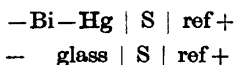# Studies on the Hydrolysis of Metal Ions

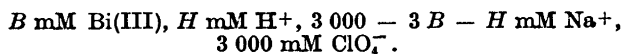## 19. The Hydrolysis of Bismuth(III) in Perchlorate Medium

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The hydrolysis of the Bi(III) ion has been studied at 25 °C in
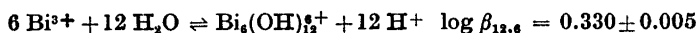3 M sodium perchlorate medium by means of the cells:

$$-Bi-Hg \mid S \mid ref+$$
$$- \quad glass \mid S \mid ref+$$

where S had the general composition,

$$B \text{ mM Bi(III)}, H \text{ mM H}^+, 3\,000 - 3\,B - H \text{ mM Na}^+,$$
$$3\,000 \text{ mM ClO}_4^-.$$

It has been possible to vary B between 50 and 0.1 mM.
The data can be explained assuming the equilibria:

$$Bi^{3+} + H_2O \rightleftharpoons BiOH^{2+} + H^+ \qquad \log \beta_1 = -1.58 \pm 0.02$$

$$6\,Bi^{3+} + 12\,H_2O \rightleftharpoons Bi_6(OH)_{12}^{6+} + 12\,H^+ \quad \log \beta_{12,6} = 0.330 \pm 0.005$$

For a summary of the work on the hydrolysis of bismuth up to 1947,
the reader is referred to a paper by Granér and Sillén [1]. Since the appearance
of their paper, in which a continuous polymerization was proposed, a photo-
metric study has been published by Souchay and Peschanski [2], who found
evidence for the formation of a complex that might be written as $Bi_4O_4^{4+}$. They
state, however, that the complexes $Bi_5O_5^{5+}$ and $Bi_6O_6^{6+}$ are just as likely. In
more basic solutions than correspond to $BiOClO_4$, Faucherre [3] has proposed
the complex $Bi_8O_{10}^{4+}$. In none of these three investigations has any evidence
been found for the simple complexes $BiOH^{2+}$ and $Bi(OH)_2^+$. Holmberg,
Kraus, and Johnson [4] have ultracentrifuged bismuth(III) solutions and
found only one complex, but it was not possible to state if the complex con-
tained 5 or 6 bismuth atoms. The present work is an electrometric investiga-
tion of bismuth(III) perchlorate solutions similar to that of Granér and Sillén
but carried out over a much broader range of concentrations.

THE METHOD OF INVESTIGATION

The experimental approach to this problem is essentially the same as similar investigations carried out in this laboratory [1,5]. In short a titrating solution rich in H^+ was added to a solution low in H^+, the total Bi(III) being kept constant. This is the only possible way in this case, since starting from the acid side would require too strong a base to be convenient. The solutions had the general composition:

[Bi(III)] : BmM, $[H^+]_{tot}$: HmM, $[Na^+]$: 3 000—$3B$—HmM, $[ClO_4^-]$: 3 000mM,

where B denotes the total Bi(III) concentration and $[H^+]_{tot}$ is the "analytical" hydrogen ion concentration assuming no hydrolysis. The following cells were used to measure $[H^+] = h$ and Bi^{3+}

$$— \text{glass} \mid h \mid \text{ref} + \qquad E = E^\circ_g — 59.16 \log h — E_j \qquad (1)$$

$$— Bi — Hg \mid Bi^{3+} \mid \text{ref} + \qquad E = E^\circ_{am} — 19.72 \log [Bi^{3+}] — E_j \qquad (2)$$

The reference half-cell was in both cases

Ag, AgCl | 10 mM Ag^+, 2 990 mM Na^+, 3 000 mM ClO_4^- | 3 000 mM $NaClO_4$

The salt bridge was of the "Wilhelm" type designed by Forsling, Hietanen, and Sillén [6].

MATERIALS AND ANALYSIS

Sodium perchlorate was prepared by neutralizing Na_2CO_3 (Merck p.a.) with $HClO_4$ (Kebo p.a.) following the directions given by Biedermann [7]. The filtered solution gave no reaction for heavy metals, NO_3^- or SO_4^{2-}. It contained, however, minute quantities of chloride. The solution was therefore evaporated and allowed to crystallize. By working with not-too-concentrated solutions and stirring vigorously during the crystallization, it is possible to obtain readily-filterable crystals. A yield of *ca.* 70 % is obtained under proper conditions. The crystals were redissolved in water and the stock solution analysed by evaporating a known weight of solution and weighing the residue as $NaClO_4$.

Perchloric acid solutions were prepared from $HClO_4$ p.a. (70—72 %) and standardized against $KHCO_3$ and standard NaOH. The sodium hydroxide was standardized both against $N_2H_4 \cdot H_2SO_4$ and $KH(IO_3)_2$.
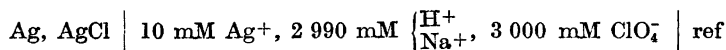
Bismuth (III) *perchlorate* was prepared by dissolving known amounts of Bi_2O_3 in standardized $HClO_4$. The Bi_2O_3 was prepared as follows: $Bi(NO_3)_3$ aq (p.a.) was re-crystallized from nitric acid and ignited in an electric resistance furnace at *ca.* 700 °C to constant weight. In this way a lemon-yellow powder was obtained which dissolved completely in *ca.* 3 M $HClO_4$ to give a colorless solution. No foreign anions could be detected in it. The bismuth perchlorate stock solution was analysed for bismuth by precipitating it as the phosphate according to Blasdale and Parle [8] or as the oxide chloride as described by Winkler [9]. Both methods gave the same result within 0.2 %. The ClO_4^- concentration was determined by passing the solution through an ion exchanger and titrating the liberated acid with NaOH. The analytical hydrogen ion concentration was obtained as the difference $[ClO_4^-] — 3[Bi^{3+}]$. The agreement between the calculated and found concentrations of ClO_4^- and Bi^{3+} was within 0.2 %.

Bismuth amalgam was prepared electrolytically using mercury (redist.) as the cathode and a platinum spiral as the anode. An attempt was made to prepare the amalgam by dissolving metallic bismuth in mercury in a CO_2 atmosphere. This failed, however, since the metal contained traces of oxide which could not be completely removed. The amalgam was kept under the acid electrolyte in an inert atmosphere. A small portion of the stock amalgam was taken out for each titration by an arrangement similar to a wash bottle. Preliminary tests showed that no electrolyte came along with the amalgam. The concentration of bismuth in the amalgam was about 0.25 % (weight).

EXPERIMENTAL DETAILS OF THE EMF MEASUREMENTS

Almost all concentrations were measured in two series with stock solutions completely independent of each other, and in each series duplicate titrations were made. The glass electrode (Blomgren) was calibrated up to 750 mM of acid, giving the sum of the liquid junction potential and the deviation of the glass electrode from ideality as a function of h. The calibration curve was the same from one time to another for acid concentrations below *ca.* 450 mM. In more acid solutions fluctuations were observed amounting to 0.5 mV.

The liquid junction potential was determined by means of the cell,

$$\text{Ag, AgCl} \;\Big|\; 10 \text{ mM Ag}^+, \; 2\,990 \text{ mM} \begin{Bmatrix} \text{H}^+ \\ \text{Na}^+ \end{Bmatrix}, \; 3\,000 \text{ mM ClO}_4^- \;\Big|\; \text{ref}$$

and found to agree with the values given by Biedermann and Sillén [10] to within 0.1 mV. For higher acidities (600 mM) the potentials were uncertain to 0.3 mV.

The amalgam electrode, which consisted of a pool on the bottom of the titration vessel, gave very constant and reproducible potentials. For identical points in each series, the difference between the emf values very seldom exceeded 0.05 mV. Under the same conditions the glass electrode showed a reproducibility of 0.2 mV. The overall reproducibility between the two series can be estimated by interpolation to be, for the amalgam electrode $0.1-0.2$ mV, and for the glass electrode $0.3-0.4$ mV. These limits, of course, contain analytical and other errors as well. Exceptions to the behavior stated above were given by the 0.1 mM titrations. Here the amalgam potential took at least half an hour to attain a constant value, and the reproducibility was only ± 0.2 mV.

Equilibrium seems to be attained immediately, and the potential remained constant within 0.05 mV for at least 3 h. It was observed that if a large amount of acid was added at one time, exactly the same potential was obtained (as fast as it could be measured), as if the same amount of acid was added during the course of about 5 h.

RESULTS AND CALCULATIONS

Since the amount of data obtained in this investigation is very large (600 equilibrium compositions were measured), it is not possible to give them all in detail. One representative titration is given in full in Table 1 and the others from the second series in compact form in Table 2. Fig. 2 shows the data from the second series. Those from the first series agree so closely that no difference would be seen in the figure. η denotes $\log \dfrac{[\text{Bi(III)}]_{\text{total}}}{[\text{Bi}^{3+}]_{\text{free}}}$ and h the hydrogen ion concentration at equilibrium. All concentrations in tables and figures, and E°_{am}, are on the mM scale, whereas E°_{g} and the final equilibrium constants are on the M scale.

Determination of E°_{am} and E°_{g}. In order to evaluate h and $[\text{Bi}^{3+}]$ from eqns (1) and (2), it is necessary to know the E°. By assuming that at sufficiently high acidities the hydrolysis is completely repressed, one can calculate the E° values by inserting the analytical concentrations. In this way it was possible to get the E° for the glass electrode, since the effect of the hydrolysis on the hydrogen ion concentration is small in the most acid solutions. The E°_{g} so obtained agreed with the E° from separate acid-base titrations substantiating the assumption made. For the amalgam electrode, a slight but definite trend in E°_{am} was always observed. Thus only a rough value was obtained, which was used for the preliminary calculations.

Table 1. Measurements with amalgam and glass electrodes. S_1 : Bi(III) : 10 mM, H^+ : 0.00 mM, Na^+ : 2970 mM, ClO_4^- : 3000 mM, S_2 : Bi(III) : 10 mM, H^+ : 1198 mM, Na^+ : 1772 mM, ClO_4^- : 3000 mM, E°_{am} = 418.1 mV.

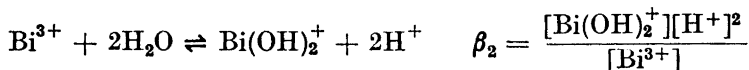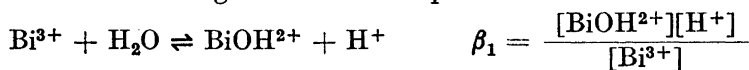| S_2 ml	E_g mV	E_{Bi-Hg} mV	H mM	E°_g mV	$\log h$ mM	$-E_j$ mV	η
0	398.4	436.74	0		1.297	0.32	1.929
0.2	393.1	433.24	4.77		1.386	0.39	1.748
0.5	387.0	429.18	11.87		1.490	0.49	1.537
0.7	383.6	426.95	16.55		1.549	0.57	1.420
1.0	379.2	424.18	23.50		1.625	0.68	1.274
1.5	373.6	420.52	34.90		1.723	0.84	1.080
2.0	369.2	417.71	46.09		1.801	1.01	0.929
2.5	365.6	415.40	57.07		1.863	1.17	0.804
3.0	362.3	413.50	67.83		1.923	1.34	0.699
3.5	359.9	411.90	78.40		1.966	1.48	0.611
4.0	357.6	410.53	88.77		2.006	1.62	0.534
4.5	355.4	409.35	98.95		2.046	1.78	0.466
5.0	353.6	408.32	108.9		2.080	1.92	0.407
5.5	351.9	407.42	118.8		2.111	2.06	0.354
6.0	350.3	406.63	128.4		2.142	2.22	0.306
6.5	349.1	405.95	137.9		2.163	2.33	0.266
7.0	347.8	405.36	147.2		2.188	2.46	0.229
7.5	346.6	404.86	156.3		2.210	2.59	0.197
8.0	345.5	404.44	165.3		2.230	2.72	0.169
8.5	344.4	404.08	174.1		2.250	2.85	0.145
9.0	343.3	403.80	182.8	296.7	2.272	2.98	0.124
9.5	342.3	403.58	191.3	296.8	2.290	3.10	0.107
10	341.5	403.42	199.7	296.9	2.305	3.20	0.093
11	340.0	403.26	216.1	297.2	2.335	3.41	0.075
12	338.5	403.24	231.9	297.2	2.365	3.64	0.062
13	337.2	403.31	247.3	297.3	2.393	3.87	0.054
14	335.9	403.43	262.2	297.3	2.418	4.10	0.048
15	334.7	403.56	276.6	297.2	2.442	4.32	0.044
17	332.7	403.85	304.1	297.2	2.483	4.70	0.039
19	331.0	404.16	330.0	297.2	2.519	5.04	0.038
21	329.5	404.44	354.4	297.1	2.550	5.35	0.036
23	328.3	404.72	377.6	297.3	2.577	5.65	0.035
25	327.3	404.97	399.4	297.4	2.601	5.93	0.034

$$E^\circ_g = 297.2 \text{ mV}$$

In the following the same notations as those of Hietanen and Sillén [11] will be used. The calculations will chiefly be based on the η function, since this is much more accurate than the Z function.

A plot of η against $\log h$ revealed two characteristic features. For higher values of η, a different curve for each Bi_{tot} was found, thus indicating polynuclearity. For low η values the curves coincided showing that only mononuclear complexes appear besides Bi^{3+}. To evaluate a more accurate E°_{am} the following method was adopted:

Table 2. Corresponding values of η and log h at equilibrium calculated with E°_{am} = 418.10 mV.

50 mM		25 mM		5 mM		2.5 mM	
η	log h	η	log h	η	log h	η	log h
1.756	1.664	2.071	1.393	1.918	1.173	2.057	0.987
1.635	1.725	1.887	1.484	1.714	1.277	1.757	1.134
1.504	1.797	1.674	1.592	1.485	1.391	1.447	1.292
1.423	1.834	1.559	1.649	1.361	1.455	1.291	1.371
1.317	1.890	1.414	1.721	1.209	1.530	1.105	1.461
1.170	1.963	1.330	1.767	1.121	1.576	0.868	1.589
1.051	2.024	1.221	1.820	1.007	1.631	0.695	1.673
0.947	2.080	1.069	1.897	0.849	1.714	0.555	1.754
0.859	2.124	0.944	1.961	0.721	1.783	0.445	1.814
0.783	2.165	0.840	2.014	0.615	1.836	0.354	1.867
0.714	2.200	0.750	2.060	0.525	1.887	0.281	1.914
0.653	2.234	0.672	2.102	0.448	1.928	0.223	1.952
0.600	2.260	0.604	2.137	0.381	1.965	0.165	1.991
0.551	2.288	0.543	2.170	0.323	2.002	0.142	2.025
0.504	2.312	0.488	2.201	0.273	2.033	0.118	2.054
0.466	2.332	0.439	2.228	0.230	2.062	0.100	2.085
0.430	2.354	0.394	2.253	0.193	2.090	0.090	2.108
0.394	2.377	0.354	2.274	0.161	2.114	0.082	2.135
0.363	2.393	0.316	2.297	0.135	2.137	0.076	2.160
0.329	2.417	0.283	2.316	0.115	2.160	0.068	2.199
0.306	2.430	0.254	2.337	0.099	2.179	0.062	2.236
0.253	2.464	0.226	2.356	0.086	2.201	0.054	2.296
0.176	2.513	0.199	2.375	0.077	2.218	0.049	2.348
0.119	2.561	0.176	2.391	0.069	2.236	0.044	2.391
0.084	2.600	0.138	2.420	0.060	2.266	0.040	2.429
0.062	2.643	0.104	2.452	0.054	2.296	0.036	2.461
0.045	2.678	0.081	2.476	0.051	2.323	0.036	2.490
0.043	2.705	0.063	2.500	0.048	2.347	0.034	2.515
0.039	2.732	0.052	2.522	0.045	2.370	0.033	2.538
0.038	2.757	0.041	2.564	0.041	2.410		
0.036	2.780	0.037	2.598	0.037	2.445		
0.035	2.800	0.034	2.628	0.034	2.476		
				0.032	2.503		

Consider the following mononuclear equilibria

$$Bi^{3+} + H_2O \rightleftharpoons BiOH^{2+} + H^+ \qquad \beta_1 = \frac{[BiOH^{2+}][H^+]}{[Bi^{3+}]}$$

$$Bi^{3+} + 2H_2O \rightleftharpoons Bi(OH)_2^+ + 2H^+ \qquad \beta_2 = \frac{[Bi(OH)_2^+][H^+]^2}{[Bi^{3+}]}$$

Together with

$$[Bi(III)]_{tot} = [Bi^{3+}] + [BiOH^{2+}] + [Bi(OH)_2^+] + \cdots\cdots$$

$$[Bi(III)]_{tot} = B \; ; [Bi^{3+}] = b \; ; [H^+] = h$$

Table 2 (continued)

1 mM		0.5 mM		0.1 mM	
η	$\log h$	η	$\log h$	η	$\log h$
2.001	0.839	2.502	0.481	2.215	0.301
1.608	1.041	2.293	0.588	1.981	0.455
1.240	1.223	2.058	0.699	1.535	0.653
1.065	1.318	1.771	0.833	1.327	0.763
0.861	1.418	1.561	0.940	1.164	0.845
0.753	1.474	1.396	1.025	1.042	0.943
0.617	1.547	1.259	1.097	0.929	0.997
0.442	1.646	1.135	1.155	0.716	1.112
0.315	1.731	0.963	1.250	0.622	1.173
0.225	1.794	0.821	1.320	0.516	1.232
0.168	1.850	0.705	1.387	0.411	1.320
0.136	1.900	0.610	1.436	0.356	1.362
0.116	1.944	0.530	1.476	0.306	1.427
0.105	1.982	0.463	1.521	0.269	1.504
0.096	2.017	0.406	1.559	0.237	1.575
0.089	2.041	0.340	1.598	0.214	1.629
0.083	2.078	0.287	1.642	0.195	1.676
0.079	2.106	0.229	1.684	0.168	1.749
0.074	2.132	0.183	1.742	0.134	1.831
0.071	2.152	0.159	1.788	0.126	1.905
0.068	2.174	0.141	1.829	0.103	1.967
0.065	2.195	0.120	1.869	0.099	2.020
0.061	2.214	0.113	1.903	0.079	2.110
0.059	2.232	0.100	1.937	0.071	2.180
0.054	2.265	0.092	1.993	0.057	2.240
0.051	2.295	0.082	2.039	0.057	2.291
0.049	2.322	0.076	2.083	0.053	2.335
0.047	2.347	0.071	2.130	0.048	2.374
0.044	2.370	0.066	2.158	0.044	2.409
0.040	2.410	0.062	2.191	0.040	2.440
0.036	2.445	0.058	2.221	0.037	2.468
0.034	2.475	0.051	2.248	0.036	2.495
0.033	2.502	0.047	2.297	0.032	2.518
0.032	2.526	0.043	2.340		
		0.040	2.378		
		0.036	2.412		
		0.034	2.443		

these equations give

$$\left(\frac{B}{b} - 1\right)h = \beta_1 + \beta_2 \cdot h^{-1} + \beta_3 \cdot h^{-2} + \ldots \ldots$$

The problem is then to find an E° value which gives a curve of the right shape when $\left(\dfrac{B}{b} - 1\right) h$ is plotted against h^{-1}. In Fig 1 three such curves are shown for different E° values, namely 418.30, 418.10 and 417.90 mV . The figure shows that the curves deviate appreciably for too high or too low E° values, leaving a range in which the correct value may be found. The "best
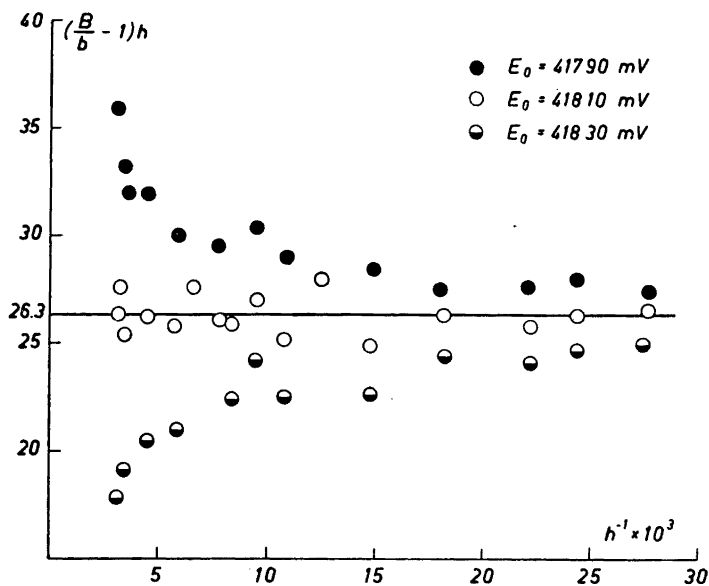
Fig 1. Determination of $E°_{am}$, β_1 and β_2. The middle curve represents $E°_{am} = 418.10$ mV and $\left(\dfrac{B}{b} - 1\right)h = 26.3$ mM.

$E°'' = 418.10$ mV was found to give an almost horizontal line with an intercept (equal to β_1) on the $\left(\dfrac{B}{b} - 1\right)h$ axis $= 26.3$ mM. Since the scatter is necessarily great a constant correct to more than 5 % cannot be expected; furthermore, it is hard to decide if the line is horizontal or has a small slope. The second mononuclear constant seems to be very small, and has not been considered in the further calculations. An analysis of the mononuclearity thus gives for the first hydrolysis stage an equilibrium constant 26.3 ± 2 mM with the second stage almost absent.

Determination of the main hydrolysis products. The recalculated η vs. log h curves (Fig 2) with $E°_{am} = 418.10$ mV revealed the following features for larger η values. The curves were almost parallel with a spacing $\left(\dfrac{\varDelta \log B}{\varDelta \log h}\right)_\eta = 2.4$ and had a slope of -2. It may be pointed out that these properties are independent of any chosen $E°_{am}$, since changing this parameter only means that the curves are shifted along the ordinate axis.

Let it be assumed that the general composition of the complexes may be written Me_qH_{-p};

$$B = b + \varSigma q\beta_{pq}b^qh^{-p} \simeq \varSigma q\beta_{pq}b^qh^{-p} \tag{3}$$

$$10\eta = \frac{B}{b} = 1 + \varSigma q\beta_{pq}b^{q-1}h^{-p} \simeq \varSigma q\beta_{pq}b^{q-1}h^{-p} \tag{4}$$

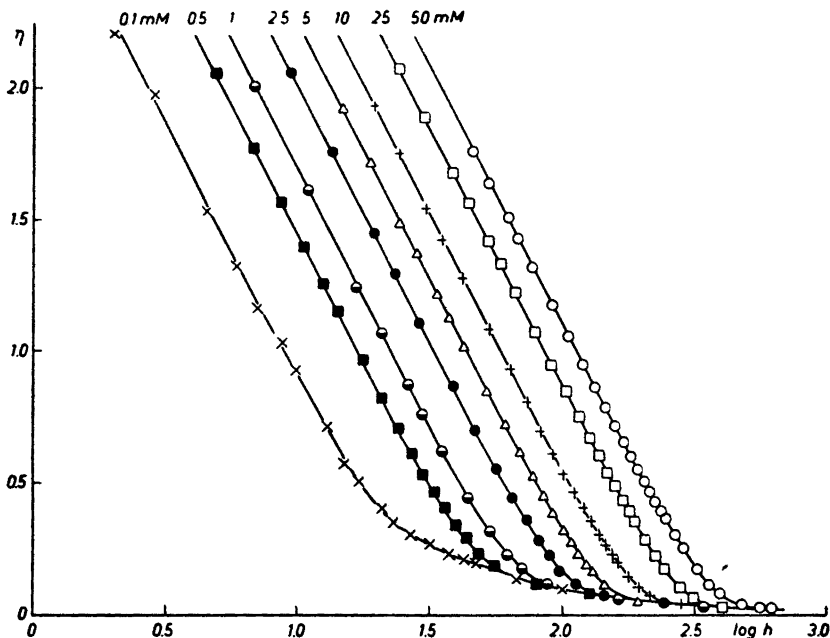*Fig 2.* $\eta = \log \dfrac{[\text{Bi(III)}]_{tot}}{[\text{Bi}^{3+}]}$ as a function of $\log h$. Curves are calculated with $\beta_1 = 26.3$ mM and $\beta_{12.6} = 2.14$ M⁷. For clarity not all of the experimental points are shown for low η values.

The curves give

$$B \text{ constant} ; \quad \eta = f(B) - 2 \log h \tag{5}$$

$$\frac{B}{b} \text{ constant} ; \quad \log B - 2.4 \log h = \text{const. or } 10\eta = f(b^{-1}h^{2.4}) \tag{6}$$

Eqns (6) and (4) give

$$\Sigma q\beta_{pq}b^{q-1}h^{-p} = f(b^{-1}h^{2.4})$$

which can be fulfilled only if

$$p = 2.4(q-1) \tag{7}$$

If (5) is rewritten as $\log B - \log b = f(B) - 2 \log h$, it is seen that $bh^{-2} = f'(B)$. This gives with (3)

$$bh^{-2} = f'(\Sigma q\beta_{pq}b^q h^{-p}) \text{ or } q = \frac{p}{2} \tag{8}$$

Eqns (7) and (8) give $q = 6$ and $p = 12$. The main complex may therefore be written $Bi_6(OH)_{12}^{6+}$ or more generally $Bi_6O_n(OH)_{12-2n}^{6+}$. The lines of argument in this discussion follow closely those of Sillén in AB I and II [12,13], and indeed the same result appears with his methods.
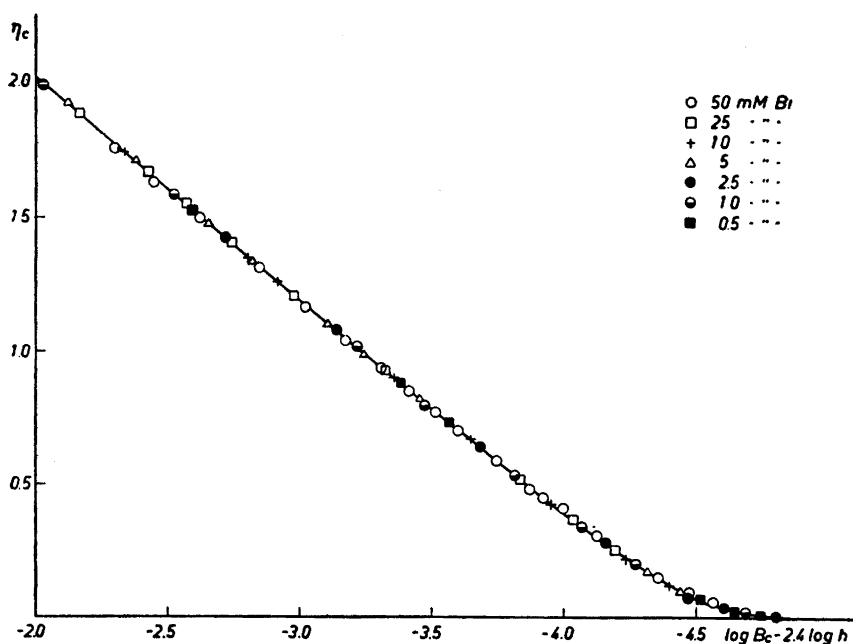
Fig 3. η_c as a function of $\log B_c - 2.4 \log h$ (see text). The curve is calculated with $\log \beta_{12,6} = 0.330$.

To evaluate the equilibrium constants for the hexamer the following method may be adopted. We define the functions B_c and η_c so that they have their usual meaning, except that the mononuclear part has been subtracted. From the relations,

$$B = b + \beta_1 b h^{-1} + 6\beta_{12 \cdot 6} b^6 h^{-12}$$

$$B_c = B - \beta_1 b h^{-1} = b + 6\beta_{12 \cdot 6} b^6 h^{-12}$$

$$\frac{B_c}{b} = 10^{\eta_c} = 1 + 6\beta_{12 \cdot 6} b^5 h^{-12} = 1 + \frac{6\beta_{12 \cdot 6}}{10^{5\eta_c}} [B_c h^{-2.4}]^5$$

it follows that η_c is a function of the single variable $\log .B_c - 2.4 \log h$. In Fig 3, η_c is shown as a function of $\log B_c - 2.4 \log h$. Since all the experimental points fall on a single curve, we might conclude that the concentrations of complexes other than $BiOH^{2+}$ and $Bi_6(OH)_{12}^{6+}$ must be small. By comparing this curve with a "normalized" one the equilibrium constant of the hexamer is obtained as $\log \beta_{12,6} = 0.330 \pm 0.005$, M scale. The uncertainty in this value lies in the E°_{am} determination.

It might at this point be asked with what certainty one can say that there are 6 Bi in the complex and not for instance 5 or 7. These complexes correspond to the spacings 2.50 and 2.33, thus lying very near to 2.4. It

was therefore decided to make calculations using these assumptions too. These calculations showed, however, that a good fit could not be obtained over the whole B range but when only a narrow concentration range in B is considered, it is not easy to draw any definite conclusions. This shows the desirability of covering as wide a concentration range as possible.

The graphic methods developed by Biedermann and Sillén [14] using "normalized" curves should be applicable to this case. On account of the preceding discussion the assumption is made that the only species present, apart from Bi^{3+}, are $BiOH^{2+}$ and $Bi_6(OH)_{12}^{6+}$. This leads to a three-parameter problem since E°_{am} is unknown in addition to the equilibrium constants. The method is based on cuts for constant η. The family of experimental curves for constant η values

$$x = \log\ B - 2.4\ \log\ h$$
$$y = \log\ h$$

are plotted and compared with a graph of the theoretical, normalized curves

$$X = \log B - 2.4\ \log\ h + \log\ k = \eta + \log\ v$$
$$Y = -\log\ a = \log\ h - \log\ \beta_1 = -\log(10^\eta - 1 - v^5)$$

where $k^5 = 6\ \beta_{12.6}$; $v = kbh^{-2.4}$.

By eliminating the parameter v, we obtain

$$Y = -\log(10^\eta - 1 - 10^{5(X-\eta)})$$

From this equation we can calculate the family of curves $Y(X)_\eta$. The two graphs are laid on top of each other to coincide as closely as possible and the differences on the x and y axes in this position give the equilibrium constants.

The correct E°_{am} is obtained by considering the smallest η values; since in this range η is dependent on $\log\ h$ only, Y must be independent of v which happens only when v equals zero. Corresponding values between η and $\log\ a$ are obtained by putting $v = 0$. A curve $\eta(\log\ a)$ may thus be found. From experimental data based on different E°_{am}, a family of curves $\eta(\log\ h)_{E^\circ_{am}}$ is obtained. It is now possible to plot $\log\ a(\log\ h)_{E^\circ_{am}}$ for each of the chosen E°_{am}. The curve for the right E°_{am} should give a straight line of slope -1. In this way the same $E^\circ_{am} = 418.1$ mV was obtained as by the earlier method. In Fig 4 the normalized curves are shown together with the experimental points in the position of "best fit". The equilibrium constants found are $\log\ \beta_1 = -1.585$ ($\beta_1 = 0.026$ M) and $\log\ \beta_{12.6} = 0.325$ (M scale), comparing favorably with the earlier results. It may be pointed out that in this method the constants may be varied simultaneously and independently of each other.

Since the Z values $\left(\dfrac{h-H}{B}\right)$ must necessarily be quite uncertain in such acid solutions as have been used in this investigation, they were thought not to be worth a separate treatment. This gap, it is hoped, will be filled by conductimetric measurements; however, there was no doubt that the limiting value of Z is 2. In addition, the quantity $\dfrac{h-H}{B-b}$ (the number of hydrogen
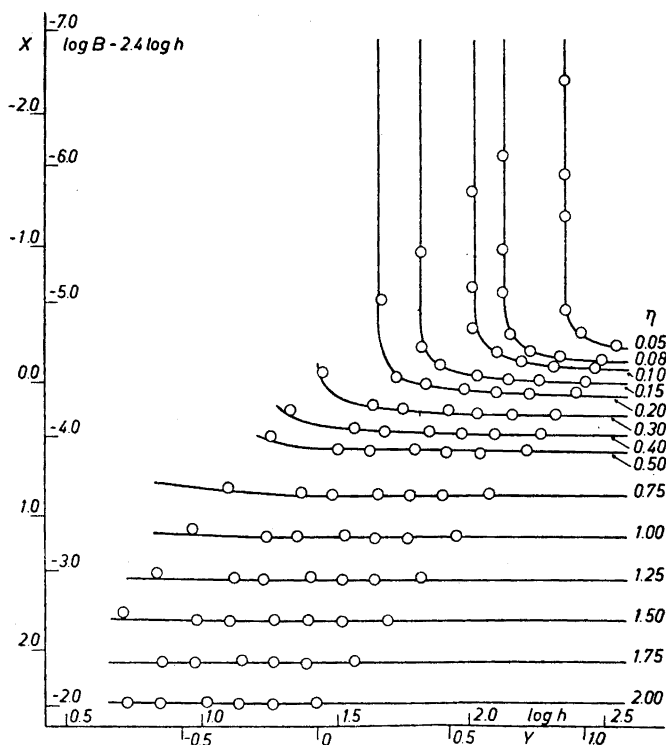
Fig 4. X, Y curves and experimental points x, y (see text) in position of »best fit». O experimental points.

ions set free by the complexed bismuth) was found to vary between 1.95 and 2.05 in the region where polynuclear species predominate. This strongly indicates that in the most hydrolysed solutions the ratio Bi:OH in the complex (es) formed is 1:2.

DISCUSSION

The present investigation of the hydrolysis of Bi^{3+} leads to a different mechanism from that proposed by Granér and Sillén [1], who used the same type of investigation. As has already been pointed out, it is difficult to decide what mechanism is the most likely, when only a rather small concentration range has been measured: a small error may completely change the picture. In the case of Granér and Sillén, who only studied the concentration range 10—50 mM of Bi(III), one probable error can be pointed out. They calculated with liquid junction potentials obtained from quinhydrone measurements. As was found later by Biedermann and Sillén [10] the quinone acts as a base [15] and the liquid junction potentials are not applicable to a quinhydrone-free system. This leads to an error of 0.1 units in η in the most unfavorable cases.

The most recent works on bismuth perchlorate all seem to indicate the presence of only one complex. Its composition was, however, not definitely established. There seems to be no doubt that the ratio Bi:O is 1:1, but the number of bismuth atoms in the complex has not hitherto been ascertained. The work of Faucherre [3] is not comparable since it was carried out in solutions of so low acidity, that they cannot be obtained when working in a strong ionic medium because of precipitation. In the present investigation the most hydrolysed solutions gave η values around 3. These points lie on the extensions of the curves in Fig. 3 and give no indication of a new reaction. The solutions were not quite stable but gave a small precipitate after standing for about a week. We hope, however, to be able to carry out titrations at lower ionic strength to find out what happens at higher pH values.

If only one complex is formed, it is hard to imagine it as a chain or a layer, since a complex with a certain, relatively high number of atoms in it would not be expected to dominate; however, for a complex containing six metal atoms one can visualise models of high symmetry. This symmetry could then account for the extreme stability and presence of only one predominating complex. These models must, however, be accepted with scepticism and need confirmation from structural data both in solution and in the solid state. Work in this direction is planned. The absence of $Bi(OH)_2^+$ is remarkable. The reason for this may be that the "hexamer" is so stable compared to $Bi(OH)_2^+$ that the equilibrium concentration of this complex is too low to be detected.

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