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The Stability of Metal Halide Complexes in Aqueous Solution

III. The Chloride, Bromide and Iodide Complexes of Bismuth

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The chloride, bromide and iodide complexes of Bi^{3+} have been studied in an acid perchlorate medium by means of emf and solubility measurements. The overall stability of these complex systems increases in the order mentioned; Bi^{3+} thus belongs to the central ions of the second group (*cf.* Ref.[1]). The first bromide complex is however a little weaker than the first chloride one. Thus Bi^{3+} also possesses certain properties of the first group central ions, as could perhaps be expected from its position in the outskirts of the second group area. The sixth complex is the one finally formed in all the systems measured; in the case of chloride and bromide the fifth complex has a remarkably wide range of existence.

With respect to the strength of their halide complexes, central ions may be divided into two groups. The first one shows decreasing stability of the complexes in the order $F^- \gg Cl^- > Br^- > I^-$, the second one in the opposite order $F^- \ll Cl^- < Br^- < I^-$. In part I of this series [1] it was pointed out that the ions of the second group were all situated within a roughly triangular area of the periodic system, centered around the noble metals. The primary aim of the present investigation has been to decide whether Bi^{3+} is also within this area, a question which was left open in the previous paper.

As Bi^{3+} is readily hydrolysed [2], the measurements have to be performed in acid solutions so that the halide complex formation is not mixed up with intricate hydrolytic reactions. In this work all solutions had $[H^+] = 1$ M, an acidity ensuring that no perceptible amounts of soluble hydroxo complexes exist at the bismuth concentrations used. Due to their very low solubility, the oxyhalides BiOCl and BiOBr are nevertheless precipitated even from solution of quite low $[Bi^{3+}]$. When further halide is added the precipitates however dissolve again owing to the strong decrease of $[Bi^{3+}]$ caused by the increasing complex formation. In the case of the iodide, the neutral third complex

BiI_3 is precipitated, as being the least soluble solid phase in the medium used. This precipitate also dissolves with the formation of higher complexes when further amounts of ligand are added.

As to methods available for the investigation, emf measurements of the concentration of free central ion, $[Bi^{3+}]$, by means of a bismuth amalgam electrode seemed most convenient (*cf.* Ref.[2]). According to the experience gained here this method worked well if the total bismuth concentration, C_M, was $\gtrapprox 0.5$ mM. Where the halide concentration, C_A, of the solutions allowed such values of C_M, the complex formation could therefore be followed by emf measurements. This turned out to be the case for the greatest part of the complex formation of the chloride and bromide systems, where only the first constant could not be determined. In the case of the iodide, on the other hand, only the constant of the final (*i. e.* the sixth) complex could be obtained in this way.

The investigation could, however, be extended to lower ligand concentrations by means of solubility determinations (*cf.*, *e. g.*, Leden[3,4]). With the method employed here, solutions of a C_M (= the solubility l) as low as ≈ 0.02 mM could be analysed. For the calculation of the stability constants, the solubility products of the solid phases BiOCl, BiOBr and BiI_3 were also needed. The determination of these quantities sometimes required the measurement of $[Bi^{3+}]$ in solutions of $C_M \approx 0.2$ or even 0.1 mM. This was often successfully accomplished especially if C_A was not too low, but great care had to be exercised in these measurements and evidently this range of C_M is not very suitable for emf measurements.

Good values of the first constant of the chloride and bromide system could be determined by these solubility measurements, which also confirmed some of the constants previously determined potentiometrically. For the iodide system values of the last three constants could be obtained. The two methods employed thus complement each other rather satisfactorily.

All values of constants found refer to the acid perchlorate medium used which had a total ionic strength $I = 2$ M. As usual, sodium perchlorate was used as supplementary neutral salt. The temperature has been kept at 20°C.

CALCULATION OF COMPLEXITY CONSTANTS FROM MEASUREMENTS OF $[Bi^{3+}]$ (=[M]) WITH THE BISMUTH AMALGAM ELECTRODE

Experimentally, the emf E of cells of the following type were measured

$$+\ \mathrm{RE}\ \left|\ \begin{array}{l} C_M \text{ mM Bi(III)} \\ C_A \text{ mM ligand} \\ [\mathrm{H}^+] = 1 \text{ M};\ I = 2 \text{ M} \end{array}\ \right|\ \text{Bi-Hg}\ -$$

where RE is a quinhydrone reference electrode. This emf can be written as

$$E = E_{RE} + E_d - E^\circ - \frac{RT}{3F} \ln f_M \cdot [\mathrm{M}] \qquad (1)$$

In this expression E_{RE} and E° are of course independent of variations of C_M and C_A and the same will be very nearly true for the liquid junction potential

E_d and the activity factor f_M in the approximately constant medium used. Hence (1) can be written

$$E = E_k - \frac{RT}{3F} \ln [\mathrm{M}] \tag{2}$$

where E_k is a constant. If the emf of the special case of $C_A = 0$, $[\mathrm{M}] = C_M$ is denoted E' we obtain:

$$E - E' = E_M = \frac{RT}{3F} \ln \frac{C_M}{[\mathrm{M}]} \tag{3}$$

From the quantity $C_M/[\mathrm{M}]$ thus found, the stability constants β were calculated by Leden's [5,6] method as developed by Fronæus [7] (*cf.* also Ref.[8]):

If only mononuclear complexes MA_n are formed then

$$C_M \, / \, [\mathrm{M}] = 1 + \sum_{n=1}^{N} \beta_n \, [\mathrm{A}]^n = X([\mathrm{A}]) \tag{4}$$

The value of [A] for a certain value of X thus found is obtained by a method of extrapolation. E_M is determined as a function of C_A in solutions containing different C_M. From the resulting family of curves values of C_A are read off for a number of values of E_M. Every value of E_M then corresponds to a certain constant value of [A], as seen from (3) and (4), andt herefore also to a constant ligand number $\bar{n}$ (*cf.* Ref. [5-8]). Thus if corresponding values of C_A and C_M are plotted for a certain E_M a straight line $C_A = \bar{n} \cdot C_M + [\mathrm{A}]$ will result, with the intercept on the C_A-axis $= [\mathrm{A}]$ and the slope $= \bar{n}$. When corresponding values of X and [A] have thus been found, the constants β are calculated from (4). Different methods of calculation have however to be used for the chloride and bromide on the one hand and the iodide system on the other.

For the chloride and bromide systems where, at the pH used in this investigation, most of the complex formation can be covered by the emf measurements, the constants are calculated in the usual way [9], by extrapolation of functions X_n. Thereby β_1 is obtained first and then successively the following constants up to β_N.

In the case of the iodide system on the other hand emf measurements can be performed only for the very last part of the complex formation due to the low solubility of the neutral complex MA_3. In the whole measurable range, MA_N is the dominating species. Its constant is conveniently calculated by forming a new function

$$X'_N = \frac{X}{[\mathrm{A}]^N} = \beta_N + \beta_{N-1} \cdot [\mathrm{A}]^{-1} + \sum_{n=2}^{N-1} \beta_{N-n} [\mathrm{A}]^{-n} + [\mathrm{A}]^{-N} \tag{5}$$

When X'_N is plotted against $1 \, / \, [\mathrm{A}]$, β_N will be found as the intercept of the X'_N -axis, and β_{N-1} as the slope of the curve at the point of intersection * (*cf.*[6] p. 16).

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* In the present case only β_N can be calculated, owing to the predominance of the highest complex in the range measured. In principle however further constants may be calculated by successively forming new functions X', in the first instance

$$X'_{N-1} = (X'_N - \beta_N) \cdot [\mathrm{A}] = \beta_{N-1} + \beta_{N-2}[\mathrm{A}]^{-1} + \sum_{n=3}^{N-1} \beta_{N-n} \cdot [\mathrm{A}]^{1-n} + [\mathrm{A}]^{1-N}$$

If the complex formation is not entirely mononuclear, (4) no longer holds, C_M / [M] being a function of both [A] and [M]. By extrapolating the C_M, C_A-lines of constant E_M to $C_M = 0$ (implying [M] = 0), corresponding values of [A] and X will nevertheless be found and hence correct values of β calculated, as shown by Fronæus (Ref.[7], p. 20). The slope of these lines will however not be $= \bar{n}$ in this case but a quantity $< \bar{n}$. By comparing the genuine complex formation function $\bar{n} = f([A])$, calculated from the found values of β with the values obtained from the C_A, C_M slopes, the existence of polynuclear complexes can thus be revealed.

CALCULATION OF COMPLEXITY CONSTANTS FROM MEASUREMENTS OF THE SOLUBILITY OF Bi(III) IN HALIDE SOLUTIONS

If only mononuclear complexes are assumed to exist in solutions of Bi(III), the solubility l can written as

$$l = [\mathrm{M}] \left(1 + \sum_{n=1}^{N} \beta_n [\mathrm{A}]^n\right) = [\mathrm{M}] \cdot X \tag{6}$$

bearing in mind that soluble hydroxo complexes certainly do not exist in the medium used [2]. Now in the cases of chloride and bromide the formula of the solid phase is MOA which we may consider as formed according to the reaction $\mathrm{M} + 2\ \mathrm{OH}^- + \mathrm{A} \rightleftharpoons \mathrm{MOA} + \mathrm{H_2O}$. Thus

$$[\mathrm{M}][\mathrm{OH}^-]^2[\mathrm{A}] = L = [\mathrm{M}][\mathrm{A}] \cdot \frac{K_w^2}{[\mathrm{H}^+]^2} \tag{7}$$

As $[\mathrm{H}^+]$ is kept constant throughout the measurements a new constant L' may be introduced:

$$[\mathrm{M}][\mathrm{A}] = \frac{L}{K_w^2} \cdot [\mathrm{H}^+]^2 = L' \tag{8}$$

Combining (6) and (8) we arrive at

$$l - \frac{L'}{[\mathrm{A}]} = L'\left(\beta_1 + \sum_{n=2}^{N} \beta_n [\mathrm{A}]^{n-1}\right) = L' \cdot X_1 \tag{9}$$

The value of [A] corresponding to a certain value of l is given by

$$[\mathrm{A}] = C_A - (C'_M - l) - \bar{n} \cdot l \tag{10}$$

where C'_M is the stoicheiometric concentration of Bi(III) added, most of it $(= C'_M - l)$ being precipitated. In all the solubility measurements, l is fairly low and $\bar{n} \cdot l$ only a correction term. Therefore a sufficiently good value of $\bar{n}$ is obtained by taking from the complex formation curve of the emf measurements the value corresponding to $[\mathrm{A}] = C_A - (C'_M - l)$. Using this value of $\bar{n}$, a value of [A] is calculated from (10). This value of [A] gives in turn a better value of $\bar{n}$ which however when inserted in (10) does not appreciably change the value of [A] already obtained.

Provided only that L' can be found, $L' \cdot X_1$ is therefore known as a function of [A]. From this function the constants β can be calculated in the same way as from the simple X-functions, *cf.* p. 000. The function $L'\cdot X_1$ has an intercept on the ordinate axis $= L'\cdot\beta_1$. The next constant β_2 is conveniently found by forming the function

$$\frac{L'X_1 - L'\beta_1}{[\mathrm{A}]} = L'\Big(\beta_2 + \sum_{n=3}^{N} \beta_n[\mathrm{A}]^{n-2}\Big) = L'\cdot X_2 \tag{11}$$

whose extrapolation to $[\mathrm{A}] = 0$ gives $L'\cdot\beta_2$. Analogously further constants may be found.

For the determination of $L' = [\mathrm{M}]\,[\mathrm{A}]$, [M] of saturated solutions of known [A] has to be measured. This is done by measuring emf of cells of the type written on p. 1112. From the values of L' thus determined it is further possible to calculate the solubility product L of the oxyhalides if K_w of the solvent medium is measured.

In the case of the iodide system where MA_3 is present as solid phase,

$$L = [\mathrm{M}][\mathrm{A}]^3 \tag{12}$$

which combined with (6) gives

$$l\ [\mathrm{A}]^3 = L\Big(1 + \sum_{n=1}^{N}\beta_n[\mathrm{A}]^n\Big) = L\cdot X \tag{13}$$

When calculating the value of [A] belonging to a certain value of l, correction must be applied for that part of the iodide which has been oxidized during the time of equilibration. Even at the lowest values of [A] used here, the iodine formed will appear mainly[10] as I_3^-. If it is assumed that this species does not form complexes with Bi^{3+}, [A] is then given by the formula

$$[\mathrm{A}] = C_A - 3(C_M' - l) - \bar{n}\cdot l - 3[I_3\ ] \tag{14}$$

Here $[I_3^-]$ is determined by analysis of a sample of the saturated solution. As to $\bar{n}$, a sufficiently correct value (*viz.* $\bar{n} = 6$) is known only in the range of [A] covered by the emf measurements where the highest complex MA_N ($= MA_6$) is practically the only one existing. At lower [A], $\bar{n} = 3$ has been used as a first approximation. This value certainly represents a lower limit of $\bar{n}$ in the range of [A] used, as shown by the following evidence. At the value of [A] where $\bar{n} = 3$ is correct, the concentration of the complex MA_3 relative to the other complexes will be at a maximum[7, p. 30]. The concentration of MA_3 in the solution is however constant, because of its presence as a solid phase. The total solubility, l, will therefore show a minimum when $\bar{n} = 3$. As seen from Fig. 1, the iodide solubility curve is in fact flattening out very much at the lowest [A] measured, but it does not reach its minimum. So $\bar{n}$ must be >3 along the whole curve.

As it can be foreseen that the upper complexes are also the dominating ones in the range covered by the solubility measurements, the constants are calculated downwards in much the same manner as that used for the potentiometric measurements. From (13) the following function is formed

$$l\,/\,[\mathrm{A}]^{N-3} = L\ \Big(\beta_N + \sum_{n=1}^{N-1}\beta_{N-n}[\mathrm{A}]^{-n} + [\mathrm{A}]^{-N}\Big) = L\cdot X_N' \tag{15}$$

When $1/[\mathrm{A}] \rightarrow 0$, $l/[\mathrm{A}]^{N-3} \rightarrow L\cdot\beta_N$. Then the following function is formed:

$$(l/[\mathrm{A}]^{N-3} - L\cdot\beta_N)\cdot[\mathrm{A}] = L\left(\beta_{N-1} + \sum_{n=2}^{N-1}\beta_{N-n}[\mathrm{A}]^{1-n} + [\mathrm{A}]^{1-N}\right) = L\cdot X'_{N-1} \qquad (16)$$

which gives $L\cdot\beta_{N-1}$ when $1/[\mathrm{A}] \rightarrow 0$. Further constants $L\cdot\beta_n$ are calculated analogously, and as L can be determined in the same way as L' of the chloride and bromide systems, all the constants β can be found. From these constants a complex formation curve is calculated allowing us to insert approximately correct values of $\bar{n}$ in (14). Better values of [A] are thus obtained giving a better set of constants β. In fact this second approximation gives the final values of β of the present system as the correction term $\bar{n}\cdot l$ of (14) is fairly small.

EXPERIMENTAL

Chemicals: All chemicals were, if not otherwise stated, of analytical grade and used without further purification.

Liquid *bismuth amalgam*, containing ≈ 1 % bismuth, was prepared [2] by dissolving Bi in Hg under water at about 90 °C. To prevent formation of oxide films it was stored under dilute perchloric acid. Before use it was washed with boiled water. During the measurements, no changes of emf due to changes of the bismuth activity in the amalgam could be detected, therefore no perceptible oxidation of the amalgam seems to occur.

Bismuth perchlorate solution was prepared by dissolving $\mathrm{Bi_2O_3}$ in an approximately 50 % excess of $\approx$ 6 M $\mathrm{HClO_4}$. By diluting this solution, a stock solution for the measurements was prepared and analysed for C_M and free acid.

The determination of C_M was carried out by precipitating and weighing BiOI, in the main according to the procedure described by Vogel [11]. Due to the slight solubility of $\mathrm{KClO_4}$, NaI had to be used instead of KI as a precipitant. It was necessary to adjust pH to about 4.5 with sodium acetate to ensure that all the originally precipitated brown-black $\mathrm{BiI_3}$ and all the yellow iodide complexes of the solution were converted into purple BiOI. The final value of the pH was checked by spots tests, as the addition of an indicator would have masked the decolourization which accompanies complete hydrolysis of the bismuth solution. The stock solution had C_M = 0.496 M.

The concentration of free acid in this solution was determined by alkalimetric titration after the removal of the bismuth by means of cation exchange, *cf.* Ref. [12]. A value of $[\mathrm{H^+}] = 0.92$ M was found, in good agreement with the value of $[\mathrm{H^+}] = 0.93$ M which was calculated from the amount of acid used in the preparation.

Two preparations of *sodium perchlorate* was used. The first one (from G. Frederick Smith) was recrystallized twice. The second one was made by neutralization of perchloric acid. The main part of the acid was neutralized by sodium carbonate, the carbon dioxide boiled off, and the last trace of acid finally neutralized with sodium hydroxide. Both the preparations contained <0.01 % of $\mathrm{Cl^-}$ and $\mathrm{ClO_3^-}$. A 2 M stock solutions was prepared by weighing the dried salt.

Stock solutions, close to 2 M, were also prepared of *perchloric, hydrochloric* and *hydrobromic acids*, as well as of *sodium chloride, bromide and iodide*, and their exact concentrations determined by analysis.

The potentiometric measurements: Two different reference electrodes were used, *viz.*:

$$\mathrm{Au}\ \left|\ \begin{array}{l}0.01\ \mathrm{M\ HClO_4}\\ 1.99\ \mathrm{M\ NaClO_4}\\ \mathrm{quinhydrone(s).}\end{array}\ \right|\ \begin{array}{l}2\ \mathrm{M}\\ \mathrm{NaClO_4}\end{array}\quad \text{and}\quad \mathrm{Au}\ \left|\ \begin{array}{l}1\ \mathrm{M\ HClO_4}\\ 1\ \mathrm{M\ NaClO_4}\\ \mathrm{quinhydrone(s).}\end{array}\ \right|\ \begin{array}{l}1\ \mathrm{M\ HClO_4}\\ 1\ \mathrm{M\ NaClO_4}\end{array}$$

denoted RE (0.01) and RE(1), respectively. RE (0.01) was used in the earlier measurements, RE(1) in the later ones. The change of RE(0.01) for RE(1) ought to improve the constancy of E_d of (1). Moreover the risk of diffusion or flow between the cell compartments should be much less.

Table 1. The validity of Nernst's law for the bismuth amalgam electrode in 2 M perchlorate medium. — Series I: $[H^+]_0 = 9.99$ mM; 2 M $NaClO_4$ in the junction between the half-cells. Series II: $[H^+] = 1$ M throughout the whole cell.

	I		II	
C_M mM	E' mV	E_k mV	E' mV	E_k mV
0.496	368.6	304.6	461.6	397.6
0.985	363.3	305.0	455.4	397.1
1.91	357.5	304.7	449.5	396.7
4.52	350.6	305.1	442.0	396.5
11.5	343.0	305.4	434.0	396.4
24.9	337.0	305.9	427.7	396.6
33.2			425.5	396.8
39.7	333.4	306.2		

First, the behaviour of the bismuth amalgam electrode in the medium used was investigated. In the amalgam half-cell, a known volume was placed of a solution containing 1 M $HClO_4$, and 1 M $NaClO_4$. Portions of bismuth perchlorate solution of the same $[H^+]$ and I were then added and the emfs of the resulting cells measured. As no complexing agent is present, these cells have $[M] = C_M$, and E_k can therefore be calculated according to (2). From Table 1 it is evident that E_k really is a constant. Thus a variation of C_M within the given limits does not cause appreciable changes of E_d or f_M. Nernst's law is obeyed in the form (2).

The main measurements were also carried out as titrations mostly in the following way. A solution, S, of known C_M but containing no ligand was prepared in the amalgam half-cell and the cell connected. Dissolved air was then expelled by bubbling nitrogen gas, free from oxygen, through the bismuth solution, the bubbling being continued through the whole titration in order to keep the solution free from air and thoroughly mixed. After E' had been read, a ligand solution T, of the same C_M, $[H^+]$ and I as the solution S, was added in portions. In the beginning a precipitate (BiOCl, BiOBr or BiI_3) was formed which however was dissolved by further addition of ligand solution. When a clear solution had thus been obtained, measurements of E could begin. Titrations were performed at four or five different values of C_M and they were continued to as high C_A as could conveniently be reached within the ionic strength used.

In order to extend the measurements to as low values of C_A as possible titrations were also performed in the opposite direction, with decreasing C_A. Portions of S were then added to a solution S′ in the electrode vessel, S′ containing a ligand concentration high enough to secure a clear solution. In this way values of E could be determined even in solutions somewhat supersaturated with respect to the slightly soluble halide. When at last precipitation really occurred, this was at once indicated by a rapid drift in the emf measured, even in cases where the precipitate was hardly visible. A value of E' could however not be directly determined in these titrations. As the value of E' varied a little between parallel titrations, being dependent on small differences in E_k between different cells, it was desirable to find the value of E' corresponding to the values of E measured in a particular titration. This was done by comparing the values of E found when titrating over a common range with increasing and decreasing C_A. The difference between E of such series leads to a fairly safe estimate of the difference between E'. The value of E' for the series with decreasing C_A can then be found as E' for its companion series was measured directly.

In the case of the iodide, a ligand solution of $[H^+] = 1$ M would have been rather unstable. In these titrations, neutral iodide solution was therefore added from one burette and perchloric acid from another. In this way iodide was kept in acid solution only in the electrode vessel, where its oxidation was minimized by the presence of an inert atmosphere.

The values of E_M given in the following tables are as a rule the mean of three titrations. In the chloride and bromide systems the values of emf measured were very stable. They were reached, moreover, almost immediately after the solutions had been mixed, with the exception of E' whose adjustment to the final value sometimes took about half an hour. The emfs could be reproduced within about ± 0.5 mV, as a rule somewhat better at lower values of C_A and somewhat worse at higher ones. In the iodide system it often took 5 — 10 min for the emfs to reach their final value; they were also markedly less reproducible, especially at high values of C_A. At the very highest values of C_A tried, they were even unstable and drifted erratically, especially if C_M was also high. Often a tarnishing of the amalgam surface was observed in such solutions and their colour gradually faded to light yellow on standing.

The solubility measurements: Solutions of 50 ml total volume, with known initial concentrations of bismuth and ligand were prepared in glass-stoppered bottles of 100 ml volume. The concentrations were chosen so that a precipitate formed. The bottles were shaken in a thermostat for about a week. After that time equilibrium had been established, as was proved by shaking a few bottles for another week. The same results were obtained in both cases.

Samples of the saturated solutions thus obtained were filtered by suction through a sintered glass disc (filter stick) direct into a pipette. The total bismuth concentration of these solutions, *i.e.* the solubility l, was then determined spectrophotometrically by the iodide method[13].

This method utilized the very intense colours of the bismuth iodide complexes, especially that of the highest. In order to bring about maximum absorption, the iodide concentration should be at least ≈ 100 mM. At this value of [A] the formation of the highest complex is practically completed, therefore further addition of iodide does not alter the absorption appreciably. The extinction curve has a maximum at 4 600 Å, where the iodide complex has a molar extinction coefficient $\varepsilon \approx 11\,000$ $M^{-1} \cdot cm^{-1}$. This very high value of ε permits a convenient determination of bismuth concentrations down to $\approx 10^{-5}$ M. The extinction values are however not very reproducible if steps are not taken to prevent the formation of I_3^- which also absorbs strongly at 4 600 Å. Following Wiegand *et al.*[13] we have successfully used hypophosphorous acid (≈ 0.3 M) to prevent the formation of I_3^-. In the absence of Bi(III) the medium used is completely colourless, and distilled water can therefore be used in the solvent absorption cell of the spectrophotmeter (Beckman DU). A calibration curve giving the connexion between C_M and the specific extinction* e was constructed by measuring solutions of known C_M. Only slight deviation from Beer's law was found.

The statement above that practically all the bismuth is present as the highest iodide complex when the iodide concentration = 100 mM may of course be invalidated if other ligands are present in the solution, competing with the iodide. This is the case when analysing chloride or bromide solutions. It was found experimentally however that if the iodide concentration was increased to 250 mM, chloride or bromide could be present in a concentration of at least 50 mM, without changing the extinction perceptibly. This could also have been expected from the values of the stability constants of the different systems, previously found by the potentiometric measurements.

The solubility l for a certain C_A could as a rule be reproduced within ≈ 10 % except at the lowest values of C_A in the chloride and iodide system where the reproducibility was very poor. This is evident from Tables 4, 7 and 10 where the solubility experiments have been tabulated.

In most cases a second sample of the saturated solutions was filtered off and used for a potentiometric determination of $[Bi^{3+}]$ in order to find L' and L. For the bromide system useful values of E_M could then be obtained in the whole range of C_A used, whereas C_A must be at least 20 or 30 mM in chloride or iodide solutions before even acceptable values of E_M could be read. At lower values of C_A, unsteady and drifting potentials were obtained. This is of course mainly due to the very low value of C_M ($= l$) in such solutions, but to judge from the figures of the chloride system, the value of C_A (or [A]) itself must also be of importance. Thus E_M can be measured for $C_A = 20$ mM, but not at lower C_A in spite of the fact that l has already reached its minimum value at $C_A = 20$ mM (Table 4).

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* $e = E/d$, where E = extinction measured and d = thickness of absorbing layer.

Table 2. The chloride system. E_M as a function of C_A for different values of C_M.

$C_M \rightarrow$ mM	2	1	0.5		20	10	2	1	0.5
C_A mM	E_M mV			C_A mM	E_M mV				
25.0*			20.0	136.4			59.3	59.9	59.7
28.6*		21.9	22.4	160.7			64.6	65.5	64.9
33.3*		25.2	25.5	184.2		63.0	69.0	69.5	69.4
40.0*		28.8	29.0	217.9		69.3	74.3	75.2	75.1
50.0*		33.7	33.6	250		74.7	80.0	80.1	80.1
57.6		36.8		300		81.9	86.6	86.8	86.7
58.8*	36.1	37.5	37.2	346	81.9	87.7	92.1	92.3	92.0
66.7*	39.1	40.4	40.3	429	91.6	96.6	100.4	100.6	100.2
71.4		41.9	42.2	500	98.7	103.2	106.7	106.8	106.3
76.9*	42.6	43.5	44.1	618	108.4	112.2	115.2	115.3	114.7
83.3*	44.7	45.7	46.1	711	114.8	118.3	121.0	120.9	120.6
84.9		46.2	46.7	818	121.3	124.5	126.9	126.9	126.4
90.9*	47.0	48.1	48.4	900	125.7	128.7	130.7	130.8	130.2
98.1		50.1	50.4	1000	130.2	133.2	135.2	135.2	134.5
100.0*	49.7	51.0	51.0	1071	133.4	136.2	138.0	137.9	137.3
111.1	53.0	53.7	53.9	1200	138.4	140.8	142.1	142.6	142.1

* These values belong to the series titrated from higher to lower values of C_A, while all other values belong to the series titrated in the opposite direction.

Evidently the bismuth species dominating at [A] = 20 mM have a more favourable electrode kinetics than those dominating at lower [A], as has also been directly proved by the impedance measurements of Randles and Somerton [14].

In the case of the iodide system a third sample of the saturated solution was filtered off and analysed by thiosulphate titration for the amount of I_3^- formed during the shaking, in order to find the true value of [A] according to (14).

In order to find L from L', K_w of the medium used was finally determined by measuring $[H^+]$ of solutions of known $[OH^-]$ by means of a hydrogen electrode. As mean of three determinations a value of $K_w = (0.75 \pm 0.05) \cdot 10^{14}$ M^{-2} was found.

RESULTS

The chloride and bromide systems: In Tables 2 and 5, E_M is given as a function of C_A with C_M as a parameter. These functions are cut at a number of E_M, thus giving corresponding values of [A] and X, Tables 3 and 6. An accurate value for the constant β_1 cannot, however, be found from the function X_1 thus formed, as the latter is not known at sufficiently low values of [A]. Reliable values of β_1 can, however, be found from the solubility measurements, where the lowest values of [A] measured are 3.94 mM for the chloride and 2.12 mM for the bromide, as compared with 23.4 mM and 8.5 mM, respectively, in the potentiometric measurements. In order to find the value of [A] corresponding to a certain value of l measured, it is, however, necessary to know beforehand $\bar{n}$ approximately as a function of [A] (*cf.* eqn. (10)). By calculating a set of provisional stability constants from the X-functions found potentiometri-

Table 3. The chloride system. Computation of the complexity constants.

Table 3 A. The functions X at low values of [A].

C_M → mM	2	1	0.5	0	X	$X_1 \times 10^{-2}$ M^{-1}	$X_2 \times 10^{-4}$ M^{-2}	$X_3 \times 10^{-5}$ M^{-3}	$X_4 \times 10^{-6}$ M^{-4}
E_M mV	C_A mM			$C_A = [\mathrm{A}]$					
20		26.0	24.8	23.6	10.8	4.13	0.77	2.1	
25		33.2	32.3	31.4	19.5	5.88	1.14	2.76	1.58
30		42.7	42.0	41.3	35.2	8.29	1.45	2.86	1.45
35		53.8	53.2	52.6	63.9	11.9	1.83	2.96	1.33
40	69.3	66.3	65.5	64.1	116	17.9	2.43	3.37	1.73
45	84.3	80.8	79.8	78.1	209	26.7	3.12	3.64	1.77
50	101.0	97.3	96.5	94.6	379	40.0	3.97	3.91	1.74
55	119.5	116.0	115.9	113.4	687	60.3	5.11	4.26	1.76

cally, using a value of $\beta_1 = 0$, complex formation functions good enough for this purpose are obtained.

For both the systems, the values of L' found are constant within the experimental error in the whole range of [A] covered. Thus the solid phases really do have a ratio M:A = 1, as postulated in (7) and (8). Furthermore, samples of the precipitates have been filtered off, and, after drying, analysed for bismuth, and in the case of the bromide, halide also. For bismuth the complexometric method of Malat *et al.*[15] has been used, and it was then found that direct titrations with EDTA could be performed for the chloride also. Bromide was determined according to Volhard. (Found for the chloride: Bi 80.4 %, calc. for BiOCl: 80.2 %. Found for the bromide: Bi 68.0 %, Br 26.23 %, calc. for BiOBr: Bi 68.4 %, Br 26.21 %.)

Table 3 B. The functions X at high values of [A].

$_M$ → nM	20	10	2	1	0	$X \times 10^{-4}$	$X_1 \times 10^{-4}$ M^{-1}	$X_2 \times 10^{-4}$ M^{-2}	$X_3 \times 10^{-5}$ M^{-3}	$X_4 \times 10^{-6}$ M^{-4}	$X_5 \times 10^{-7}$ M^{-5}
E_M nV	C_A mM				$C_A = [\mathrm{A}]$						
60		166.5	140.0	137.3	134.5	0.124	0.92	6.70	4.79	1.88	4.61
65		192.0	162.5	160.5	157.4	0.225	1.43	8.92	5.50	2.06	5.08
70		221	190.0	185.2	182.3	0.407	2.23	12.12	6.50	2.32	5.81
80	330	283	253	250	246	1.34	5.45	22.1	8.85	2.68	5.77
90	414	365	328.5	326	320	4.39	137	42.8	13.3	3.45	6.84
100	515	464	425.5	423	417.5	14.4	344	82.4	19.7	4.16	6.95
110	640	589	544.5	541.5	538	47.1	875	163	30.3	5.20	7.32
120	794	739	695	695	686	155	2 260	329	47.9	6.65	7.85
130	996	929	882	882	872	506	5 800	665	76.1	8.46	8.25

Table 4. The chloride system. The solubility l as a function of [A]. Determination of the constant L', with subsequent calculation of the complexity constants β_1 and β_2.

C_M' mM	C_A mM	E_M mV	$[M] \times 10^3$ mM	l mM	[A] mM	$L' \times 10^9$ M^2	$L' \cdot X_1 \times 10^6$ M	$L' \cdot X_2 \times 10^5$
1	5			0.108	3.94		55.2	
1	5			0.0792	4.02		(27.5)	
1	7.5			0.0857	6.47		53.5	
1	7.5			0.0949	6.52		63.0	
1	10			0.0857	8.98		62.5	
1	10			0.0871	8.99		64.0	
1	12.5			0.0880	11.48		69.9	
1	15			0.1036	13.89		88.6	
1	20			0.0949	18.91		83.9	
1	20	38.1	10.81	0.0958	18.91	204	84.8	
1	25	38.2	10.69	0.1045	23.88	255	95.8	201
1	25	38.4	10.45	0.123	23.89	250	114	276
2	30	41.8	6.97	0.116	27.85	194	108.5	215
2	35	42.3	6.56	0.149	32.9	215	143	288
2	40			0.168	37.7		162.5	304
2	40	45.2	4.66	0.165	37.8	176	159.5	296
2	50	47.1	3.72	0.1985	47.6	177	194	306
2	60	47.8	3.42	0.328	57.2	196	342	484

Table 5. The bromide system. — E_M as a function of C_A for different values of C_M.

$C_M \rightarrow$ mM	5	2	1	0.5		10	5	2	1
C_A mM	E_M mV				C_A mM	E_M mV			
8.3 *				13.7	111.1	71.2	80.8	87.1	88.9
10.0 *			15.5	16.3	136.4	82.2	90.4	95.8	97.4
12.5 *			18.6	20.2	160.7	91.0	98.2	103.0	104.5
14.9			22.6	23.5	184.2	98.4	104.7	109.0	110.3
16.7 *			24.4	26.1	217.9	107.2	112.7	116.5	117.6
20.8 *				31.5	250.0	114.5	119.1	122.7	123.5
25.0 *			35.0	36.5	300	123.9	127.8	130.8	131.6
29.4		37.0	40.0	41.4	346	131.4	134.6	137.3	137.9
35.7 *				47.6	429	142.2	144.7	146.9	147.6
41.6 *			51.7	52.6	500	150.1	152.5	154.0	154.5
43.7 *		50.5	53.1	54.4	618	160.3	162.1	163.6	164.1
45.5 *			54.6	55.8	711	167.4	168.9	170.2	170.6
50.0 *			58.2	59.2	818	174.4	175.7	176.6	177.1
57.6	51.2	60.7	63.2	64.1	900	179.2	180.8	180.8	181.3
71.4	60.5	68.9	71.4	72.2	1000	184.3	186.0	185.6	186.1
84.9	68.4	76.1	78.1		1071	187.8	189.3	188.6	189.1
98.1	75.0	82.0	83.8		1200	193.3	194.6	193.4	194.1

* See note of Table 2.

Table 6. The bromide system. Computation of the complexity constants.

Table 6 A. The functions X at low [A].

C_M mM	5	2	1	0.5	0						
E_A mV	C_A mM				C_A = [A]	X	$X_1 \times 10^{-2}$ M^{-1}	$X_2 \times 10^{-4}$ M^{-2}	$X_3 \times 10^{-6}$ M^{-3}	$X_4 \times 10^{-8}$ M^{-4}	$X_5 \times 10^{-9}$ M^{-5}
15			9.9	9.2	8.5	5.94	5.81	4.71	2.25		
20			13.2	12.3	11.4	10.75	8.55	5.92	2.74		
25			16.7	15.8	14.9	19.5	12.4	7.11	2.90		
30			20.7	19.6	18.5	35.2	18.5	9.03	3.35		
35			24.9	23.7	22.5	63.8	27.9	11.60	3.92		
40		32.5	29.5	28.2	26.7	116	42.9	15.4	4.72	1.02	
45		37.7	34.7	33.2	31.7	209	65.7	20.2	5.49	1.10	
50		43.3	40.0	38.6	37.0	379	102	27.0	6.55	1.23	
55	63.0	49.4	46.1	44.5	42.3	686	162	37.8	8.26	1.48	2.32
60	70.6	56.7	52.8	51.3	48.9	1242	254	51.5	9.95	1.63	2.31
65	78.9	64.6	60.6	59.0	56.1	2250	401	71.0	12.1	1.80	2.32

Table 6 B. The functions X at high values of [A].

C_M mM	10	5	2	1	0					
E_M mV	C_A mM				C_A = [A]	$X_1 \times 10^{-5}$ M^{-1}	$X_2 \times 10^{-6}$ M^{-2}	$X_3 \times 10^{-7}$ M^{-3}	$X_4 \times 10^{-8}$ M^{-4}	$X_5 \times 10^{-9}$ M^{-5}
70	109	88	73	69	64.5	0.63	0.976	1.47	1.92	2.20
80	131	109	94	89.5	84.5	1.58	1.87	2.18	2.33	2.16
90	157	135	119	114.5	109.5	4.01	3.66	3.32	2.85	2.14
100	190	167	150	145	140	10.2	7.29	5.19	3.56	2.18
110	230	206	188	183	178	25.6	14.4	8.09	4.45	2.23
120	278	255	235	230	224	69.0	30.8	13.7	6.03	2.47
130	337	314	294	289	283	179	63.3	22.4	7.85	2.60
140	411	388	368	363	358	464	130	36.3	10.1	2.68
150	499	476	459	452	447	1 220	273	61.0	13.6	2.94
160	615	588	570	564	558	3 200	574	103	18.4	3.21
170	749	725	709	701	696	8 410	1 210	174	25.0	3.52
180	914	886	884	873	873	22 000	2 520	288	33.0	3.72
190	1 123	1 091	1 109	1 094	1 101	57 100	5 180	470	42.6	3.82

The mean value of L' is found to be $(208 \pm 20) \times 10^{-9}$ M^2 for the chloride and $(303 \pm 10) \times 10^{-9}$ M^2 for the bromide. Using these values of L', β_1 is calculated from the corresponding values of l and [A], according to (9). The values of β_1 thus found are then used for calculating X_2 from the potentiometrically found X_1. From X_2 (Tables 3 and 6), β_2 is found by extrapolation to [A] = 0. Further X-functions are then formed and the corresponding constants determined. For both the chloride and the bromide the function X_5 is found to be a straight line, the sixth complex thus being the highest one existing in the range of [A] investigated. The complex formation curves, as

Table 7. The bromide system. The solubility l as a function of [A]. Determination of the constant L', with subsequent calculation of the complexity constants β_1 to β_4.

C_M' mM	C_A mM	E_M mV	$[M] \times 10^3$ mM	l mM	[A] mM	$L' \times 10^9$ M^2	$L' \cdot X_1 \times 10^6$ M	$L' \cdot X_2 \times 10^3$	$L' \cdot X_3$ M^{-1}	$L' \cdot X_4$ M^{-2}
1	3	15.2	164	0.202	2.12	345	59			
1	3	17.4	126.5	0.200	2.12	266	57			
1	4	19.0	104.7	0.169	3.07	314	70			
1	4	20.4	88.5	0.183	3.08	269	85	9.7		
1	5	22.8	66.7	0.164	4.02	265	89	8.5		
2	7.5	26.0	45.5	0.147	5.46	247	82	6.8		
4	10	24.3	55.7	0.150	5.95	329	99	7.4		
2	10	27.7	37.2	0.182	7.87	292	144	11.3	0.74	
2	10	27.4	38.6	0.166	7.88	302	128	9.3	0.48	
2	10	29.2	31.1	0.171	7.88	244	133	9.9	0.56	
2	12.5	28.5	33.8	0.207	10.28	346	177	11.9	0.62	
2	12.5	28.5	33.8	0.216	10.27	347	186	12.8	0.71	
2	15			0.267	12.63		243	14.9	0.75	
5	20			0.309	14.51		288	16.0	0.72	
2	20	33.0	19.8	0.461	17.15	340	443	22.6	1.00	33
2	20	33.6	18.5	0.418	17.23	318	400	20.0	0.84	23
5	25	33.8	18.0	0.534	18.94	342	518	24.4	1.00	30
5	25	35.2	15.3	0.525	18.95	290	509	24.0	0.98	29
5	25			0.502	19.00		486	22.7	0.91	25
5	27.5			0.659	21.14		645	27.9	1.06	29
5	27.5			0.667	21.12		653	28.4	1.09	31
5	30			0.797	23.25		784	31.4	1.12	29
10	45			1.63	30.8		1616	50.7	1.47	34
10	50			2.17	34.1		2165	61.9	1.65	36

calculated from the constants found, show very distinct tendencies of asymptotically approaching $\bar{n} = 6$, Fig. 2. The coordination number of bismuth in these two halide systems thus seems to be $N = 6$. In fact even the sixth complex is a little reluctant to form from the fifth one. In addition to the values of β_1 used in connexion with the potentiometric data, values of some of the higher constants can also be determined from the solubility measurements (*cf.* eqn. (11)). In this way β_2 of the chloride system and β_2 to β_4 of the bromide system are calculated and found to be in reasonable agreement with the values found potentiometrically, as seen from Table 11, where all the constants are tabulated.

As C_M must be kept rather low in the potentiometric measurements in order to avoid precipitation as much as possible, the determination of the slopes of the C_A, C_M lines of constant E_M becomes rather uncertain, all the more as the error in E_M is not very small (*cf.* p. 1118). In such cases the slopes found cannot be expected to coincide completely with the complex formation curve even if the complex formation is in fact entirely mononuclear. As seen from Fig. 2, discrepancies are found for the chloride system especially, but they can most certainly be explained by the poor accuracy of the slope values. The general trends of these nevertheless coincide with the curve found from the

Table 8. The iodide system. E_M as a function of C_A for different values of C_M.

$C_M \rightarrow$ mM	10	5	2	1	$C_M \rightarrow$ mM	10	5	2	1
C_A mM	E_M mV				C_A mM	E_M mV			
60.2				232.7	346	304.7	312.7	320.4	324.4
73.9				243.5	375	310.0	317.1	324.5	328.6
87.2			245.5	252.5	424	317.4	324.0	331.0	335.1
100.2			253.2	259.9	465	322.8	329.0	335.6	339.9
124.8		253.4	265.4	271.6	499	327.1	333.2	339.4	343.6
147.9		263.3	274.5	280.1	553	333.1	338.8	344.6	349.0
180.2	264.9	274.4	285.5	290.4	595	337.1	342.9	348.3	352.7
209.7	274.9	283.2	293.8	298.5	627	340.0	345.7	350.8	355.5
245.5	284.6	292.7	302.5	306.7	675	344.0	349.5	354.8	359.0
278	291.9	300.2	308.8	313.0	715	352.0	352.3	357.6	362.3
314	299.0	307.2	315.2	319.4					

stability constants and no doubt the complex formation is mononuclear for both systems.

The iodide system: In Table 8, E_M is given as a function of C_A at different C_M. A fairly high value of C_A is necessary in order to prevent precipitation of BiI_3 even at C_M as low as 1 mM. As the values of E_M obtained for a certain C_A are remarkably high the system must be strongly complex. Only the highest complexes can therefore be expected to exist in the range of [A] covered by the emf measurements. The calculation should in such a case start with β_N (*cf.* p. 1113). From the results of the chloride and bromide systems, it may be

Table 9. The iodide system. Calculation of β_6 from potentiometric measurements

$C_A \rightarrow$ mM	10	5	2	1	0	$X \times 10^{-12}$	$X'_6 \times 10^{-19}$ M^{-6}
E_M mV	C_A mM				C_A = [A]		
245			86	74	62	4.32	7.8
250			94	82	70	7.82	6.7
255		128	103	91	83	14.2	4.3
260		139	113	100	92	25.6	4.2
265	180	152	123	110	107	46.4	2.9
270	193	166	135	121	119	84.1	3.0
275	209	182	148	134	131	152.3	3.0
280	227	199	162	148	145	276	3.0
285	247	216	177	163	158	499	3.2
290	268	235	194	179	176	904	3.1
300	318	278	234	216	212	2960	3.3
310	375	331	282	262	255	9720	3.5
320	443	394	342	319	315	$3.19 \cdot 10^4$	3.3
330	525	472	415	386	386	$10.45 \cdot 10^4$	3.2
340	626	564	502	466	468	$34.3 \cdot 10^4$	3.3
350		683	614	565	541	$112.2 \cdot 10^4$	4.5

Table 10. The iodide system. The solubility l as a function of [A]. Determination of the solubility product L, with subsequent calculation of the complexity constants β_6 to β_4.

C'_M mM	C_A mM	E_M mV	$[M] \times 10^{17}$ M	l mM	$[I_3^-]$ mM	[A] mM	$L \times 10^{18}$ M^4	$L \cdot X'_6$ M^{-2}	$L \cdot X'_5$ M^{-1}
1	7.5			0.0255	0.14	4.08		375	1.51
1	10			0.0239	0.19	6.41		90.8	0.547
1	10			0.0130	0.09	6.72		42.8	0.252
1	12.5			0.0277	0.14	9.05		37.4	0.289
1	15			0.0450	0.25	11.20		32.0	0.297
1	15			0.0437	0.10	11.65		27.6	0.258
1	17.5			0.0506	0.35	13.38		21.2	0.210
1	20			0.0580	0.60	15.11		16.8	0.171
1	20			0.0663	0.44	15.57		17.6	0.188
1	20			0.0731	0.33	15.86		18.3	0.203
1	22.5			0.0867	0.27	18.52		13.6	0.150
1	25			0.0892	1.10	18.53		14.0	0.158
1	25			0.1077	0.42	20.5		12.5	0.144
1	25			0.0980	0.36	20.8		11.0	0.114
1	30			0.151	1.07	23.5		11.7	0.145
1	30	197.9	6220	0.163	0.59	24.9	0.96	10.6	0.127
1	30			0.185	0.50	25.1		11.8	0.158
1	35			0.236	0.59	29.7		9.1	0.106
1	40	207.4	2010	0.337	0.85	33.6	0.76	8.9	0.114
1	40			0.349	0.67	34.1		8.8	0.113
1	40	208.3	1810	0.340	0.15	35.7	0.82	7.5	0.070
1	50	209.5	1570	0.596	1.19	41.8	1.15	8.2	0.111
2	65	218.8	520	1.077	1.24	52.3	0.75	7.6	0.107
3	80	225.0	249	1.82	0.84	63.3	0.63	7.2	
5	100	226.7	203	2.44	1.80	72.6	0.78	6.4	
5	100	227.7	181	2.65	1.08	74.1	0.74	6.5	
10	150	233.9	87	5.82	1.08	99.8	0.86	5.9	

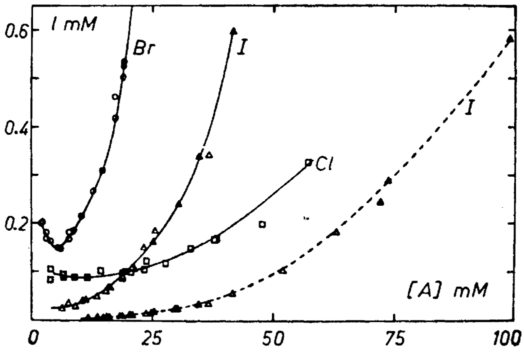

Fig. 1. The solubility l of Bi(III) as a function of [A] in halide solutions. Squares, circles and triangles refer to the chloride, bromide and iodide systems respectively. The dashed curve of iodide refers to values of l ten times greater than those given on the ordinate axis.

assumed that $N = 6$ also for the iodide. In Table 9, where corresponding values of X and [A] are found, the function X_6' is also given, calculated according to (5). It is found to be a constant, $= \beta_6$, from the highest value of [A] down to $[A] \approx 80$ mM, thereby confirming that $N = 6$. For $[A] < 80$ mM, X_6' increases as lower complexes become perceptible, but further constants cannot be safely calculated from the present figures.

A substantial extension of the measured range of [A] is obtained by the solubility measurements, Table 10. A value of $[A] \approx 4$ mM can be reached, as compared with $[A] \approx 60$ mM in the emf measurements. In that range of [A] (>25 mM) where [M] can be measured and thus values of L determined (from eqn. (12)), L is found to be constant within the experimental errors (Table 10). Thus the solid phase really is MA_3, as postulated in (12). Using the established value of $N = 6$, $L \cdot X_6' = l \,/\, [A]^3$ is then calculated, *cf.* eqn. (15), and from the extrapolation to $1 \,/\, [A] = 0$, $L \cdot \beta_6$ and hence β_6 is found. Then $L \cdot X_5'$ is formed according to (16), and from this function β_5 and β_4 are found from the intercept on the axis and the slope at the point of intersection. The function is not linear, so the third complex must be present in appreciable amounts, at least in the solutions of lowest [A]. The accuracy of l is not good enough however to permit the calculation of a further constant from a function $L \cdot X_4'$, formed analogously to $L \cdot X_5'$.

The constants found are given in Table 11. As can be seen, the two values of β_6 found agree tolerably well. We believe, however, that the figure found by the solubility measurements is the more reliable one, on the following grounds. As pointed out above (p. 1118) a reaction involving the amalgam electrode is evidently taking place in iodide solutions of high [A]. From the bleaching of the solutions it is obvious that Bi(III) is being reduced by the metallic Hg. Such a reduction is rendered possible by the formation of very strong iodide complexes of Hg(II) which greatly stabilize this oxidation state relative to Hg(0). A calculation based on the data of Sillén[16] for Hg(II) and those of the present paper for Bi(III) also confirms that the reduction is possible. On the other hand Sillén's data seem to indicate that the existence of Hg(I) in appreciable amounts (as solid Hg_2I_2) is not to be expected at those values of [A] where a perceptible reduction of Bi(III) can take place. Similar calculations for the chloride and bromide system prove that no reduction of Bi(III) is to be feared in these cases, as is also experimentally confirmed.

Even at lower values of C_A where the function of the amalgam electrode is not obviously erratic, minor irregularities occur which may indicate the beginning of its break-down. Thus the corresponding values of C_M and C_A at constant values of E_M do not fall as well as they should along straight lines. Moreover the best straight lines which can be drawn have slopes much greater than $\bar{n}$. Obviously the values of E_M measured cannot be considered as quite realiable, and more weight should therefore be placed on the measurements of solubility.

The observed slopes of course do not suggest any polynuclear complex formation, being greater than $\bar{n}$. As their value seems doubtful however, no conclusions ought to be drawn. But from the behaviour of the other halide systems it may perhaps be concluded that the iodide system also is probably mononuclear.

CONCLUSIONS. COMPARISON WITH PREVIOUS WORK

The halide complexes of Bi^{3+} increase in strength in the order $Cl^- < Br^- < I^-$, and Bi^{3+} thus belongs to the second group of central ions, *i. e.* those centered about the noble metals. This is evident from Table 11 and also from Fig. 2, where the complex formation curves are drawn as calculated according to Ref.[9], p. 785.

Fig. 2 also shows that the curves of the chloride and bromide systems are similar, implying that the complex formation proceeds in much the same way

Table 11. The logarithms of the stability constants β and the solubility products L, with maximum random errors indicated. Comparison with the results of other investigations.

		log β_n (M^{-n})						log L (M^4)
n →		1	2	3	4	5	6	
Present authors								
Cl^-	emf		3.5 ±0.2	5.35 ±0.06	6.10 ±0.15	7.72 ±0.06	7.56 ±0.12	BiOCl −34.93 ±0.09
	sol	2.36 ±0.10	3.8 ±0.3					
Br^-	emf		4.45 ±0.06	6.30 ±0.06	7.70 ±0.08	9.28 ±0.04	9.38 ±0.08	BiOBr −34.77 ±0.06
	sol	2.26 ±0.06	4.26 ±0.10	6.18 ±0.12	7.8 ±0.2			
I^-	emf						19.4 ±0.4	BiI_3 −18.09 ±0.10
	sol				14.95 ±0.2	16.8 ±0.2	18.8 ±0.2	
Babko and Golub *								
Cl^-	emf				5.42	7.5	6.42	
Br^-	emf				7.82	7.3	7.9	
I^-	emf						11.51	
Newman **								
Cl^-	sp	2.43 ±0.01	4.4	5.8	6.2	6.7		

* β_4 and β_5 measured in 1.5 M HNO_3 for the chloride, in 1.2 M HNO_3 for the bromide. β_6 of all systems measured in 0.6 M HNO_3. The solutions also contain KNO_3 to a total $I = 2.3$ or 3 M. Temperature 20°C.

** The first two consecutive constants (β_n/β_{n-1}) were measured in 1 M $HClO_4$, the three following ones in a medium of the same $[H^+]$, but with $I = 5$ M.

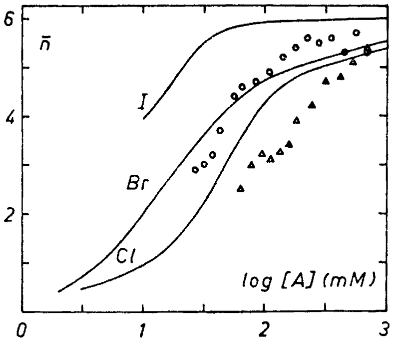

Fig. 2. The complex formation functions of the bismuth chloride, bromide and iodide systems. The curves are calculated from the values of β found. The points obtained from the slopes of the C_A, C_M-lines of constant E_M are indicated by circles for the bromide and by triangles for the chloride system.

in these two systems. A characteristic feature is the slow formation of the sixth complex, which means that the fifth one has a broad range of existence. This stands out well in Fig. 3, where the distribution of Bi(III) on the different complexes is given as a function of log [A] (*cf.* Ref.[9], p. 787). The graphical representation is the one first used by Bjerrum [17], *cf.* also J. Bjerrum [18] (p. 287). A still more interesting thing is that the value of β_1 for bromide is about the same as that for chloride (or even a little less). In this respect Bi^{3+} thus behaves as an intermediate between the two groups of central ions, in accord with its position in the outskirts of the second group. As the formation curve of the bromide is much steeper than that of the chloride, the overall complexity of the former system is nevertheless considerably stronger. As to the solubility products of the oxyhalides, that of the bromide seems to be just greater than that of the chloride, which is also contrary to the general rule for halide systems of the second group ions, as exemplified by the halides of Cu^+, Ag^+, Hg_2^{+2} and Hg^{2+}.

In the iodide system, on the other hand, the fifth complex does not have a wide range of existence, instead the formation curve goes steeply up $\bar{n} = N = 6$. Moreover the difference in stability between the iodide and bromide complexes is much greater than between the bromide and chloride ones.

Quantitative investigations of the complex formation in solutions of the bismuth halides have also been performed by Babko and Golub [19] and by Newman [20]. Babko and Golub measured [Bi^{3+}] by means of bismuth metal electrodes, as well as measuring the corresponding [Cl^-] or [Br^-] by silver halide electrodes. The pure metal electrodes did not give emfs as reproducible as those of the present amalgam electrodes, in accordance with the general observation that electrodes of hard metals are not easy to get working satisfactorily. The measurements were performed in nitrate media of such high acidity that a definite risk of oxidation of the metal electrode certainly must have existed, especially in solutions of high halide concentration where bismuth is much less noble than in non-complexing media. In the case of iodide, moreover, it was necessary to add sulphite in order to prevent oxidation of the ligand. This addition, however, is objectionable, as sulphate and sulphite are

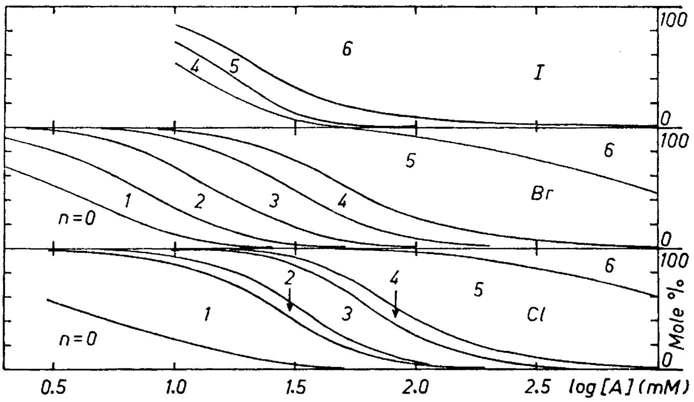

Fig. 3. The distribution of bismuth between the various complexes as a function of [A].

thereby introduced as new ligands in the solution whose concentration of acid is simultaneously reduced.

Dissociation constants, K_n, have been calculated for the three highest complexes of the chloride and bromide systems and for the highest (= sixth) iodide complex. The corresponding stability constants, $\beta_n = 1/K_n$, are as a rule perceptibly lower than those found by the present authors, Table 11. As to the chloride and bromide systems, they are nevertheless of the same order of magnitude. The value of β_6 of the iodide system is however quite different.

Newman has measured spectrophotometrically the consecutive constants of the first five complexes of the chloride system, as well as constants for mixed chloride bromide complexes containing one bromide ion. The constants β calculated from his data, Table 11, agree on the whole tolerably well with ours, especially if the differences of method and medium are taken into account. The most remarkable discrepancy is found for β_5. The sixth complex has escaped discovery because the measurements were not extended into that range of [A] where it exists in perceptible amounts, according to the present investigation.

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Note added in proof: Slightly revised, Newman's [20] work has recently been definitively published (Newman, L. and Hume, D. N. *J. Am. Chem. Soc.* **79** (1957) 4571, 4576, 4581.

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