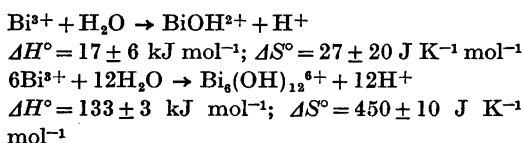


A Thermochemical Study of Hydrolysed $\text{Bi}(\text{ClO}_4)_3$ Solutions

ÅKE OLIN

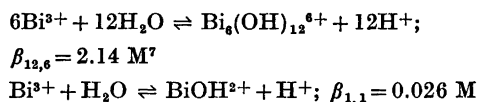
Institute of Chemistry, University of Uppsala, P.O.B. 531, S-751 21 Uppsala, Sweden

The enthalpy and entropy changes of the hydrolysis reactions of Bi^{3+} have been determined by enthalpy titrations with hydrolysed $\text{Bi}(\text{ClO}_4)_3$ solutions in 3 M $(\text{Na})\text{ClO}_4$ at 25 °C. The results were:



The measurements also indicate that at least one further complex is present in small amounts in addition to the species $\text{Bi}_6(\text{OH})_{12}^{6+}$ and BiOH^{2+} found earlier from emf measurements. It is tentatively identified as $\text{Bi}_3(\text{OH})_4^{5+}$.

From emf measurements¹ on hydrolysed bismuth(III) perchlorate solutions in 3 M $(\text{Na})\text{ClO}_4$ medium the following reactions and equilibrium constants were suggested



Some years ago a calorimetric study was made on this system using the titration technique developed by Schlyter.² When the enthalpy changes of the above reactions were calculated by the methods described in Ref. 3, it was found that the estimated standard deviation in the heat evolved per addition was somewhat larger than expected from the calorimetric measurement uncertainties. This cast some doubt on the correctness of the hydrolysis scheme proposed from the emf data, particularly as the interpretation of such data is uncertain when high powers are present in the expressions for the equilibria. It was therefore decided to postpone further treatment of the calorimetric

data until more evidence had been accumulated to establish the correctness of the formulas of the species present. A bismuth(III) hydroxide perchlorate formed from equilibrium solutions has now been shown from a crystal structure determination⁴ to contain discrete hexameric units with the same structure as suggested from X-ray diffraction studies on solutions.⁵ With the composition of the main complex now firmly established, the calculations on the data from the enthalpy titrations have been resumed and the results will be presented here.

EXPERIMENTAL

The experiments were carried out in the apparatus described by Schlyter² as a series of titrations in which a strongly acid $\text{Bi}(\text{ClO}_4)_3$ solution, T, was added to a hydrolysed bismuth(III) perchlorate solution, S, in the calorimeter. The compositions of S and T were chosen so that in each titration $[\text{Bi}(\text{III})] = B$, and $[\text{ClO}_4^-] = 3.000 \text{ M}$ were kept constant. The analytical hydrogen ion concentrations, H , in the solutions were $(B, H_S, H_T/\text{mol dm}^{-3})$; 0.010, -0.01020, 2.655; 0.025, -0.02552, 2.892; 0.050, -0.05105, 2.809; 0.100, -0.1306, 2.580; 0.0, 2.980.

Two titrations were made for each value of B . The results from the runs with $B=0$ were used to correct the heat evolved per addition, Q , for the heat of dilution of the perchloric acid in the titrant. The preparation and analysis of the chemicals and stock solutions were made as described in Ref. 1.

CALCULATIONS

The data have been treated with the least squares computer program LETAGROP KALLE,⁶ which searches for a set of parameters that minimizes the error square sum $U = \sum(Q_{\text{calc}} - Q_{\text{exp}})^2$. The parameters to be determined are primarily the enthalpy changes, $l_{p,q}$,

Table 1. Results from the least squares refinements *i*–*v*. Only parameters followed by the estimated standard deviation within parenthesis have been varied. The values of $l_{p,q}$ are in kJ mol^{-1} , $\sigma(Q)$ and δQ in J, and $\beta_{q,p}$ in $\text{M}^{(p-q+1)}$.

Refinement	$\beta_{12,6}$	$l_{12,6}$	$\beta_{1,1} \times 10^2$	$l_{1,1}$	$\sigma(Q)$	δQ	$\beta_{4,3}$	$l_{4,3}$
<i>i</i>	2.14	132	2.60	16	0.29			
		(1)		(2)				
<i>ii</i>	2.1	132	3.0	17	0.28			
	(0.2)	(1)	(0.2)	(3)				
<i>iii</i>	2.14	125	2.60	12	0.23	0.42		
		(1)		(2)		(0.08)		
<i>iv</i>	2.14	133	2.60	17	0.22		0.16	54
		(1)		(2)			(0.02)	(4)
<i>v</i>	2.14	133	2.60	14	0.23		0.16	56
		(0.5)		(2)				(4)

of the hydrolysis reactions $q\text{Bi}^{3+} + p\text{H}_2\text{O} \rightleftharpoons \text{Bi}_q(\text{OH})_p + p\text{H}^+$. For convenience, charges will be omitted on the complex. The equilibrium constants, $\beta_{p,q}$, can also be treated as adjustable parameters by the program as well as (constant) errors in the analyses of the solutions and in the measurement of Q . In order to save computer time only one of the titrations for each value of B was included in the calculations. Moreover, data for $B=0.1$ M were excluded at first, since most of the data for this B value refer to solutions with so high and varying acidities that it appeared doubtful if the basic assumption of constant activity factors was valid. The selected

titrations comprise 56 data points (V/cm^3 , Q/J). V denotes the volume of titrant added.

The calculations will be reported as a series of refinements (*i*–*v*) in which the $l_{p,q}$ have been computed under various assumptions. The results are collected in Table 1 for ease of comparison. A number within parenthesis is the estimated standard deviation (esd.) calculated by the program. If the value of a parameter is not followed by an esd. the parameter was kept constant during the refinement. $\sigma(Q)$ is the esd. of $Q_{\text{calc}} - Q_{\text{exp}}$.

i. $l_{12,6}$ and $l_{1,1}$ were calculated assuming the equilibrium constants from the emf measure-

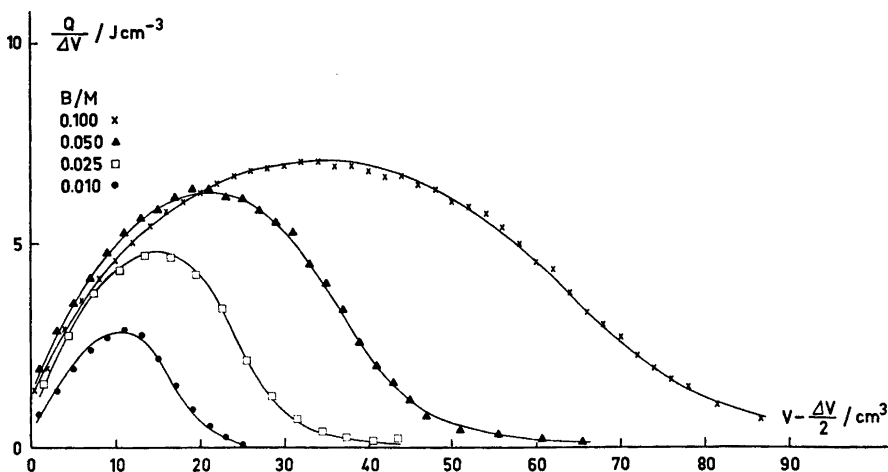


Fig. 1. The heat evolved in an experimental point per cm^3 of titrant added, $Q/\Delta V$, as a function of $V - \Delta V/2$. V is the total volume of titrant. The curves have been drawn through the $Q/\Delta V$ values calculated with the parameters from refinement *v*.

ments to be correct. The $\sigma(Q)$ is larger than the value expected from the calorimeter measurement uncertainties, 0.15–0.20 J, and the differences between Q_{calc} and Q_{exp} are systematic at the highest acidities. More heat is evolved than expected from the model. On the whole, however, there is a reasonable agreement between Q_{calc} and Q_{exp} and the fact that the former follows the rather unusual course of Q_{exp} (see Fig. 1) points to the essential correctness of the data and their interpretation. The heats evolved at high acidities moreover confirm that complexes other than $\text{Bi}_6(\text{OH})_{12}^{6+}$, viz. BiOH^{2+} , must also be present. From the emf measurements this was not so easily recognized at high values of B on account of the large liquid junction potentials.

ii. $l_{p,q}$ and $\beta_{p,q}$ were varied simultaneously. The program partly failed to find the minimum in U (see "slumpskott" in LETAGROP program description). The values of the standard deviations are therefore approximate. A recalculation of $\beta_{12,6}$ and $\beta_{1,1}$ from the data given in Ref. 1 was made with the program LETAGROP VRID, version ETITR.⁷ The following values were obtained: $\beta_{12,6} = 2.14(0.04) \text{ M}^7$ and $\beta_{1,1} = 2.64(0.04) \times 10^{-2} \text{ M}$. These values agree very well with those obtained graphically in the original work. $\sigma(E)$ was 0.18 mV for 134 data points (every second was used). The first four points in the 0.0001 M titration and the first point in the 0.0005 M titration showed large deviations between E_{calc} and E_{exp} . If these points were rejected $\sigma(E)$ dropped to 0.13 mV. Since there is good agreement between the equilibrium constants obtained from the emf and the calorimetric measurements the discrepancies in the heat data at high acidities are not likely to be caused by erroneous equilibrium constants. They may rather be caused by the presence of small amounts of additional complexes or systematic errors.

iii. Analytical and systematic errors in the calorimetric measurements. Since $\text{Bi}^{3+}(\text{aq})$ is a rather strong acid the deviations at high acidities can not be removed by the introduction of analytical errors of reasonable magnitude. No calculations were therefore made on this assumption. One calculation on the 0.05 and 0.025 M titrations was performed with an assumed, constant error in Q , δQ . Despite the improvement in $\sigma(Q)$ the result is difficult to accept,

since, it is hard to find a reasonable explanation for a δQ as large as 0.4 J.

iv. Additional complexes present. In this series of refinements it was assumed that in addition to $\text{Bi}_6(\text{OH})_{12}^{6+}$ and BiOH^{2+} , $\text{Bi}_q(\text{OH})_p$ was present. The following pairs of p and q were tested: (p,q) , (2,1), (2,2), (3,2), (4,2), (3,3), (4,3), (5,3), (6,3), (4,4). These pairs include most of the p,q combinations found in the hydroxo complexes of metal ions. $\beta_{p,q}$ was estimated from the deviations between Q_{calc} and Q_{exp} at high acidities on the assumption that $l_{p,q}/p = 12.5 \text{ kJ mol}^{-1}$. This is a rounded-off value based on $l_{12,6}$ and $l_{1,1}$. The (V,Q) data were next subjected to a least squares treatment in which $\beta_{12,6}$ and $\beta_{1,1}$ were kept constant and the other parameters varied. These calculations ruled out the combinations (2,1), (2,2), (3,3), and (4,4), which either failed to converge or decrease $\sigma(Q)$. The compatibilities of the remaining combinations with the emf data were next tested by calculating $\Delta E = E_{\text{calc}} - E_{\text{exp}}$ using the β values from the calorimetric data. This test definitely ruled out (4,2) and (6,3) which showed large ΔE . (3,2) showed smaller but systematic deviations and was also rejected, which left (4,3) and (5,3) as possible species. No choice between these alternatives could be made from the error square sums. The value of $l_{5,3} = 38(8) \text{ kJ mol}^{-1}$ is smaller than expected, since $l_{p,q}/p$ in most systems has been found to be almost constant.⁸ With one additional complex, $\text{Bi}_3(\text{OH})_4^{5+}$ would hence be the most likely alternative and only data for this complex have been entered in Table 1.

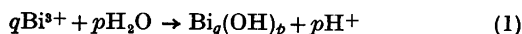
A refinement of the emf data with $\text{Bi}_3(\text{OH})_4^{5+}$ included gave $\beta_{12,6} = 2.09(0.04) \text{ M}^7$, $\beta_{1,1} = 2.60(0.04) \times 10^{-2} \text{ M}$, and $\beta_{4,3} = 0.20(0.07) \text{ M}^2$, and $\sigma(E) = 0.11 \text{ mV}$ (five points excluded). $\beta_{12,6}$ and $\beta_{1,1}$ are thus almost unaffected by the introduction of $\text{Bi}_3(\text{OH})_4^{5+}$ and within one standard deviation the same value of $\beta_{4,3}$ is obtained from the emf and calorimetric measurements.

v. Data from one titration with $B = 0.1 \text{ M}$ were included in the refinement. $\sigma(Q)$ for 98 data points became 0.23 J, which may be compared with the value 0.32 J if $\text{Bi}_3(\text{OH})_4^{5+}$ is left out. The agreement between Q_{calc} and Q_{exp} is shown in Fig. 1.

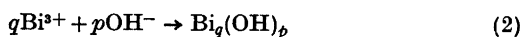
DISCUSSION

From Table 1 one may conclude that despite the various assumptions made, the values of $l_{12,6}$ and $l_{1,1}$ stay fairly constant. Since the relative amount of BiOH^{2+} increases with decreasing B the value of $l_{1,1}$ obtained from refinements *i*, *ii*, and *iv* will be used. The presence of $\text{Bi}_3(\text{OH})_4^{5+}$ is only tentative. The concentration of any additional complex is at most a few percent of B and its presence and composition hence difficult to establish. Further discussion of the data for $\text{Bi}_3(\text{OH})_4^{5+}$ will therefore not be made.

Table 2 contains some thermodynamic quantities for $\text{Bi}_6(\text{OH})_{12}^{6+}$ and BiOH^{2+} calculated per mol of complex formed. Symbols without a subscript refer to the reaction



Quantities for the reaction



have subscripted symbols. In the calculations of these quantities, ΔH° for $\text{H}_2\text{O} \rightarrow \text{H}^+ + \text{OH}^-$ was taken as 54.8 kJ mol^{-1} and ΔS° as $-88 \text{ J K}^{-1} \text{ mol}^{-1}$.

The enthalpy and entropy parts of the free energy change for reaction (2) are both favourable. This is also the case for other metal ions. Reckoned per mol of hydroxide, the values of $-\Delta H^\circ$ and ΔS° are amongst the largest hitherto observed and they make $\text{Bi}^{3+}(\text{aq})$ one of the strongest acids of its kind. $-\Delta H^\circ_{\text{OH}/p}$ for hydroxo complexes of divalent metal ions are with few exceptions less than 35 kJ mol^{-1} ,⁸ which is considerably less than 44 kJ mol^{-1} found for $\text{Bi}_6(\text{OH})_{12}^{6+}$. Although a direct com-

Table 2. Thermochemical data for hydroxo complexes of Bi^{3+} . Unsubscripted quantities refer to the reaction $q\text{Bi}^{3+} + p\text{H}_2\text{O} \rightarrow \text{Bi}_q(\text{OH})_p + p\text{H}^+$ and subscripted, to the reaction $q\text{Bi}^{3+} + p\text{OH}^- \rightarrow \text{Bi}_q(\text{OH})_p$. The limits of error correspond to 3 σ .

	$\text{Bi}_6(\text{OH})_{12}^{6+}$	BiOH^{2+}
$\Delta G^\circ / \text{kJ mol}^{-1}$	-1.89 ± 0.14	9.01 ± 0.15
$\Delta H^\circ / \text{kJ mol}^{-1}$	133 ± 3	17 ± 6
$\Delta S^\circ / \text{J K}^{-1} \text{ mol}^{-1}$	450 ± 10	27 ± 20
$\Delta H^\circ_{\text{OH}} / \text{kJ mol}^{-1}$	-525	-38
$\Delta S^\circ_{\text{OH}} / \text{J K}^{-1} \text{ mol}^{-1}$	1500	115

parison of these figures is somewhat hazardous because of probable variations in the coordination numbers of the oxygen atoms, a larger value for the bismuth complex is reasonable on account of the higher charge of the Bi^{3+} ion. The entropy change, again reckoned per mol of hydroxide, is generally less than $100 \text{ J K}^{-1} \text{ mol}^{-1}$ for divalent metal ions.⁸ The corresponding value for $\text{Bi}_6(\text{OH})_{12}^{6+}$ is $125 \text{ J K}^{-1} \text{ mol}^{-1}$. The greater reduction in net charge per metal ion which occurs for the bismuth complex probably causes the increase in $\Delta S^\circ_{\text{OH}/p}$. The standard entropy of $\text{Bi}^{3+}(\text{aq})$, $-190 \pm 10 \text{ J K}^{-1} \text{ mol}^{-1}$,⁹ is lower than for most divalent ions, which also can be expected to contribute to a higher ligational entropy for Bi^{3+} .

The wide variety of compositions found for the hydrolysis products of metal ions make correlations of the thermodynamic data for hydroxo complexes with such quantities as charge and size difficult to detect and few relationships of this type have been proposed. Messmer and Baes¹⁰ suggested the relation; $\Delta S^\circ_{\text{OH}}(\text{corr})/p = 28 + 1.0Z^2 \text{ cal K}^{-1} \text{ mol}^{-1}$, where Z is the charge of the uncomplexed metal ion and $\Delta S^\circ_{\text{OH}}(\text{corr})$ is the entropy change corrected for the cratic part.¹¹ For $\text{Bi}_6(\text{OH})_{12}^{6+}$ this quantity is $41 \text{ cal K}^{-1} \text{ mol}^{-1}$, which is larger than predicted. The value of the constant term (28) appears, however, to be somewhat too low to judge from the data presented by Arnek.⁸

REFERENCES

- Olin, Å. *Acta Chem. Scand.* 11 (1957) 1445.
- Schlyter, K. *Trans. Roy. Inst. Technol. Stockholm* (1959) No. 132.
- Carell, B. and Olin, Å. *Acta Chem. Scand.* 16 (1962) 2357.
- Sundvall, B. *Acta Chem. Scand. A* 28 (1974) 1036.
- Danforth, M. D., Levy, H. A. and Agron, P. A. *J. Chem. Phys.* 31 (1959) 1458.
- Arnek, R. *Ark. Kemi* 32 (1970) 81.
- Brauner, P., Sillén, L. G. and Whiteker, R. *Ark. Kemi* 31 (1969) 365.
- Arnek, R. *Ark. Kemi* 32 (1970) 55.
- Vasil'ev, V. P. and Ikonnikov, A. A. *Zh. Fiz. Khim.* 45 (1971) 292.
- Mesmer, R. E. and Baes, C. F., Jr. *Inorg. Chem.* 6 (1967) 1951.
- Gurney, R. W. *Ionic Processes in Solution*, McGraw Hill, New York 1953.

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