

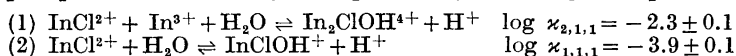
On the Hydrolysis of the Indium(III) Ion in Chloride Solutions

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The hydrolysis equilibria of the indium chloride complex species, InCl^{2+} and InCl_2^+ at 25°C, have been studied by measuring the $[\text{In}^{3+}]$ with the indium amalgam half-cell as a function of the chloride ion concentration, the measurements being made at a series of $\log [\text{H}^+]$ levels ranging from -2.69 to -3.38 . The test solutions were made to contain a total molarity of 3 M by adding NaClO_4 . The indium concentration of the test solutions was varied between 5×10^{-4} and 0.1 M, and at each $[\text{In(III)}]$ and $\log [\text{H}^+]$ level the chloride ion concentration was increased stepwise to 0.35 M.

The emf data, which indicate that only a small part of the indium chloride complexes can be transformed to hydrolysis products before precipitation occurs, may be explained by assuming the equilibria



On the basis of these equilibrium constants it may be seen that the main product of the hydrolysis is the species $\text{In}_2\text{ClOH}^{4+}$.

No other mechanism involving only two chloride bearing hydrolysis products could be found which would explain the data.

The hydrolysis equilibria of the indium ion has received much attention in this laboratory. A detailed investigation in perchlorate medium was made in 1956 by Biedermann¹ who used the indium amalgam and glass half-cells to measure both the $[\text{In}^{3+}]$ and $[\text{H}^+]$ of a series of solutions in which the indium concentration, B , was varied within the wide limits 5×10^{-4} and 0.1 M. The quite steep $\log([\text{In(III)}]/[\text{In}^{3+}])$ and Z versus $\log [\text{H}^+]$ plots obtained have been interpreted by assuming the mononuclear ions InOH^{2+} and $\text{In}(\text{OH})_2^+$ as well as the formation of a series of polynuclear species of the general composition $\text{In}(\text{In}(\text{OH})_2)_t$, where t may take any one of a series of integral values. The mononuclear species have been found to become important only in solutions containing less indium than 1 mM. Of the polynuclear hydrolysis products $\text{In}_2(\text{OH})_2^{4+}$ may be supposed to predominate except at acidities near to the point of precipitation where species containing considerably more

than two indium atoms appear to be present in appreciable amounts. The interpretation of Biedermann's data at the lowest acidities is a difficult problem due to the fact that to distinguish between model functions representing the formation of highly polynuclear species an experimental accuracy is required that is not accessible by present methods.

The hydrolysis of the indium ion in the 3 M NaCl medium was studied in 1961 by Biedermann, Li and Yu² mainly with the intention of finding out, whether mixed complexes which bear chloride as well as hydroxyl ions are formed in appreciable amounts. Although serious experimental difficulties were encountered due to the low solubility of indium hydroxide (it would have been more practical to study solutions saturated with indium hydroxide), they were able to conclude that the main reaction products have the composition InOH^{2+} and $\text{In}_2(\text{OH})_2^{4+}$ with an unspecified number of coordinated chloride ions. As they kept the chloride ion concentration constant throughout, their evidence for the presence of chloride ions in the hydrolysis products is indirect, being based on the comparison of the results obtained in 3 M NaClO_4 and 3 M NaCl media.

In the present work the more ambitious task was undertaken of finding the true composition of the hydrolysis products in chloride solutions. Thus the concentration of both the hydrogen ion and the chloride ion in the test solutions had to be varied.

The main complication one has to meet when mixed complex formation is to be studied is that the equilibria in the two-component systems have to be known with a high degree of accuracy. With this in mind, the present author has conducted prior to undertaking this work an investigation of the complex formation equilibria between indium and chloride ions. The results of this work have been summarized in a preceding report.³

Whatever the final conclusions to which a more sophisticated analysis⁴ of the indium hydrolysis data in the vicinity of the solubility limit of the indium hydroxide might lead, the interpretation of the results in the main range of hydrolysis is not likely to be seriously affected.

Biedermann's measurements¹ have been repeated by the present author and an agreement to within 0.1 mV has been found in the entire $[\text{In(III)}]$ and $\log[\text{H}^+]$ range. Moreover, in cooperation with the late Lars Gunnar Sillén and Georg Biedermann preliminary least square calculations have been made on both sets of measurements. These lead to the conclusion that at a low degree of hydrolysis the ions $\text{In}_2(\text{OH})_2^{4+}$, InOH^{2+} , and $\text{In}(\text{OH})_2^+$ predominate and that the magnitudes of their formation constants are not likely to differ significantly from the values reported in 1956. A report on our least square computations is to be published soon.

It will emerge from the following discussion that for our purposes a formally correct explanation of the mechanism of In^{3+} hydrolysis is sufficient, and the uncertainty concerning the composition of the highly polymerized species does not affect the present conclusions.

THE METHOD OF INVESTIGATION

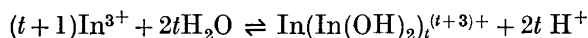
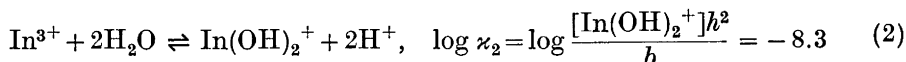
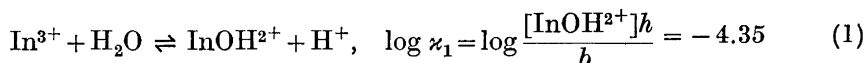
In this work the hydrolysis equilibria have been studied by measuring with the indium amalgam half-cell at a series of acidity levels the indium ion concentration as a function of the chloride and total indium concentrations. The $\log b = f(A)_{B,h}$ data so obtained have been analyzed in two steps.

In the first, the number of the chloride and the indium ions present in the reaction products, and the corresponding apparent formation constants, K_n , have been evaluated. These represent the hydrogen ion concentration dependent "formation constants" of all species containing a certain number of indium and chloride ions irrespective of whether the species are hydrolyzed or not. Next, the functional dependence on hydrogen ion concentration of the apparent formation constants has been examined, so that the number of hydroxyl groups coordinated to the hydrolysis products and the corresponding true equilibrium constants could be finally ascertained.

This approach makes it possible to employ the methods developed for the study of complex formation with a single ligand, and consequently the data treatment is much simplified. On the other hand the maintenance of a constant acidity level involves some experimental complications if it is to be achieved manually. These complications will, however, be eliminated by the introduction of automatic digital control methods which are now being developed in this laboratory.⁵

Three types of equilibria need to be considered in the test solutions.

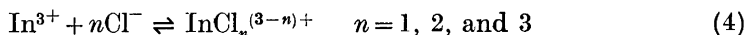
(1) The hydrolysis of the (hydrated) In^{3+} ion. This can be described¹ by the equations



$$\log \beta_{(t+1),2t} = \log \frac{[\text{In}(\text{In}(\text{OH})_2)_t]h^{2t}}{b^{(t+1)}} = \log k_0 + t \log k = -0.52 - 4.69t \quad (3)$$

Here the notation usual in this laboratory $b = [\text{In}^{3+}]$ and $h = [\text{H}^+]$ has been used, the symbol t representing a variable which can assume a series of integer values.

(2) The complex formation between In^{3+} and Cl^- ions. According to the results reported in the preceding publication³ the following equilibria have to be taken into account:

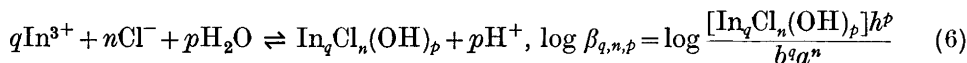


$$\log \beta_1 = \log \frac{[\text{InCl}^{2+}]}{ba} = 2.58, \quad \log \beta_2 = \log \frac{[\text{InCl}_2^+]}{ba^2} = 3.84,$$

$$\log \beta_3 = \log \frac{[\text{InCl}_3]}{ba^3} = 4.2 \quad (5)$$

In eqns. (4) and (5) the symbol a represents the concentration of the free chloride ions.

(3) The hydrolysis of the complexes which are being sought. For convenience these equilibria will be generally formulated as



with charges omitted on the reaction products.

The mass balance conditions may then be put into the form

$$B = b(1 + \kappa_1 h^{-1} + \kappa_2 h^{-2}) + S_1 + b \sum_1^3 \beta_n a^n + b(a \sum_p \beta_{1,1,p} h^{-p} + a^2 \sum_p \beta_{1,2,p} h^{-p} + a^3 \sum_p \beta_{1,3,p} h^{-p}) + S_2 \quad (7)$$

$$A = a + b \sum_1^3 n \beta_n a^n + b(a \sum_p \beta_{1,1,p} h^{-p} + 2a^2 \sum_p \beta_{1,2,p} h^{-p} + 3a^3 \sum_p \beta_{1,3,p} h^{-p}) + S_3 \quad (8)$$

Here S_1 , S_2 , and S_3 represent sums containing polynuclear terms of the type $q\beta_{q,p}b^q h^{-p}$, $qb^q a^n \beta_{q,n,p} h^{-p}$, and $nb^q a^n \beta_{q,n,p} h^{-p}$, respectively.

The first two members occurring in eqn. (7) have always been known throughout the experiments since b was measured, h was kept constant and the formation constants of the chloride-free hydrolysis products were taken as given earlier. For compactness these two first members will be denoted by $B_0 = B_0(h, b)$.

It is also convenient to rearrange the mononuclear terms and introduce the apparent formation constant

$$K_n = \beta_n + \sum \beta_{1,n,p} h^{-p} = K_n(h) \quad (9)$$

which represents the formation constant for all species containing a single indium and n chloride ions, hydrolyzed or not. In the general case, a similar rearrangement of the polynuclear terms and the substitution of the corresponding apparent formation constants $K_{q,n} = \sum \beta_{q,n,p} h^{-p}$ would lead to a significant simplification of the notation. Arguments will be presented in a later section that the $\log b(A)_{B,h}$ data obtained in this work can be satisfactorily explained by assuming the formation of a single polynuclear hydrolysis product which coordinates chloride. Anticipation of this result greatly simplifies the unavoidably awkward symbolism required to describe mixed complex formation, and therefore it is suggested, pending justification, that already at this stage the mass balance equations be written as

$$B = B_0 + b \sum_n a^n K_n + Qb^Q a^N \alpha_{Q,N} \quad (7a)$$

$$A = a + b \sum_n n a^n K_n + Nb^Q a^N \alpha_{Q,N} \quad (8a)$$

where for convenience $\sum \beta_{Q,N,p} h^{-p}$ is denoted by $\alpha_{Q,N}$, and $\beta_{Q,N,p}$ represents the formation constants of the chloride-containing polynuclear species having the composition $\text{In}_Q\text{Cl}_N(\text{OH})_p$.

It is clear from eqns. (7a) and (8a) that the n , N , and Q values prevailing at a certain acidity level can be found and the magnitudes of the corresponding

apparent formation constants can be estimated by recalculating the primary data $\log b(A)_{B,h}$ to the form

$$R = \frac{B - B_0}{A} = R(A, B)_h$$

and by examining the function $R = R(A, B)_h$.

This will be the subject of the first part of the section concerned with the determination of the composition of the reaction products. The second part describes the method used to evaluate the p and $\beta_{q,n,p}$ values.

Eqns. (7a) and (8a) also form the basis for the contention in the introduction concerning the mechanism of the hydrolysis of the hydrated indium ion. A formal description of the hydrolysis process which, like Biedermann's hypothesis, affords a correct value for the term B_0 is sufficient for finding the acid properties of the chloride species.

CHOICE OF EXPERIMENTAL CONDITIONS

In all the test solutions the total molarity was kept at the 3 M level by the addition of NaClO_4 . This solvent salt and molarity level were chosen with the intention of enabling us to use the results obtained in previous investigations^{1,3} concerning the chloride complex formation and the hydrolysis of the hydrated In^{3+} ion.

The general composition of the test solutions may be written as B mM In(III) , H mM H^+ , $(3000 - 3B - H)$ mM Na^+ , A mM Cl^- , $(3000 - A)$ mM $\text{ClO}_4^- = \text{TS}$ where H denotes the analytical proton excess and A represents the total concentration of chloride ions.

The B values studied ranged from 5.0×10^{-4} to 1.0×10^{-1} M. The lower limit 5.0×10^{-4} M was determined by the experimental difficulties discussed in detail in a preceding publication.³ The upper limit 1.0×10^{-1} M which is higher than that chosen in the indium chloride study was taken because it was desirable to investigate solutions containing a high concentration of polynuclear species.

Unfortunately, only a narrow $\log h$ range extending from -2.7 to -3.4 has been accessible for the study of the hydrolysis. The higher limit was, of course, set by the acid properties of the indium ion. At $\log h$ values exceeding -2.7 the fraction of In(III) present as hydrolysis products becomes negligible. The low solubility of indium hydroxide does not permit the investigation of less acidic solutions.

In each series of measurements, where B and h were maintained constant, the chloride concentration was increased in small steps until A attained the value of about 330 mM. The upper limit corresponds to a replacement of 11 % of the perchlorate ions of the medium by the chloride ions. The maximum A value was chosen with the object of reaching at all B levels the value of 3 for the ratio A/B . This made it possible to investigate the hydrolysis of both the InCl_2^+ and InCl_2^+ species, whereas much higher A/B values would be required to convert a considerable part of indium ions to the neutral InCl_3 complex, the hydrolysis of which was thus not taken up in the present work.

The equilibrium concentration of the indium ions b was determined by measuring the emf of the cell



where RE is the symbol for the reference half-cell



and In (in Hg) denotes a dilute indium amalgam in which the indium concentration (0.01 % in weight) was kept constant throughout a series of measurements.

The constancy of $\log h$ was controlled by measuring at the same time the emf of the cell



where GE is the symbol for a glass electrode.

The emf's of the cells (A) and (B) at 25°C may be written

$$E_A = E_{0,A} - 19.72 \log b + E_j(h) + E_j(a) \quad (10)$$

and

$$E_B = E_{0,B} - 59.16 \log h + E_j(h) + E_j(a) \quad (11)$$

In equations (10) and (11) $E_{0,A}$ and $E_{0,B}$ represent constants which have been evaluated by measuring E_A and E_B in chloride free solutions of such a high acidity that the hydrolysis could be neglected. $E_j(h)$ is the symbol for the liquid junction potential arising between the test solution and the 3 M NaClO₄ because of the replacement of Na⁺ by H⁺ ions, while $E_j(a)$ denotes the part of the liquid junction potential caused by the replacement of ClO₄⁻ by Cl⁻ ions. For $E_j(h)$ Biedermann and Sillén's data⁶ were used, while the $E_j(a)$ values were taken from the preceding publication.³

The primary data, $\log(B/b) = f(A)_{B,h}$, obtained with cell (A) are collected in Table 1.

The emf measurements were carried out as potentiometric titrations as usual in this laboratory. A typical example of a series is shown in detail in Table 2. This has been included to demonstrate the technique adopted and the precision which generally has been attained. The first part of the series, in which no chloride is added, serves for the determination of the constants $E_{0,A}$ and $E_{0,B}$. No series has been accepted when a deviation in $E_{0,A}$ exceeding 0.02 mV was observed.

In the second part, in which the chloride complex formation and the hydrolysis were studied, several solutions had to be employed in order to maintain h and B constant. Each point was reached by first adding a solution containing Cl⁻ and then adding an acid indium perchlorate solution in small steps to restore the acidity level. Upon introducing Cl⁻, the acidity always decreased because of the replacement of the hydroxyl groups coordinated to the hydrolysed species by the chloride ions.

The experimental approach described in connection with the study³ of the complex formation between indium and chloride ion has been followed in every detail. However, as more experience has now been obtained, especially as regards the treatment of the amalgams and the technique of the emf de-

Table 1. Survey of the measurements.

The indium amalgam half-cell data

$B = 5.00 \times 10^{-4}$ M; $-\log h = 3.379$: $\log(B/b)$, $A \times 10^3$ M; 0.0685, 0.102; 0.0806, 0.209; 0.0918, 0.297; 0.1055, 0.414; 0.1161, 0.504; 0.1278, 0.614; 0.1450, 0.780; 0.1658, 0.975; 0.2059, 1.390; 0.2571, 1.959; 0.3053, 2.543; 0.3545, 3.203.

$B = 5.00 \times 10^{-3}$ M; $-\log h = 3.110$: $\log(B/b)$, $A \times 10^3$ M; 0.1131, 0.970; 0.1592, 1.953; 0.2231, 3.114; 0.2713, 4.021; 0.3190, 4.887; 0.3829, 6.130; 0.4427, 7.306; 0.6040, 10.984; 0.7663, 15.262; 0.9093, 19.969; 1.0305, 24.681; 1.1456, 29.882.

$B = 5.00 \times 10^{-3}$ M; $-\log h = 3.379$: $\log(B/b)$, $A \times 10^3$ M; 0.2434, 1.109; 0.2799, 2.158; 0.3180, 3.158; 0.3545, 4.117; 0.3976, 5.183; 0.4569, 6.648; 0.5178, 8.126; 0.5959, 10.116; 0.7196, 13.493; 0.8525, 17.689; 0.9950, 23.063; 1.1101, 28.078; 1.2212, 33.554.

$B = 1.00 \times 10^{-2}$ M; $-\log h = 3.113$: $\log(B/b)$, $A \times 10^3$ M; 0.1521, 0.901; 0.1750, 1.739; 0.2054, 2.787; 0.2505, 4.300; 0.2972, 5.730; 0.3398, 6.954; 0.3788, 8.089; 0.4219, 9.312; 0.5355, 12.510; 0.6420, 15.653; 0.7592, 19.415; 0.8611, 23.062; 1.0361, 30.356; 1.2186, 39.760.

$B = 1.00 \times 10^{-2}$ M; $-\log h = 3.360$: $\log(B/b)$, $A \times 10^3$ M; 0.3438, 0.670; 0.3550, 1.256; 0.3661, 2.027; 0.3874, 3.144; 0.4032, 4.030; 0.4224, 5.063; 0.4442, 6.114; 0.4660, 7.108; 0.4879, 8.090; 0.5147, 9.160; 0.5376, 10.091; 0.6202, 13.299; 0.6993, 16.290; 0.8215, 20.941; 0.9924, 28.171.

$B = 2.50 \times 10^{-2}$ M; $-\log h = 3.109$: $\log(B/b)$, $A \times 10^3$ M; 0.3058, 3.287; 0.3524, 7.636; 0.3966, 11.186; 0.4579, 15.560; 0.5639, 19.634; 0.6613, 26.995; 0.8824, 38.028; 1.0852, 49.129; 1.2627, 60.492; 1.4413, 73.909; 1.6000, 87.707; 1.7384, 101.629; 1.8388, 112.934.

$B = 5.00 \times 10^{-2}$ M; $-\log h = 2.753$: $\log(B/b)$, $A \times 10^3$ M; 0.1562, 6.876; 0.3063, 22.400; 0.5497, 41.455; 0.8733, 62.433; 1.0858, 76.925; 1.2754, 91.766; 1.5102, 112.607; 1.7785, 142.021; 2.1436, 193.146.

$B = 5.00 \times 10^{-2}$ M; $-\log h = 2.677$: $\log(B/b)$, $A \times 10^3$ M; 0.1435, 9.175; 0.2804, 21.929; 0.5518, 42.428; 0.8788, 63.015; 1.0584, 75.125; 1.2835, 92.431; 1.5173, 113.347; 1.8272, 148.020; 2.1309, 191.388.

$B = 1.00 \times 10^{-1}$ M; $-\log h = 2.780$: $\log(B/b)$, $A \times 10^3$ M; 0.2891, 14.648; 0.3575, 33.994; 0.4382, 51.149; 0.6086, 78.014; 0.8433, 105.839; 1.1284, 135.934; 1.4656, 174.320; 1.7374, 210.556; 2.0412, 258.347; 2.2983, 310.291.

$B = 1.00 \times 10^{-1}$ M; $-\log h = 2.705$: $\log(B/b)$, $A \times 10^3$ M; 0.1978, 5.699; 0.2196, 13.189; 0.2982, 32.324; 0.3991, 51.647; 0.5695, 76.375; 0.8215, 104.730; 1.1152, 135.103; 1.4570, 173.587; 1.7445, 212.692; 2.0483, 259.709; 2.3049, 311.688.

Table 2. An example of a series of measurements.

Measurements with the amalgam and glass electrode half-cells						
v_2 ml	v_3 ml	b mM	h mM	$-E_j(h)$ mV	$-E_{0,A}$ mV	$E_{0,B}$ mV
(1) 10.00 mM In ³⁺ , 19.95 mM H ⁺ , 3000 mM ClO ₄ ⁻	50.0 ml					
(2) 20.00 mM In ³⁺ , 20.00 mM H ⁺ , 3000 mM ClO ₄ ⁻	v_2 ml					
(3) 202.07 mM NaHCO ₃ , 3000 mM ClO ₄ ⁻	v_3 ml					
(4) 10.00 mM In ³⁺ , 1.00 mM H ⁺ , 82.52 mM Cl ⁻ , 2917.5 mM ClO ₄ ⁻	v_4 ml					
(5) 53.05 mM NaHCO ₃ , 3000 mM ClO ₄ ⁻	v_5 ml					
0	0	9.578	19.95	0.34	564.31	365.24
1.00	1.00	9.578	15.68	0.26	564.31	365.20
2.00	2.00	9.578	11.73	0.20	564.30	365.22
3.00	3.00	9.578	8.06	0.14	564.31	365.23

Table 2. Continued.

At this point 2.11 ml of solution (2) were added in order to restore the $[\text{In}^{3+}]$ (which decreased during the preparation of the amalgams by electrolysis) to 10.00 mM. Then 11.00 ml of sol. (2), 3.50 ml of sol. (3), and 7.50 ml of sol. (5) were added to attain the desired hydrogen ion concentration level at which an appreciable hydrolysis is taking place and the second part of the titration was started.

v_1 ml	v_4 ml	$-E_A$ mV	E_B mV
1.00	0.68	610.53	166.29
2.00	1.30	610.75	166.24
3.25	2.15	610.97	166.26
5.00	3.45	611.39	166.26
6.50	4.55	611.70	166.22
8.15	5.90	612.08	166.22
9.75	7.35	612.51	166.19
11.25	8.80	612.94	166.20
12.65	10.30	613.37	166.19
14.00	12.00	613.90	166.18
15.15	13.55	614.35	166.18
18.50	19.33	615.98	166.18
20.75	25.30	617.54	166.20
22.75	35.66	619.95	166.18
24.00	55.00	623.32	166.20

termination, the present emf data are believed to be of somewhat higher precision. Both E_A and E_B are considered to have been determined with an uncertainty not exceeding 0.01 mV.

RESULTS

The sets of $\log(B/b) = f(A)_{B,h}$ data, summarized in Table 1, form the basis of the calculations presented in this section.

Determination of the apparent formation constants. The determination of the composition of the predominant indium chloride complex species, as far as the number of indium and chloride ions prevailing in the reaction products and their apparent formation constants are concerned, was carried out by first comparing the $\log(B/b)$ data, suitably recalculated, with normalized projection maps of the type described in the preceding paper.³ In a second stage, the results obtained were refined by the generalized least square computer program Letagrop.⁸

First, at each acidity level, the $\log b(A)_{B,h}$ data were recalculated by graphical interpolation to the form $\log b = f(\log(B - B_0))_{R,h}$ where $R = (B - B_0)A^{-1}$ designates the average number of indium atoms bound per chloride ion, and they were then compared with a series of model functions representing various mechanisms.

In order to estimate the concentration of the chloride and hydroxyl bearing species, each group of recalculated data was compared with the model constructed by assuming no mixed species formation. The comparison showed

clearly that appreciable amounts of mixed species are only formed in the region of high R and high B values. This conclusion has been corroborated by calculating the E_A values with the known hydrolysis and complex formation constants given in eqns. (1)–(5). The measured experimental values, E_A , have been found to deviate appreciably from the calculated values only at low values of the ratio $[\text{Cl}^-]_{\text{tot}}/[\text{In(III)}]_{\text{tot}}$, the deviations increasing with B and attaining a value of about 2 mV for $B = 0.1$ M.

Thus only a small fraction of indium ions are converted to chloride-containing hydrolysis products prior to the formation of a precipitate of indium hydroxide. An attempt was then made to explain the deviations from pure hydrolysis and chloride complex formation by a simple model.

With the hypothesis that only mononuclear chloride bearing species $\text{InCl}(\text{OH})_p$ and $\text{InCl}_2(\text{OH})_p$, where p may take any value, are present, no agreement was found in the region where mixed species were shown to be of importance. We have thus to assume the presence of polynuclear reaction products as well. A single polynuclear species of the composition $\text{In}_Q\text{Cl}_N(\text{OH})_p$ was supposed to be formed, and models with Q values ranging from 2 to 4 were tried and for each choice of Q the N values 1, 2, and 3 were assumed.

A satisfactory fit has been obtained only by assuming the formation of $\text{In}_2\text{Cl}(\text{OH})_p$. It is now recalled that at this stage, when data pertaining to a certain hydrogen concentration level are considered, the value of p has to be regarded as an unknown variable.

To illustrate the calculations, the construction of the model for the final hypothesis will be described briefly. The basic ideas have been discussed in detail in several papers from this laboratory.

The actual hypothesis leads, using the mass balance conditions (7a) and (8a), to the following equation for R

$$R = \frac{B - B_0}{A} = \frac{K_1b + K_2ba + 2\alpha_{2,1}b^2}{1 + K_1b + 2K_2ba + \alpha_{2,1}b^2} \quad (12)$$

Introducing instead of b and a the new independent variables

$$u = K_1b \quad \text{and} \quad v = K_2K_1^{-1}a \quad (13)$$

the expression for R will take the form

$$R = \frac{u + uv + 2\varrho u^2}{1 + u + 2uv + \varrho u^2} \quad (14)$$

where for brevity $\alpha_{2,1}K_1^{-2}$ is set equal to ϱ .

Eqn. (14) shows that, when at a constant R level a value is chosen for ϱ , v becomes a function of u only, thus one of the independent variables can be eliminated. After this step has been taken it is easy to calculate model functions to be compared with the data ($\log(B - B_0)$, $\log b$) $_R$, which are obtained by interpolation. Large scale plots of $\log b$ versus $\log R$ were made at each B (and of course h) level and the data were interpolated at R steps differing by about 0.1 units. The corresponding model functions

$$\log u = \log K_1 + \log b$$

and

$$\log Y = \log v + \log(u + uv + 2\varrho u^2) = \log(B - B_0) + \log K_2 - \log K_1$$

are seen to differ from the experimental $\log(B - B_0)$ versus $\log b$ plots by the constants $\log K_1$ and $\log(K_2 K_1^{-1})$. Thus if a correct value is chosen for ϱ , which determines the shape of the model functions, then by lateral and vertical translations the data can be made to agree with the set of functions $\log Y(\log u)$. The fit obtained with the hypothesis expressed by eqn. (12) is illustrated in Figs. 1a and 1b.

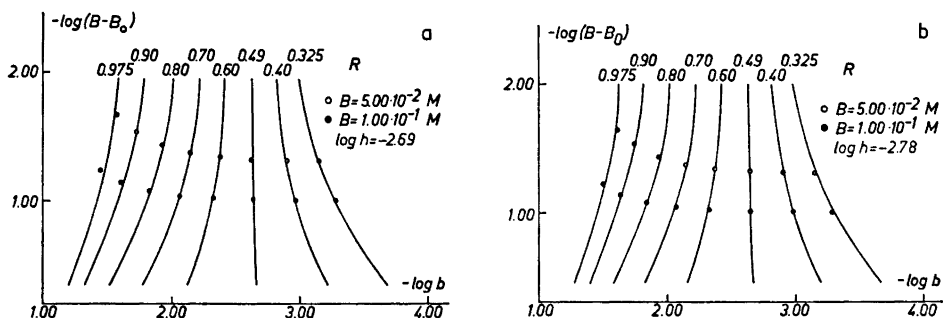


Fig. 1. $\log(B - B_0)$, cf. eqn. (7a), as a function of $\log b$ at a series of R , cf. eqn. (12), levels. (a) $-\log h = 2.69$, (b) $-\log h = 2.78$. The curves have been calculated with the equilibrium constants shown in the first row of Table 3.

The main feature of the projection map method is that the *same* set of data may be compared with several hypotheses, and since the uncertainty of the data of the type employed here can be estimated directly, one can easily decide whether the experimental precision is sufficient to distinguish between different models. Comparison with different hypotheses is of particular importance in a case as unfavorable as the present one, when the reaction products sought never attain a high concentration.

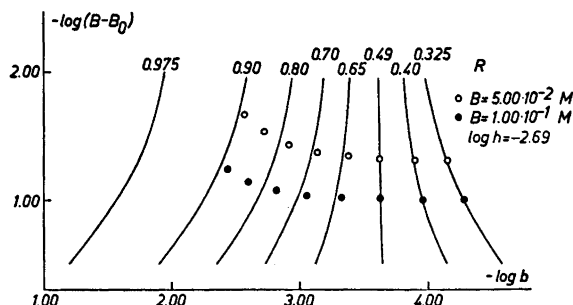
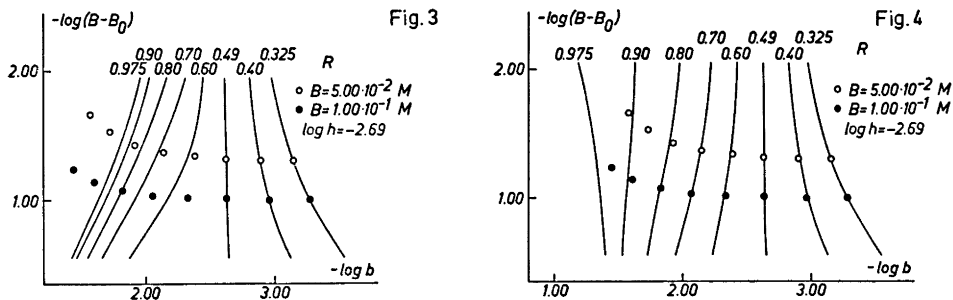


Fig. 2. Comparison of the $\log(B - B_0)$ versus $\log b$ data with the hypothesis that all chloride containing hydrolysis products are mononuclear. The model functions are shown in the position of optimum fit.



Figs. 3 and 4. Comparison of the $\log(B - B_0)$ versus $\log b$ data with the hypothesis that trinuclear hydrolysis products of the composition $\text{In}_3\text{Cl}_n(\text{OH})_p$ are present. Fig. 3, $n = 1$ and Fig. 4, $n = 2$. The model functions are shown in the position of optimum fit.

Figs. 2 – 4 illustrate the results obtained with the following assumptions: all chloride species are mononuclear (Fig. 2); trinuclear reaction products are formed containing one (Fig. 3) or two chloride ions (Fig. 4) besides the mononuclear species. Comparison was also made with models representing the hypothesis that tetranuclear species are present. The fit was even poorer than in Figs. 3 and 4.

The deviations which are seen to exceed by far the experimental uncertainty, represented by the diameter of the circles, indicate that the data are of an accuracy which is sufficient to exclude the formation of appreciable amounts of species other than $\text{InCl}(\text{OH})_p$, $\text{InCl}_2(\text{OH})_p$, and $\text{In}_2\text{Cl}(\text{OH})_p$.

Determination of the true formation constants. To ascertain the values of p and the formation constants of the chloride complexes the hydrogen ion concentration dependence of the apparent constants $K_1 = \beta_1 + \sum_p \beta_{1,1,p} h^{-p}$, $K_2 = \beta_2 + \sum_p \beta_{1,2,p} h^{-p}$ and $\alpha_{Q,N} = \beta_{2,1,p} h^{-p}$ have been examined. Plots of $\log(K_1 - \beta_1)$ and $\log \alpha_{Q,N}$ versus $-\log h$ could be well approximated with a straight line of slope unity, indicating that in both cases one hydroxyl group is coordinated to the complexes and thus that they have the composition $\text{In}_2\text{ClOH}^{4+}$ and InClOH^+ . On the other hand, the $\log(K_2 - \beta_2)$ versus $-\log h$ plot did not show any trend exceeding the experimental uncertainty, hence with data of the present precision no evidence can be found for the hydrolysis of the species InCl_2^+ .

Table 3. Survey of the values of the formation constants.

Method	$\log \beta_{1,1,1}$	$\log \beta_{2,1,1}$
Normalized projection maps	-1.3 ± 0.1	$0.3_8 \pm 0.1$
Letagrop	$-1.2_8 \pm 0.07$	$0.3_1 \pm 0.06$
Proposed values	-1.3 ± 0.1	0.3 ± 0.1

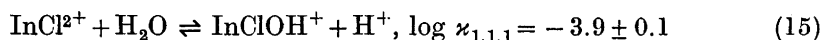
The $\log \beta_{1,1,1}$ and $\log \beta_{2,1,1}$ values obtained by these calculations are given in Table 3. In the estimation of the uncertainty for $\log \beta_{1,1,1}$ and $\log \beta_{2,1,1}$ the narrow $\log h$ range available, the accumulated errors arising from the use of the equilibrium constants κ_1 , κ_2 , $\beta_{q,p}$ and β_n and the experimental inaccuracy have all been taken into account.

*Treatment of the data with Letagrop.*⁷ The least square calculations were undertaken with two main objectives. First, an attempt was made to refine the magnitudes of the graphically obtained constants $\beta_{1,1,1}$ and $\beta_{2,1,1}$. Only these constants were assumed as variables and the sum $U = \sum (E_{A,\text{calc}} - E_A)^2$, where $E_{A,\text{calc}}$ represents a value of the indium amalgam half-cell calculated with a certain choice for the magnitudes of the mixed complex formation constants, has been minimized by employing Sillén and Warnqvist's most recent version of the Letagrop program.⁸ The results, summarized in Table 3, are seen not to differ significantly from the values for $\log \beta_{2,1,1}$ and $\log \beta_{1,1,1}$ obtained with the projection maps.

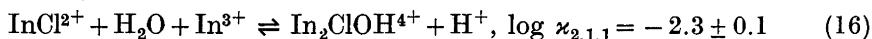
To express the fit in quantitative terms the deviation $E_{A,\text{calc}} - E_A$ was computed for each experimental point. For none of them was the deviation found to exceed 0.1 mV.

In the second part of the Letagrop calculations a series of hypotheses were tried concerning the composition of the hydrolysis products of the chloride complexes. The number of indium atoms as well as the number of chloride and hydroxyl ions coordinated were varied in a systematic fashion; in each case only two species were assumed to be formed. An average deviation not exceeding 0.1 mV could, however, be obtained solely with the model deduced by the projection maps. Hence, as long as one does not want to introduce more than two chloride bearing hydrolysis products, there is little doubt that an acceptable fit can be achieved only by assuming the formation of the species InClOH^+ and $\text{In}_2\text{ClOH}^{4+}$.

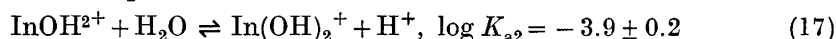
The results of the present work may be easier to visualize when they are expressed in terms of hydrolysis instead of formation constants. We obtain, since $\log \beta_1 = 2.58$, for



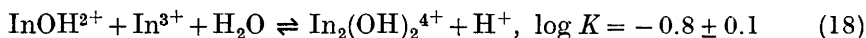
and for



By comparing these values with the corresponding hydrolysis constants¹ of the chloride-free species



and



we may first conclude that with the data of present precision no difference can be detected between the strength of the mononuclear (aquo) acids InCl^{2+} and InOH^{2+} .

As far as mononuclear protolysis is concerned indium(III) appears to show many similarities to thallium(III) and mercury(II). For these three ions K_{a2} has been found^{1,9,10} to be close to the acidity constant of the mono-

chlorocomplex.^{11,12} Thus the acid properties are not seriously influenced when a hydroxide ion in the coordination sphere is replaced by a chloride ion. On the other hand, there does not seem to be experimental evidence for the formation of soluble hydrolysis products bearing two chloride ions such as $\text{InCl}_2(\text{OH})_p$ and $\text{TlCl}_2(\text{OH})_p$.

We may infer from eqns. (16) and (18) that InCl^{2+} shows a much weaker tendency to form binuclear hydrolysis products than the InOH^{2+} ion. Were the two indium atoms in a binuclear species bound together by a single hydroxyl group, the difference between $\log K$ and $\log \kappa_{2,1,1}$ would be expected to be rather small since the foregoing discussion of the mononuclear hydrolysis mechanism appears to indicate that the second water molecule in the coordination sphere of the indium ion is not much affected by the formation of the monochlorocomplex. It seems plausible to suggest that the two indium atoms in the binuclear species form several bonds (perhaps including metal-metal bonds as well) which become weakened when chloride replaces the hydroxyl ion.

To devise experiments for a detailed study of the hydrolysis of the more chloride-rich indium complexes would bring us nearer to an understanding of the conditions enabling the indium ion to participate in a polynuclear mechanism.

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