaOH to mixtures of NaClO₄ and Bi(ClO₄)₃ solutions as described by Holmqvist³ and Prytz and Nagel¹¹. These authors found from the analysis a salt of composition Bi₂(OH)₃OClO₄. In addition to this salt Prytz and Nagel found a yellow salt, which precipitated when a large amount of NaClO₄ was added to a bismuthyl perchlorate solution. Its composition was given as Bi₃(OH)₃O₂(ClO₄)₂. This salt was not obtained in the present investigation.

The crystals were dissolved by adding water. On standing overnight, however, the solution became turbid. After filtration and standing the turbidity developed again. Since no impurities were found in the distilled water used, carbon dioxide from the air was suspected as interfering. This was confirmed by passing in CO₂. The formation of the insoluble carbonate is a slow process, and a pronounced turbidity appears only after one

or two h. The final stock solution was filtered through a bacteria filter (Jena G 5), and some acid added. The solution was analyzed and thereafter stored and handled under nitrogen. When stored under nitrogen the solution remained clear.

The Bi_2O_3 used was obtained by igniting twice recrystallized $\text{Bi}(\text{NO}_3)_3$ (Baker p.a.). *Bismuth amalgam* was prepared and handled as described previously². The bismuth concentration in the amalgam was 0.5 % (weight).

The emf measurements

The log h measurements were made with a Radiometer glass electrode, which had been checked against the quinhydrone electrode in an acetate buffer also containing 0.1 M NaClO_4 . The potential between the two electrodes remained constant throughout the log h range -2 to -6 . Thus the glass electrode behaved as a perfect hydrogen electrode. The bismuth amalgam electrode consisted of a pool on the bottom of the titration vessel.

Since E_{am}° could not be determined we could find only relative concentrations of unhydrolysed bismuth from the potentials. In order to compare titrations made at different times, a certain titration was repeated at regular intervals, and the average potential change (at most 0.4 mV) from the first of these standard titrations, for identical points, was taken as the shift in E_{am}° and used as a correction to the measured E .

All potentials were recorded with a Radiometer valve potentiometer (PHM 3) with the exception of the liquid junction potential measurements, where a Cambridge potentiometer was used.

The equilibria were rapidly attained. No time effects were present. This was established by comparing titrations for the same total bismuth concentration but starting from different analytical hydrogen ion concentrations. The Z and η' curves for the two titrations, in the log h region where they overlapped, were identical within the limits of the experimental error.

The glass electrode measurements showed, between identical titrations, a reproducibility which in general lay within the accuracy of the instrument (± 0.2 mV). The agreement between titrations on solutions made up from the two stock solutions was better than 0.01 Z units in most of the range studied. In the most acidic region, the spread in the glass electrode measurements, however, caused a somewhat larger uncertainty in Z .

The behavior of the amalgam electrode changed remarkably during the titration. As log h decreased the electrode became more and more sensitive to shakings and vibrations. The time required to attain a stable potential increased and finally no constant potentials were obtained. The last few potentials recorded were uncertain to at least 0.5 mV since the potential fluctuated by this amount. A swirling motion of the amalgam changed the potential by more than 20 mV and it regained the previous value after 1–2 h. This may be contrasted with the behavior at log $h = -2$ and higher. In this region the cell attained the equilibrium value immediately and shaking did not affect the potential at all.

RESULTS AND CALCULATIONS

Owing to the pronounced hydrolysis of Bi^{3+} it is not possible, when working with 0.1 M $(\text{Na})\text{ClO}_4$ medium, to add enough acid to repress this reaction. Thus E° values could not be obtained by inserting analytical concentrations in eqns. (1) and (2). Instead, E_g° had to be determined in HClO_4 – NaClO_4 mixtures, whereas E_{am}° remains unknown. Therefore only changes in the concentration of Bi^{3+} can be determined and not absolute values.

From eqn. (2) we find $\log b = \frac{E_{\text{am}}^{\circ}}{19.72} - \frac{(E_{\text{am}} + E)}{19.72}$ and from the definition of η ;

$$\eta = \log B - \log b = \log B + \frac{(E_{\text{am}} + E_j)}{19.72} - \frac{E_{\text{am}}^{\circ}}{19.72} \quad (6)$$

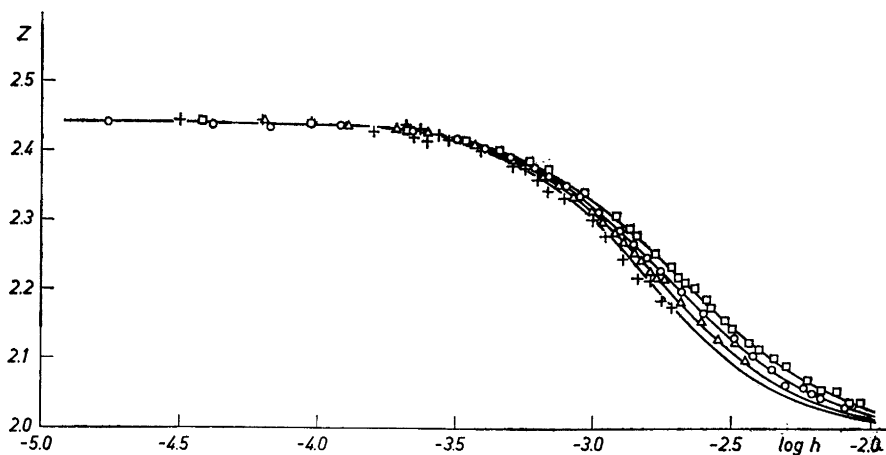


Fig. 1. Average number, Z , of protons split off by one Bi(III) as a function of $\log h$. The lines are calculated with $\log \kappa_{20,3} = -3.5$, $\log K_1 = -3.2$ and $\log K_2 = -2.6$. \square 4 mM Bi(III); \circ 2 mM Bi(III); \triangle 1 mM Bi(III); $+$ 0.5 mM Bi(III); $\delta = 0.01$ mM OH^- .

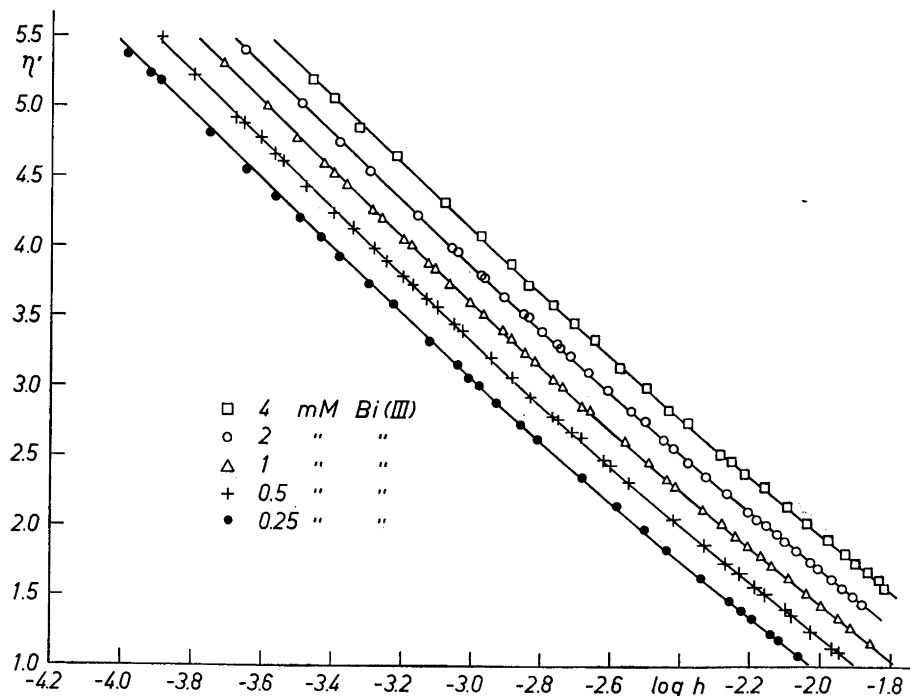


Fig. 2. $\eta' = \log \frac{[\text{Bi(III)}]_{\text{tot}}}{[\text{Bi}^{3+}]} + \nabla$ as a function of $\log h$. The lines are calculated with $\log \kappa_{20,3} = 3.5$, $\log K_1 = -3.2$ and $\log K_2 = -2.6$.

Table 1. Corresponding values of $\log h$, Z and η' . In general only points where both Z and η' were measured simultaneously are given.

Bi(III) = 4 mM

$-\log h$	Z	η'	$-\log h$	Z	η'	
4.427	2.442	} in 0,1 M (Ba)ClO ₄	2.662	2.206	3.339	
4.035	2.437		2.576	2.169	3.142	
3.681	2.424		2.500	2.138	2.990	
3.460	2.410		5.200	2.437	2.122	2.837
3.326	2.394		4.866	2.383	2.102	2.721
3.225	2.380		4.653	2.290	2.082	2.528
3.085	2.350		4.318	2.255	2.076	2.482
2.976	2.321		4.080	2.219	2.051	2.381
2.913	2.303		3.902	2.158	2.043	2.254
2.890	2.294		3.882	2.097	2.040	2.148
2.838	2.277	3.750	2.040	2.020	2.026	
2.770	2.249	3.588	1.981	2.028	1.904	
2.713	2.230	3.451	1.881	—	1.702	
			1.835	—	1.620	

Bi(III) = 2 mM

$-\log h$	Z	η'	$-\log h$	Z	η'	
4.758	2.441	} in 0,1 M (Ba)ClO ₄	2.611	2.162	2.988	
4.379	2.437		2.544	2.130	2.836	
4.038	2.435		2.449	2.110	2.633	
3.916	2.433		—	2.380	2.085	2.470
3.654	2.422		5.407	2.317	2.060	2.349
3.495	2.410		5.021	2.270	2.054	2.252
3.384	2.398		4.742	2.207	2.046	2.121
3.298	2.386		4.539	2.156	2.034	2.019
3.227	2.373		4.357	2.104	2.032	1.902
3.161	2.359		4.230	2.060	—	1.816
3.059	2.333	3.992	2.008	—	1.705	
2.976	2.309	3.804	1.971	—	1.629	
2.900	2.285	3.637	1.940	—	1.563	
2.839	2.250	3.510	1.911	—	1.507	
2.757	2.222	3.312	1.884	—	1.451	
2.665	2.185	3.109				

Bi(III) = 1 mM

$-\log h$	Z	η'	$-\log h$	Z	η'
4.195	2.436	—	2.822	2.232	3.189
3.891	2.429	5.724	2.768	2.205	3.062
3.718	2.421	5.303	2.740	2.204	3.016
3.595	2.414	5.009	2.659	2.172	2.824
3.505	2.404	4.786	2.577	2.115	2.646
3.430	2.393	4.598	2.491	2.112	2.463
3.365	2.384	4.446	2.441	2.089	2.347
3.290	2.375	4.259	2.391	—	2.251
3.261	2.366	4.198	2.351	—	2.159
3.200	2.357	4.050	2.285	—	2.027
3.178	2.350	4.015	2.209	—	1.860
3.127	2.339	3.888	2.143	—	1.728
3.066	2.321	3.741	2.094	—	1.632
3.003	2.299	3.604	2.040	—	1.515
2.968	2.285	3.518	1.996	—	1.429
2.918	2.271	3.407	1.952	—	1.343
2.889	2.256	3.336	1.916	—	1.267
2.850	2.241	3.249	1.856	—	1.145

Table 1. Continued

Bi(III) = 0,5 mM

$-\log h$	Z	η'	$-\log h$	Z	η'
4.535	2.430	—	2.765	2.162	2.796
4.204	2.426	—	2.711	2.154	2.680
4.019	2.422	5.763	2.689	2.096	2.640
3.889	2.418	5.489	2.620	2.104	2.482
3.798	2.408	5.225	2.600	2.072	2.440
3.653	2.400	4.881	2.557	2.082	—
3.619	2.412	4.774	2.545	2.094	2.320
3.566	2.404	4.657	2.530	2.042	—
3.546	2.388	4.612	2.415	—	2.030
3.478	2.394	4.429	2.339	—	1.879
3.400	2.380	4.247	2.270	—	1.747
3.341	2.376	4.130	2.233	—	1.670
3.284	2.344	3.988	2.187	—	1.564
3.247	2.350	3.902	2.158	—	1.524
3.200	2.338	3.790	2.104	—	1.407
3.167	2.322	3.729	2.030	—	1.260
3.132	2.308	3.638	1.967	—	1.133
3.048	2.294	3.450	1.949	—	1.103
3.027	2.280	3.400	1.903	—	1.011
2.944	2.262	3.207	1.849	—	0.905
2.883	2.214	3.070			

Bi(III) = 0.25 mM

$-\log h$	η'	$-\log h$	η'
3.894	5.193	2.679	2.363
3.754	4.828	2.581	2.150
3.651	4.554	2.503	1.988
3.565	4.356	2.440	1.841
3.495	4.209	2.339	1.638
3.434	4.072	2.258	1.481
3.382	3.930	2.224	1.405
3.298	3.738	2.195	1.344
3.228	3.591	2.141	1.233
3.122	3.332	2.118	1.192
3.041	3.165	2.060	1.075
3.009	3.068	1.996	0.949
2.927	2.891	1.933	0.837
2.858	2.734	1.884	0.731
2.809	2.627	1.813	0.599

The measured E_{am} ranged between 500 and 400 mV. In the following calculations E_{am}° was arbitrarily replaced by 360.6 mV, which gave a convenient quantity η' defined as (∇ = unknown constant)

$$\eta' = \log B + \frac{(E_{am} + E_j)}{19.72} - \frac{360.6}{19.72} = \eta + \frac{(E_{am}^{\circ} - 360.6)}{19.72} = \eta + \nabla \quad (7)$$

In order to be able to find possible reactions giving rise to Z values above 2 it is necessary to make some assumptions as to what species are formed

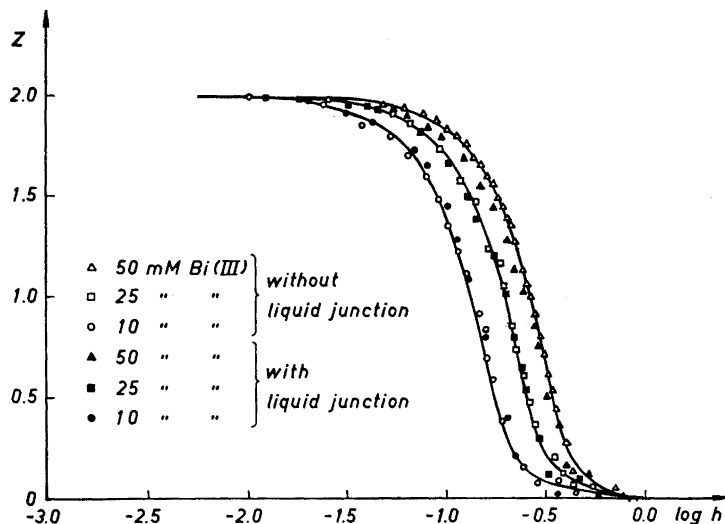


Fig. 3. Average number, Z , of protons split off by one Bi^{3+} in 3 M $(\text{Na})\text{ClO}_4$ as a function of $\log h$. The lines are calculated with $\log \beta_{12,6} = 0.33$ and $\log \beta_{11} = -1.58$.

in earlier stages of the hydrolysis. Previous measurements of η with 3 M $(\text{Na})\text{ClO}_4$ medium² have indicated that the main complex formed is $\text{Bi}_6(\text{OH})_{12}^{6+}$, and that in addition some BiOH^{2+} is formed. Assuming only these two complexes it was possible to explain quantitatively the data over a wide range of concentrations. This hypothesis has been the basis for the present calculations.

The experimental results are shown graphically in Figs. 1 and 2 and numerically in Table 1.

With 0.05 M $\text{Ba}(\text{ClO}_4)_2$ — to be strict, 0.1 M $(\text{Ba})\text{ClO}_4$ — as medium only $\log h$ measurements with $[\text{Bi(III)}]_{\text{tot}} = 4$ and 2 mM were made. The data obtained in general agreed to 0.005 Z units with those found with 0.1 M $(\text{Na})\text{ClO}_4$ as medium. Therefore only a few data in the low $\log h$ region not covered by the measurements with the latter medium are given.

The η' values in the most acid region are characterized by parallel curves for the various B values, a slope $(\Delta\eta'/\Delta \log h)_B$ close to -2 , and $(\Delta \log B/\Delta \log h)_{\eta'} = 2.4$ to 2.5. Thus the curves have the same properties as found with 3 M $(\text{Na})\text{ClO}_4$, which makes it likely that the same complex, $\text{Bi}_6(\text{OH})_{12}^{6+}$, predominates also at lower ionic strengths. With decreasing $\log h$, $(\Delta\eta'/\Delta \log h)_B$ decreases, and the curves tend to become closer together, as seen along the $\log h$ axis.

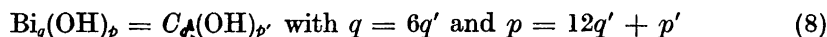
The Z curves clearly indicate that $\text{Bi}_6(\text{OH})_{12}^{6+}$ is in equilibrium with larger complexes, since the curves are separate and do not cross. The curves do not show a pronounced shelf at $Z = 2$ but turn fairly sharply downwards after having passed this value. Unfortunately it is not possible to follow the hydrolysis in 0.1 M $(\text{Na})\text{ClO}_4$ for much smaller values than $Z = 2$, for the experimental

accuracy declines rapidly as the acidity increases. That there is a short separation between the reactions occurring above and below $Z = 2$ is evident from Fig. 3, which shows some Z curves from measurements with 3 M(Na)ClO₄. They exhibit a pronounced bending off towards $Z = 2$. These measurements are described in an appendix to the present paper. Holmberg, Kraus and Johnson¹² also found $Z_{\text{lim}} = 2.0$ from $\log h$ measurements.

An upper limit seems to exist for Z around 2.44. The solutions had a very low buffer capacity in this region. A small change in analytical composition led to a large $\log h$ change and finally precipitation started. It is remarkable that this limiting value is different from 2.5 which is the ratio OH:Bi in the solid phase^{3,11}. The divergence of the limiting value from 2.5 is not likely to be due to an experimental error, since it was obtained with two independent stock solutions both in NaClO₄ and Ba(ClO₄)₂. Moreover protons were set free when the precipitate was formed, as is expected if the ratio OH:Bi = 2.5 in the solid phase and < 2.5 in the solution.

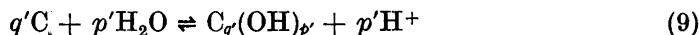
Elucidation of possible hydrolysis products. The formulas of the products formed by the hydrolysis of the Bi₆(OH)₁₂⁶⁺ ion are difficult to find with certainty mainly for two reasons. Firstly, only low total metal ion concentrations could be measured, which causes the Z values in general to be uncertain to 0.01 unit. When we have polynuclear complexes present the spacing between the Z curves is very important in finding possible species to explain the data. With a small concentration range considerable uncertainty is introduced. Secondly high powers are present in the expression for the law of mass action for the complexes formed. This leads to a scatter of the experimental points used in the calculations.

It is convenient to consider the complexes as built up from Bi₆(OH)₁₂⁶⁺ (C) and OH⁻(-H⁺) and not from Bi³⁺ and OH⁻. The complex Bi_q(OH)_p is therefore written as



where p' and $6q'$ are whole numbers.

$\kappa_{p',q'}$ denotes the equilibrium constant for the reaction



The expression (9) is so general that it includes all conceivable species, also Bi³⁺ ($q' = 1/6$, $p' = -2$) and BiOH²⁺ ($q' = 1/6$, $p' = -1$) known to exist in small amounts.

The law of mass action gives

$$C = c + \sum q' \kappa_{p',q'} c^q h^{-p'} \quad (10)$$

$$CZ' = \sum p' \kappa_{p',q'} c^q h^{-p'} \quad (11)$$

The concentration of Bi₆(OH)₁₂⁶⁺, c , is found from the amalgam data. We start with the equation

$$\frac{[\text{Bi}_6(\text{OH})_{12}^{6+}] \cdot h^{12}}{[\text{Bi}^{3+}]^6} = \beta_{12,6} \text{ or } \log c = \log \beta_{12,6} + 6 \log b - 12 \log h \quad (12)$$

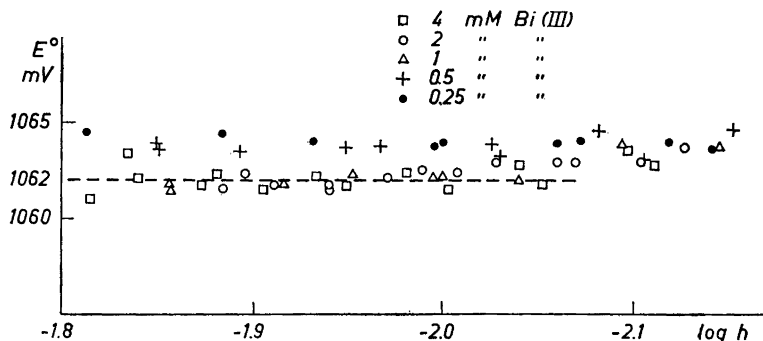


Fig. 4. The values of E° found from eqn. (13) as a function of $\log h$.

Inserting $\log b$ and $\log h$ from eqns. (1) and (2) we get

$$19.72 \log c = 19.72 \log \beta_{12,6} + 6E_{\text{am}}^\circ - 4E_{\text{g}}^\circ + 4E_{\text{g}} - 6E_{\text{am}} - 2E_{\text{j}} = E^\circ + 4E_{\text{g}} - 6E_{\text{am}} - 2E_{\text{j}} \quad (13)$$

In this equation both $\beta_{12,6}$ and E_{am}° are unknown but by inserting $B/6$ for c , $E^\circ = 19.72 \log \beta_{12,6} + 6E_{\text{am}}^\circ - 4E_{\text{g}}^\circ$ can be found from the potentials in the most acid region where $\text{Bi}_6(\text{OH})_{12}^{6+}$ is the predominating species. Since the amalgam data are presented as η' , an equation from which c can be calculated using η' will be given.

$$\eta' = \log B - \log b + \nabla \text{ or } \log b = \log B - \eta' + \nabla \quad (14)$$

Inserting this expression for $\log b$ in (12)

$$\log c = \log \beta_{12,6} + 6\nabla + 6 \log B - 6\eta' - 12 \log h \quad (15)$$

is obtained. $\log \beta_{12,6} + 6\nabla$ is found by inserting $B/6$ for c as indicated above.

Fig. 4 shows the values of E° obtained from eqn. (13) in the region where $\text{Bi}_6(\text{OH})_{12}^{6+}$ may be expected to predominate. It is seen that for the three highest concentrations E° comes out quite constant $= 1062 \pm 0.5$ mV, which is almost better than could be expected, considering the factors 4 and 6 in eqn. (13). The lower concentrations yield an E° ca. 2 mV higher. This is not unexpected since $\text{Bi}_6(\text{OH})_{12}^{6+}$ is certainly not the sole species present. If for example the equilibrium constants were the same as given in Ref.² for 3 M (Na)ClO₄, we may estimate that for $B = 0.25$ mM, 5–7 % of the bismuth(III) is present as Bi^{3+} and BiOH^{2+} at $\log h = -2$. For the highest values of B we may also have disturbances from species more hydrolysed than $\text{Bi}_6(\text{OH})_{12}^{6+}$ as indicated by the $(\Delta\eta'/\Delta \log h)_B$ values which are smaller than -2 . In the calculations on the 0.5 mM titrations we have used the value of E° found for the higher concentrations, but only used the data in the low $\log h$ region where an error in E° is not so serious. No calculations have been performed on the 0.25 mM titrations and the reason for this is, that beside the uncertainty

in E° , these data must be subject to large errors since $(\Delta\eta'/\Delta \log h)_B$ does not decrease regularly with decreasing $\log h$ values. This contradicts the law of mass action.

When we know c , the quantity $CZ'/(C-c)$, which is the average number of OH^- per $\text{Bi}_6(\text{OH})_{12}^{6+}$ unit in the complexes, can be calculated. The $CZ'/(C-c)$ ($\log h$) curves for the 4 and 2 mM titrations coincided or very nearly so, whereas the 1 and 0.5 mM titrations were slightly off the curve. However, if the NaClO_4 contained a basic impurity, δ , of the order of 0.01 mM, the $CZ'/(C-c)$ ($\log h$) curves for the different B coincide.

If only one complex had been formed, $CZ'/(C-c)$ should have come out as a constant equal to p'/q' . The hypothesis that only one complex is formed is ruled out, since $CZ'/(C-c)$ is found to be variable.

The same conclusion is reached from consideration of Z data alone¹³. Eqns. (10) and (11) give

$$C = c + q' \kappa_{p',q'} c^{q'} h^{-p'} \quad (10a)$$

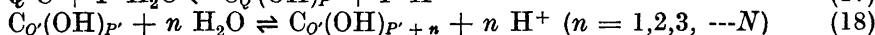
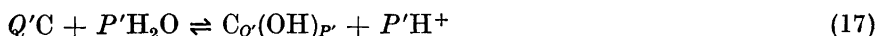
$$CZ' = p' \kappa_{p',q'} c^{q'} h^{-p'} \quad (11a)$$

and after elimination of c

$$\log X = \log h - \frac{1}{p'} \log(p' \kappa_{p',q'} C^{q'-1}) = \frac{1}{p'} \log \frac{(p' - Z'q')^{q'}}{p'^{q'} Z'} \quad (16)$$

Comparison with $Z'(\log X)$ curves calculated for different q' and choosing p' to give a $Z_{\text{lim}} \approx 2.4$, showed no fit. The theoretical curves are steeper than the experimental ones, which means that intermediate complexes must be present.

The fact that the $CZ'/(C-c)$ ($\log h$) curves are independent of C , suggests that the complexes formed are homonuclear. The hydrolysis can then be represented by the reactions



where Q' , P' and N are unknown. With $\overline{\kappa_{P',Q'}} = \kappa$ and $\kappa_{P'+n, Q'} = \alpha_n \kappa$ the law of mass action gives

$$C = c + Q' \kappa c^{Q'} h^{-P'} (1 + \alpha_1 h^{-1} + \alpha_2 h^{-2} + \dots) \quad (19)$$

$$CZ' = \kappa c^{Q'} h^{-P'} (P' + (P' + 1)\alpha_1 h^{-1} + (P' + 2)\alpha_2 h^{-2} + \dots) \quad (20)$$

For the complex of highest Z , $C_Q(\text{OH})_{P'+N}$ or $\text{Bi}_Q(\text{OH})_{P'+N}$, the following relations must be fulfilled

$$(P' + N)/Q = 2.44 \pm 0.02 \text{ or } (P' + N)/6Q' = 0.44 \pm 0.02; Q > 6; P, Q, N, P',$$

and $6Q'$ whole numbers.

A tentative value for Q' is found from eqn. (19). If homonuclear complexes are formed and the correct value of Q' is chosen $\log(C-c) - Q' \log c = f(h)$ when plotted as a function of $\log h$ should give one curve independent of C . Different Q' values were tested starting from $Q' = 7/6$. This test excluded all values of Q' except $7/6$ and $9/6$. $Q' = 8/6$ is ruled out since there is no corre-

sponding P' that gives a Z_{lim} in agreement with experiment. For $Q' > 9/6$ the experimental data fall less and less satisfactorily on a single curve.

With the help of the Q' values $7/6$ and $9/6$ a tentative value for N can be found. The experimental $CZ'/(C-c)$ ($\log h$) curve ranges between 2.7 ± 0.1 and 1.3 ± 0.2 , with these limits as asymptotes. These limiting values should be equal to $(P' + N)/Q'$ and P'/Q' . For $Q' = 7/6$ we should have $P' = 1.5 \pm 0.2$ and $P' + N = 3.15 \pm 0.1$. For $Q' = 9/6$ we find $P' = 1.95 \pm 0.3$ and $P' + N = 4.05 \pm 0.15$. We may thus conclude $N = 2$.

Determination of α_1 and α_2 . Eqns. (19, 20) with $N = 2$ give after elimination of c

$$Q' \left(\frac{CZ'}{C-c} \right) - P' = \frac{\alpha_1 h^{-1} + 2\alpha_2 h^{-2}}{1 + \alpha_1 h^{-1} + \alpha_2 h^{-2}} = n \tag{22}$$

Experimental $\bar{n}(\log h)$ were compared with normalized curves for the right hand side of the equation according to Sillén¹⁴. The sets tested were $P' = 1$, $Q' = 7/6$ (or $P = 15$, $Q = 7$) and $P' = 2$, $Q' = 9/6$ (or $P = 20$, $Q = 9$). Both combinations reasonably fitted the normalized curves, and α_1 and α_2 were determined for each set.

Determination of κ . To determine κ and to make possible a choice of best values for P and Q the following equations were developed. Replacing $1 + \alpha_1 h^{-1} + \alpha_2 h^{-2}$ by $\varphi(h)$ in eqn. (19) and $P' + (P' + 1)\alpha_1 h^{-1} + (P' + 2)\alpha_2 h^{-2}$ by $\omega(h)$ in eqn. (20) for simplification, eliminating c and introducing the new variables y and x defined by

$$y = Z' \frac{\varphi(h)}{\omega(h)}, \quad x = \log h - \frac{1}{P'} \log \varphi(h) - \frac{(Q'-1)}{P'} \log C \tag{23, 24}$$

we get

$$X = x - \frac{1}{P'} \log \kappa = \frac{1}{P'} \log \frac{(1-Q' y)^{Q'}}{y} \tag{25}$$

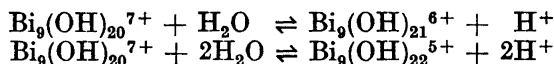
Experimental $y(x)$ curves calculated with eqns (23, 24) and the previously determined constants α_1 and α_2 may be compared with normalized $y(X)$ curves from eqn. (25). If a fit is obtained, $P'^{-1} \log \kappa$ is the difference between the coordinates on the x and X axes in this position. This comparison ruled out the set $P' = 1$, $Q' = 7/6$ but gave a good fit for the set $P' = 2$, $Q' = 9/6$ if we allow for a $\delta = 0.01$ mM OH^- .

The same calculations were carried out for complexes $\text{Bi}_{11}(\text{OH})_{25+n}$ for $N = 2$. A fairly good fit was obtained if δ is assumed to be 0.02 mM OH^- , which is, however, larger than the estimated error in the experimental value for $\delta = 0.00 \pm 0.01$ mM OH^- or H^+ .

Sillén's "core and links" approach^{15,16} to the explanation of polynuclear complex formation will be briefly discussed since it has been successfully applied to the hydrolysis of many metal ions. If this assumption is valid it should be possible to represent the complexes by the formula $\text{Bi}_6(\text{OH})_{12} [\text{Bi}_6(\text{OH})_{12}(\text{OH})_t]_n$, where t is a constant and n varies. nt and $6n$ must, of course, be whole numbers. This hypothesis requires that the $Z(\log h)_B$ curves should be parallel, and that $(\Delta \log B / \Delta \log h)_Z = t$ is constant. These characteristics

are not shown by the present data especially at high Z values. It may still be instructive to apply this hypothesis to the data, since the curves are sufficiently close together that a fairly small experimental error can distort the curves. In these calculations $t = 6$ was used in order to conform with a limiting value 2.5 for Z , and n arbitrarily assumed to take the values 0, 1/6, 2/6...1. The t value used is greater than the experimental average value which is closer to 5. The calculations indicated that the complexes with the smallest n predominate, but no satisfactory explanation of the data was afforded by this approach using simple assumptions about how the equilibrium constants vary with n . It is, however, not unlikely that a number of complexes with different values of q , as for instance in a "core + links" series, could also be made to fit the data, if no relation is assumed to exist between the equilibrium constants.

The determination of the equilibrium constants for the final choice of complexes, $\text{Bi}_9(\text{OH})_{20}^{7+}$, $\text{Bi}_9(\text{OH})_{21}^{6+}$, and $\text{Bi}_9(\text{OH})_{22}^{5+}$, will be given in some detail using the methods indicated in the general discussion. We start with the determination of α_1 and α_2 which are the equilibrium constants for the reactions'



This was accomplished by a combination of the η' and Z' data. We plotted the left hand side of eqn. (22), $1.5 CZ'/(C-c)-2$, as a function of $\log h$ and compared the plot with normalized curves for the right hand side of the same equation. The normalization is brought about by the following substitutions

$$v^2 = \alpha_2 h^{-2} \text{ and } k = \alpha_1 \alpha_2^{-1/2} \quad (26, 27)$$

which give

$$\bar{n} = \frac{\alpha_1 h^{-1} + 2\alpha_2 h^{-2}}{1 + \alpha_1 h^{-1} + \alpha_2 h^{-2}} = \frac{kv + 2v^2}{1 + kv + v^2} \quad (28)$$

Curves \bar{n} ($-\log v$) were calculated for different values of k to find the value which gave the best agreement between the experimental and normalized curve. When this value was found, $\log \alpha_2$ was determined as twice the difference between the coordinates on the $\log h$ and $-\log v$ axes when the two curves overlapped and $\log \alpha_1$ was determined from eqn. (27). The best value of k was found to be 0.5. This value is, however, not very accurate owing to the scatter among the experimental points (Fig. 5).

The values found for $\log \alpha_1$ and $\log \alpha_2$ were

$$\begin{aligned}\log \alpha_1 &= -3.2 \pm 0.2 \\ \log \alpha_2 &= -5.8 \pm 0.1\end{aligned}$$

Knowing α_1 and α_2 we proceeded to determine $\kappa_{20,9}$ from eqns. (23, 24 and 25). For each experimental point $\varphi(h)$ and $w(h)$ were first computed and then y and x . The plot $y(x)$ was compared with the theoretical $y(X)$ curve calculated from eqn. (25) with $Q' = 9/6$ and $P' = 2$, and examined for a fit. In this position twice the difference between the x and X coordinates gives $\log \kappa_{20,9}$ (Fig. 6).

$$\log \kappa_{20,9} = -3.5 \pm 0.1$$

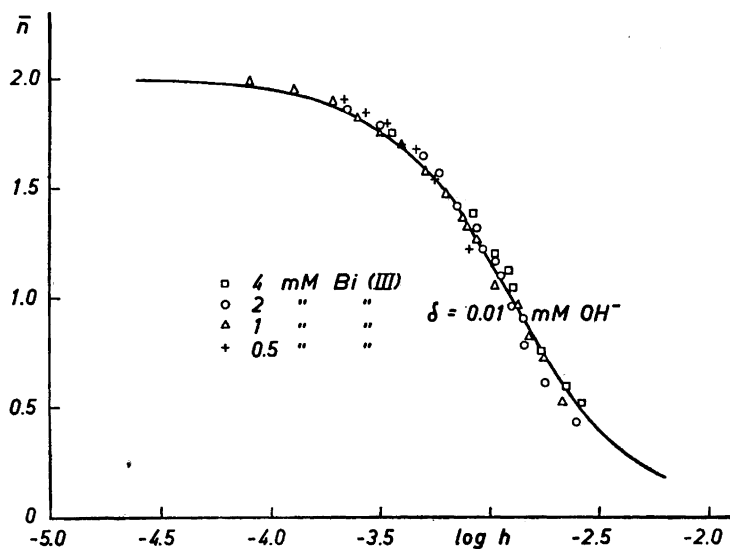


Fig. 5. Determination of α_1 and α_2 by curve fitting according to eqn. (28). The line represents the normalized curve in position of best fit.

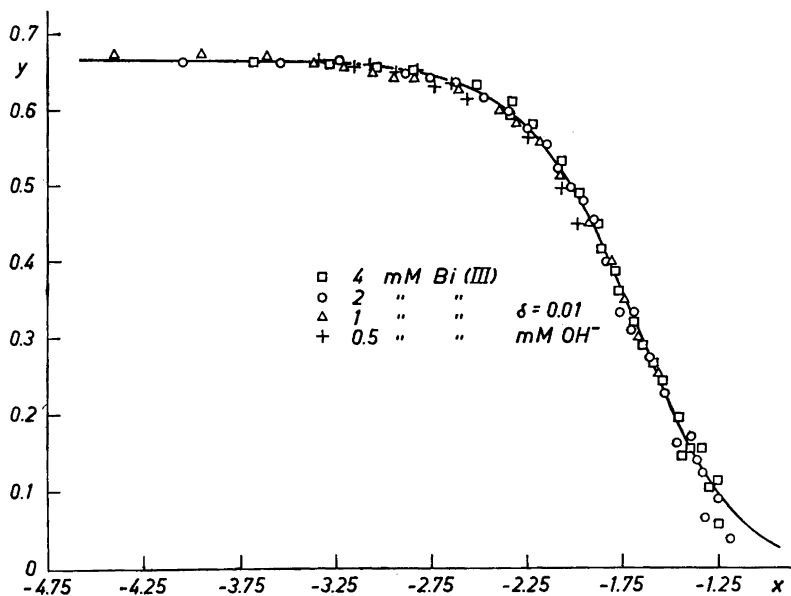


Fig. 6. Determination of $\kappa_{20,9}$ by curve fitting according to eqn. (25). The line represents the normalized curve in position of best fit.

Log $\kappa_{20,9}$ was also calculated from the amalgam data using eqn. (19) from which we find

$$\log \kappa_{20,9} = \log(C-c) - 1.5 \log c + 2 \log h - \log \varphi(h) - \log 1.5 \quad (19a).$$

$\varphi(h)$ was computed with the values for α_1 and α_2 already determined. The mean value obtained for $\log \kappa_{20,9}$ was

$$\log \kappa_{20,9} = -3.45 \pm 0.1$$

When taking the mean value a few values from the most hydrolysed solutions were excluded. It is not surprising that the $\log \kappa_{20,9}$ values calculated from these points are erroneous. The estimated uncertainty in the amalgam potentials of at least 0.5 mV leads to an uncertainty in $\log \kappa_{20,9}$ of 0.23.

The data may also be represented by $\log \kappa_{20,9}$ and the two acidity constants (K_1 and K_2) of $\text{Bi}_9(\text{OH})_{20}^{7+}$. We find that $\log K_1 = \log \alpha_1$ and $\log K_2 = \log \alpha_2 - \log \alpha_1$.

The numerical values are

$$\begin{aligned} \log K_1 &= -3.2 \pm 0.2 \\ \log K_2 &= -2.6 \pm 0.2 \end{aligned}$$

Finally the experimental $Z(\log h)_B$ and $\eta'(\log h)_B$ curves were compared with the theoretical ones calculated with the equilibrium constants given (Figs 1 and 2).

Comparison with Faucherre's measurements

The only previous work on the hydrolysis of the "bismuthyl ion", which contains enough data to warrant a calculation of the species formed, is that by Faucherre. With some hesitation he gives $\text{Bi}_8(\text{OH})_{20}^{4+}$ as a possible complex. To make a comparison with the present data easier, Faucherre's data were converted to give Z as a function of $\log h$. This cannot be accomplished very accurately, since he presents only a small graph showing $\log h$ as a function of the analytical composition of the solutions. The most notable difference between the two sets of data is the disagreement between the limiting values for Z . Whereas in the present work Z values larger than 2.44 to 2.45 were not obtained and the form of the curves indicates that this is a limiting value, he found Z values at least larger than 2.46 before precipitation started. In this region his curves are still bending quite steeply upwards so that the limiting value 2.5 for Z proposed by him is reasonable. Some doubt may be raised concerning the complex $\text{Bi}_8(\text{OH})_{20}^{4+}$. If we accept $\text{Bi}_4\text{O}_4^{4+}$ as the "mother complex", as was done by Faucherre, and calculate a theoretical curve for the combination $\text{Bi}_4\text{O}_4^{4+}$ and $\text{Bi}_8\text{O}_{10}^{4+}$, it is found that the agreement is poor between Faucherre's experimental data and the calculated curve even if we consider the previously mentioned uncertainty in the Z values. The theoretical curve is too steep for this explanation of the data. This was the situation met with when the present data were tested for the hypothesis that only one complex is formed.

DISCUSSION

It is not easy to discuss the plausibility of the proposed hydrolysis mechanism. On hydrolysis, the metal ions seem to be quite individualistic in their behavior so we have little or no help from analogies with other cations. The mechanism proposed shows some parallelism with that found for the VO_2^+ ion by Rossotti and Rossotti¹⁷ but is widely different from what has been found for other ions. The VO_2^+ ion hydrolyses to the decavanadate $\text{H}_2\text{V}_{10}\text{O}_{28}^{4-}$, which splits off two hydrogen ions.

One intriguing feature of the mechanism proposed is the discrepancy between the number of OH^- groups bound per Bi(III) in the aqueous complexes and in the solid phase. However, the relationship between the solid phase described as $\text{Bi}_2(\text{OH})_3\text{OClO}_4$ and the complexes in solution may not be simple, since protons were set free when the salt started to precipitate. It would be desirable to know the crystal structure of this salt. It may contain structural units that could give hints as to what is happening in the solution.

APPENDIX

In this appendix some $\log h$ measurements on bismuth(III) in 3 M $(\text{Na})\text{ClO}_4$ will be described briefly. They were carried out with the cell — glass/0.01 M Ag^+ , B M Bi(III) , H M H^+ , $(2.99-3B-H)$ M Na^+ , 3 M ClO_4^-/Ag , AgCl +

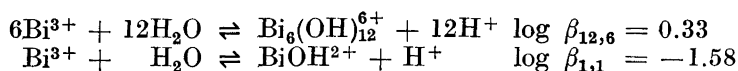
$$E_g = E_g^\circ - 59.15 \log h + \epsilon$$

where ϵ is a correction term for the deviation of the glass electrode from ideality. The electrode used had the slope 59.15 up to $\text{H}^+ = 350$ mM. After 350 mM H^+ , deviations from this slope became apparent. At 750 mM H^+ , which was the highest acidity used, ϵ reached -0.4 mV.

The above cell was used in an effort to reduce the uncertainty in the measured potentials by elimination of the liquid junction. Since Bi^{3+} starts to hydrolyse in fairly acid solutions small differences in the measured emf cause large differences in Z .

The results are shown in Fig. 3. When the new data were compared with older ones, obtained from cells with liquid junctions, discrepancies were observed. These discrepancies were found to be caused by the E_g° chosen. When $59.15 \log h$ was plotted as a function of H it was found that the plots for the two cells were perfectly superposable but slightly displaced from each other. The difference was 0.2 mV for the 10 and 25 mM Bi(III) and 0.5 mV for 50 mM. The rather large difference in the latter case merely reflects the difficulty of obtaining good E_g° values in very acid solutions where the liquid junction potential is large and corrections have to be applied to the glass electrode.

In Fig. 3 the drawn curves have been calculated with the equilibrium constants previously found from η data²



we thus find that the number of protons set free by the hydrolysis of Bi(III) in 3 M (Na)ClO₄ can be satisfactorily accounted for by the formation of Bi₆(OH)₁₂⁶⁺ and BiOH²⁺.

Note added in proof. After the completion of this work I was told by Dr. R.S. Tobias (private communication; results to be published in *J. Am. Chem. Soc.*) that from log *h* measurements in 1 M (Na)ClO₄ he had suggested the formation of Bi₆O₆⁶⁺ and Bi₆O₆(OH)₃³⁺. The agreement is good on Bi₆O₆⁶⁺ (which is equivalent to Bi₆(OH)₁₂⁶⁺ but the present data cannot be explained on the assumption that Bi₆O₆(OH)₃³⁺ is formed as a main species in the latter stages of the hydrolysis of the Bi³⁺ ion.

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