ACTA CHEMICA SCANDINAVICA 15 (1961) 555–564

Studies on the Hydrolysis of Metal Ions

Part 34. The Hydrolysis of the Indium(III)ion, In^{3+}, in 3 M (Na^+) Cl^- Medium

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The hydrolysis equilibria of In(III) have been studied at 25°C in the ionic medium 3 M(Na^+)Cl^- by measuring the hydrogen ion concentration with a glass electrode. The [In(III)] ranged from 1×10^{-3} to 4×10^{-2} M, and the hydrogen ion concentration was varied from values high enough for the hydrolysis to be negligible to those low enough for a precipitate to be formed. The data could be explained by assuming the equilibria:

$$In^{3+} + H_2O \rightleftharpoons InOH^{2+} + H^+ \qquad \log k_{a1} = -6.9_5 \pm 0.1$$
$$2\,In^{3+} + 2\,H_2O \rightleftharpoons In_2(OH)_2^{4+} + 2\,H^+ \qquad \log \beta_{22} = -10.1_5 \pm 0.1$$

Comparison with the equilibrium constants for the formation of the species $InOH^{2+}$ and $In_2(OH)_2^{4+}$ in 3 M(Na^+)ClO_4^-, given in a previous work [1], indicates that in 3 M (Na^+)Cl^- medium the species denoted by the collective formulas "$InOH^{2+}$" and "$In_2(OH)_2^{4+}$" are in reality mainly mixed Cl^-–OH^--complexes (just as "In^{3+}" denotes mainly Cl^- complexes).

The hydrolysis equilibria of the In(III) ion at 25°C have been previously studied by Biedermann [1] who used 3 M (Na^+)ClO_4^- as the ionic medium. The extensive data obtained were explained by assuming the formation of the mononuclear ions $InOH^{2+}$ and $In(OH)_2^+$, and of polynuclear species of the general composition $In(In(OH)_2)_n^{(3+n)+}$, where n is an integer which may take an unlimited series of values. The following equilibrium constants were determined:

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* This investigation was started by N. Li and G. Biedermann who carried out a number of preliminary experiments in Stockholm. The main part of the experimental work was then done by N. Li and J. Yu in Pittsburgh. The theoretical interpretation is the responsibility of all the authors.

$$In^{3+} + H_2O \rightleftharpoons InOH^{2+} + H^+; \ \log k_{a1} = \log\{[InOH^{2+}]h[In^{3+}]^{-1}\} = -4.42 \quad (1)$$

$$In^{3+} + 2H_2O \rightleftharpoons In(OH)_2^+ + 2H^+; \ \log k_2 = \log(k_{a1}k_{a2}) = \log\{[In(OH)_2^+]h^2[In^{3+}]^{-1}\} = -8.3 \quad (2)$$

$$(n+1)In^{3+} + 2nH_2O \rightleftharpoons In(In(OH)_2)_n^{(3+n)+} + 2nH^+;$$
$$\log K_n = \log\{[In(In(OH)_2)_n^{(3+n)+}]h^{2n}[In^{3+}]^{-(n+1)}\} = -0.52 - n4.69 \quad (3)$$

On the basis of these constants it can be shown that for $[In(III)] > 10^{-3}M$ the predominant hydrolysis products are the polynuclear species.

In the present work, the hydrolysis equilibria of In(III) have been investigated in the ionic medium 3 M $(Na^+)Cl^-$. A study of the hydrolysis in this solvent seemed to be of interest for several reasons.

A number of investigators [2-4] have found evidence that In^{3+} forms strong mononuclear complexes with Cl^-. Thus, a comparison of the results obtained in Cl^- and ClO_4^- media may indicate the influence of chloride complex formation on the hydrolysis equilibria. It must be pointed out that, from equilibrium measurements in a constant ionic medium, one may only determine the number of those ions in the products formed whose concentrations are varied. However, no information can be obtained on the number of medium ions bound to the complexes because the concentration of the medium ions is always essentially constant. Thus, if we write $[In_p(OH)_q]$, the "concentration of the species $In_p(OH)_q$" in 3 M $(Na^+)Cl^-$, this symbol is really an abbreviation for the sum

$$[In_p(OH)_q] = \sum_r \sum_s \sum_t [In_p(OH)_qNa_rCl_s)(H_2O)_t] \quad (4)$$

A more detailed discussion on the limitations of the ionic medium method has been given by Sillén [5].

A study of indium solutions containing chloride also has some practical value. Metallic indium is dissolved most easily in a HCl solution, and therefore the starting material in many analytical and preparative methods is an indium solution with an excess of chloride ions.

METHOD OF INVESTIGATION

All the indium solutions studied were made up to contain 3 M Cl^- by adding sodium chloride, so they had the general composition, B M In(III), H M H^+, $(3.000 - 3B - H)$ M Na^+, 3 M Cl^- = solution S, where B denotes the total concentration of indium and H is the hydrogen ion concentration assuming no hydrolysis. A series of B values ranging from 0.001 to 0.04 M were investigated. We have not been able to obtain sufficiently accurate data for $B < 0.001$ M; this failure is explained by the very low buffer capacity of such dilute indium solutions. It has been of little interest to study solutions of $B >$ about 0.05 M, because the acidity range where appreciable hydrolysis occurs but no precipitate is formed becomes very narrow in concentrated indium solutions.

The hydrolysis equilibria were investigated by measuring the hydrogen ion concentration with the cell

$$-RE \,|\, \text{solution S} \,|\, GE + \quad (A)$$

where GE denotes a glass electrode and RE is the reference half-cell

$$\text{Ag, AgCl} \mid 3\ \text{M NaCl saturated with AgCl(s)} \mid 3\ \text{M NaCl} \mid$$

The emf of cell (A) may be written at 25°C

$$E = E_0 + 59.15 \log h + 59.15 \log f(\text{H}^+) - E_j \tag{5}$$

where E_0 is a constant, h the hydrogen ion concentration at equilibrium, $f(\text{H}^+)$ the activity factor of hydrogen ions and E_j the liquid junction potential at the junction, solution S | 3 M NaCl. The standard state is defined so that $f(\text{H}^+)$ as well as the activity factors of the other reacting species tend to unity when the composition of the solution approaches 3 M NaCl. We have assumed that the activity factors may be regarded as constants. It is probable that no serious error is introduced by this assumption since the concentration of the reacting ions was always kept low in comparison with that of the medium ions.

By measuring the emf of the cell

$$\text{RE} \mid h\ \text{M H}^+,\ (3.000-h)\ \text{M Na}^+,\ 3.000\ \text{M Cl}^- \mid \text{GE}$$

as a function of h, it was found that for, $h<0.01$ M, E_j becomes less than 0.1 mV. Since the hydrolysis proved to be inappreciable for $\log h > -3$, E_j could be neglected in hydrolyzed solutions when h was calculated with eqn. (5).

Each series of measurements was performed, as is usual in the Stockholm laboratory, as a potentiometric titration. In each series B was kept constant and, by adding a NaOH solution (containing 3 M Cl^-), H was decreased from values where the hydrolysis is negligible to the point where a lasting precipitate was formed. The E data obtained in the region where $H = h$ served to calculate E_0. The analytical excess of hydrogen ions of the indium stock solution was calculated by the equation: $[\text{H}^+] = [\text{Cl}^-] - 3\,[\text{In(III)}]$.

In most cases E_0 was found to be constant within ± 0.2 mV when $\log H$ was decreased by one unit; this result indicates that the H value calculated from the analytical data is of sufficient accuracy.

In this way, for each series of measurements, we could calculate the average number of hydrogen ions set free per indium atom,

$$Z = \frac{h - H}{B} \tag{6}$$

as a function of $\log h$. The composition of the hydrolysis products and the corresponding equilibrium constants were ascertained by the study of the family of functions $Z(\log h)_B$. This forms the subject of the "Results" section.

EXPERIMENTAL

Materials and analysis

Indium chloride solutions were prepared from indium metal of 99.93 % purity supplied by Kings Products Co. The metal was dissolved in an excess of a concentrated HCl solution which had been purified by distillation. A large part of the excess HCl, which was required to dissolve the metal rapidly, was then removed by evaporation using an infrared lamp.

In(III) in the indium chloride stock solution was determined by precipitating hydrous indium oxide with a slight excess of NH_3 aq; the precipitate was washed with hot water, dried at 120°C and was finally ignited at 1 000°C until a constant weight was attained. Some current work by one of us (G. Biedermann) indicates that the precipitate ignited at 1 000°C contains some excess oxygen or water. An error of about 0.2 % is therefore introduced when the ignited oxide is assumed to have exactly the composition of In_2O_3. If rapid analyses are required In(III) may be determined as the oxide, but, for the most accurate work, the sulfide method [6] is to be preferred.

Cl^- in the indium stock solution was determined gravimetrically as AgCl. The analytical excess of the hydrogen ions, H, was calculated from $H = [Cl^-] - 3\,[In(III)]$.

It is essential for the proper functioning of $Cl^- \mid AgCl$, Ag half-cells that solutions containing less than 0.001 % Br^- should be used [7]. The *NaCl* solution used in the reference half-cell was therefore prepared from a batch of concentrated HCl and Na_2CO_3 of p.a. quality in which no Br^- ions could be detected using the test of Ref.[7]. The neutral 3 M NaCl solution made from these substances was shaken for several days with an excess of AgCl to attain a saturated solution.

The *NaCl stock solution* used to prepare solution S was made from NaCl p.a. Since this batch of NaCl proved to contain traces of HCl, the stock solution (about 4 M) was carefully neutralized with dilute NaOH using bromothymol blue as indicator.

The *hydrochloric acid* solution was standardized against $KHCO_3$, and the *NaOH* solution against potassium hydrogen phthalate. When the NaOH solution was titrated with the hydrochloric acid the equivalence point found by a Gran plot [8] has agreed within ± 0.1 % with the value calculated on the basis of the standardizations.

N_2 was taken from a cylinder and passed through 3 M NaCl to obtain the vapor pressure of solution S.

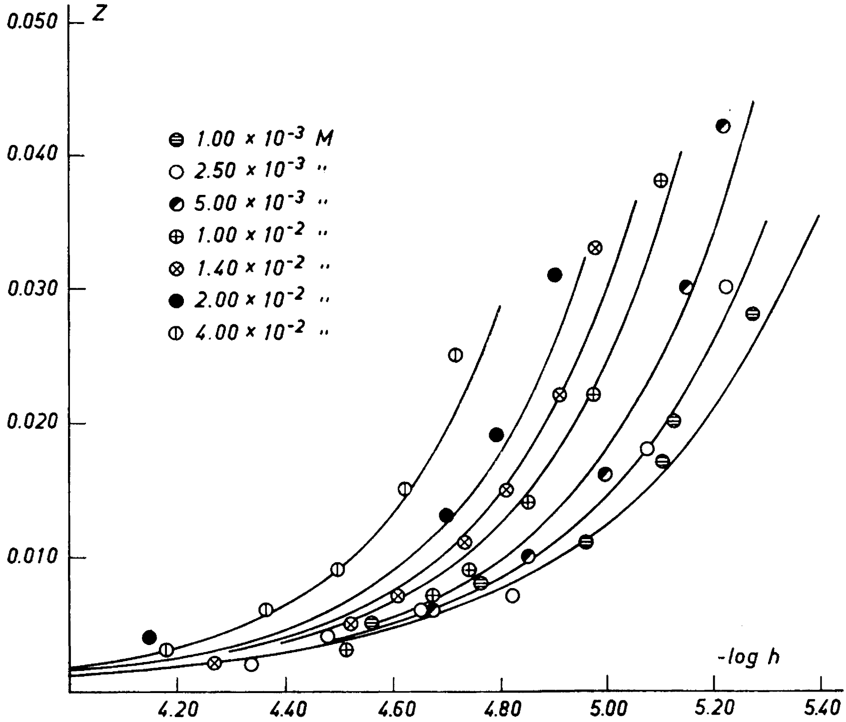

Fig. 1. Z, the average number of hydrogen ions set free by In(III), as a function of log h. The curves are calculated with log $k_{a1} = -6.9_5$ and log $\beta_{22} = -10.1_5$.

Emf measurements

All emf measurements were made in a thermostat at 25.0 ± 0.1°C. E was determined with a valve potentiometer Radiometer PHM3, Copenhagen. The reading accuracy of this instrument has been ± 0.1 mV.

The cell arrangement was that described by Forsling, Hietanen and Sillén [9]. Beckman glass electrodes of type No 40498 were employed. AgCl, Ag electrodes were prepared by the method normally used [1] in the Stockholm laboratory.

RESULTS

All the data are summarized in Table 1, and a graphical representation of the experimental results is given in Fig. 1. At Z values exceeding 0.04—0.05, this limit depending somewhat on B, no stable E values could be attained because of the slow formation of a colloidal precipitate which became visible in a couple of hours.

Since $Z(\log h)_B$ is seen in Fig. 1 to be a function of B as well as of h, polynuclear hydrolysis products must be present in considerable amounts. To find the composition of the polynuclear species and the corresponding equilibrium constants, Sillén's method [10] will be followed.

When smoothed curves were drawn through the $Z(\log h)_B$ data these were found for $B \geq 0.01$ M to be approximately parallel, and, for a constant value of Z, the spacing of the curves $\Delta \log B / \Delta \log h$ was about 2. Using the arguments given by Sillén [10], these results indicate that for $B \geq 0.01$ M the main products of the hydrolysis are polynuclear ions having the general composition $In(In(OH)_2)_n^{(3+n)+}$ (n = integer).

If these conclusions are correct, then Z should be a function of the single variable $\log B - 2 \log h$. The plot $Z(\log B - 2 \log h)$ is shown in Fig. 2; clearly the data for $B \geq 0.01$ M form a single curve which represents the limiting curve for the polynuclear mechanism involving the formation of the species $In(In(OH)_2)_n$.

Table 1. Survey of measurements.

$B = 1.00 \times 10^{-3}$ M		$B = 2.50 \times 10^{-3}$ M		$B = 5.00 \times 10^{-3}$ M		$B = 1.00 \times 10^{-2}$ M		$B = 1.40 \times 10^{-2}$ M		$B = 2.00 \times 10^{-2}$ M		$B = 4.00 \times 10^{-2}$ M	
$-\log h$	Z	$-\log h$	Z	$-\log h$	Z	$-\log h$	Z	$-\log h$	Z	$-\log h$	Z	$-\log h$	Z
4.560	0.005	4.339	0.002	4.673	0.006	4.515	0.003	4.269	0.002	4.151	0.004	3.823	0.001
4.763	0.008	4.479	0.004	4.854	0.010	4.674	0.007	4.525	0.005	4.702	0.013	4.182	0.003
4.962	0.011	4.655	0.006	5.001	0.016	4.744	0.009	4.611	0.007	4.796	0.019	4.367	0.006
5.107	0.017	4.823	0.007	5.156	0.030	4.855	0.014	4.735	0.011	4.905	0.031	4.500	0.009
5.130	0.020	5.080	0.018	5.226	0.042	4.980	0.022	4.813	0.015			4.624	0.015
5.278	0.028	5.230	0.030			5.108	0.038	4.915	0.022			4.720	0.025
								4.981	0.033				

Plots of $Z(\log B - \log h)$ and $Z(\log B - 3 \log h)$ were also tested, but in these cases no limiting curve could be obtained. Thus the accuracy of the data is sufficient to exclude the hypothesis that the polynuclear ions have the composition $In(InOH)_n$ or $In(In(OH)_3)_n$.

Next we made the assumption that a *single polynuclear* species is formed with $n = 1$, *i.e.* $In(In(OH)_2)^{4+}$. This seemed to be reasonable because only very low Z values could be studied. With this hypothesis, Z is given by the equation

$$Z = \frac{2\,\beta_{22}\,b\,h^{-2}}{1 + 2\,\beta_{22}\,b\,h^{-2}} \qquad \beta_{22} = \frac{[In_2(OH)_2^{4+}]\,h^2}{b^2} \qquad b = [In^{3+}] \tag{7}$$

and B, the total concentration of In(III), is equal to

$$B = b(1 + 2\,\beta_{22}\,b\,h^{-2}) \tag{8}$$

It can be seen from (7) and (8) that Z and Bh^{-2} are both functions of the same variable $b\,h^{-2}$, thus Z is a function of $B\,h^{-2}$. This conclusion is the basis of the arguments used above for the composition of the polynuclear species.

The correctness of the assumptions represented by (7) and (8) was tested by comparing the experimental data Z *versus* $(\log B - 2 \log h)$ with the normalized [11] form of (7), Z *versus* $\log X$ where

$$Z = \frac{2\,v}{1 + 2\,v} \qquad X = B\,h^{-2}\,\beta_{22} = v\,(1 + 2\,v) \tag{9}$$

and

$$v = \beta_{22}\,b\,h^{-2} \tag{10}$$

When the plot $Z = Z(\log X)$ was superimposed on the data $Z(\log B - 2 \log h)$ a good agreement was found for $B \geq 0.01$ M, and the difference $\log X - (\log B - 2 \log h)$ in the position of best fit gave $\log \beta_{22} = -9.9 \pm 0.1$. The $Z(\log B - 2 \log h)$ curve calculated with $\log \beta_{22} = -9.9$ is seen in Fig. 2 to represent, to a good approximation, the experimental data for $B \geq 0.01$ M.

To explain the positive deviations of the $Z(\log B - 2 \log h)$ data from the limiting polynuclear curve for $B \leq 0.005$ M it was assumed that in these dilute indium solutions the only important hydrolysis products are $In_2(OH)_2^{4+}$ and the mononuclear ion $InOH^{2+}$. Then B and Z will be given by the equations

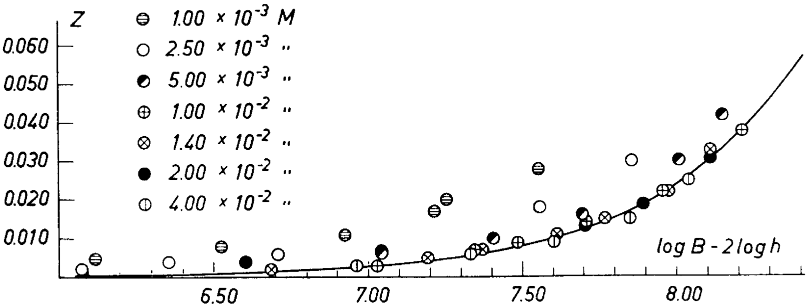

Fig. 2. Z as a function of $\log B - 2 \log h$. The limiting curve for the polynuclear mechanism is calculated with $\log \beta_{22} = -9.9$.

$$Z = \frac{k_{a1}h^{-1} + 2\beta_{22}\, b\, h^{-2}}{1 + k_{a1}h^{-1} + 2\beta_{22}\, b\, h^{-2}};\ k_{a1} = [\mathrm{InOH}^{2+}]\, h\, b^{-1} \tag{11}$$

$$B = b\,(1 + k_{a1}\, h^{-1} + 2\,\beta_{22}\, b\, h^{-2}) \tag{12}$$

which are the corrected forms of the approximate eqns. (7) and (8). The hypothesis represented by (11) and (12) was checked by calculating k_{a1} in the Z range 0.01 to 0.04 for each experimental point corresponding to $B = 1$, 2.5, and 5×10^{-3} M. The equation used was:

$$k_{a1} = \frac{Z\,h}{1-Z} - 2\,\beta_{22}\, B\,(1-Z)\, h^{-1} \tag{13}$$

which is obtained from (11) and (12) by eliminating b.

The calculated k_{a1} values have shown no trend with B or h and as the average value we have estimated $\log k_{a1} = -6.9 \pm 0.1$.

The hypothesis that there are practically only In^{3+}, $In_2(OH)_2^{4+}$ and $In(OH)_2^{+}$ present was also tried. When $k_2 = k_{a1}k_{a2}$ was calculated from an equation corresponding to (13) a trend with h was found which greatly exceeded the experimental uncertainty.

The β_{22} value calculated with (7) and (8) must be regarded as a first approximation because we have neglected the mononuclear species. Similarly k_{a1} may be slightly in error since an approximate value for β_{22} has been used when applying (13). To refine these approximate results a method of calculation is needed which yields independent numerical values for β_{22} and k_{a1}. It would be preferable to apply the approach proposed by Biedermann and Sillén [12] but the low accuracy of the present data makes such a treatment too uncertain. Instead we have attempted to use the easily normalizable function:

$$\begin{aligned} a = Z\, h^2 B^{-1}(1-Z)^{-2} &= \beta_{22}\,(2 + k_{a1}\,\beta_{22}^{-1}\, h\, B^{-1}(1-Z)^{-1}) = \\ &= \beta_{22}\,(2 + k_{a1}\,\beta_{22}^{-1}\, w) \end{aligned} \tag{14}$$

which is obtained from (11) and (12) by eliminating $b = B\,(1-Z)$, substituting it into (12) and rearranging the resulting equation. Thus if $InOH^{2+}$ and $In_2(OH)_2^{4+}$ are the sole products of hydrolysis a should be a function of the single variable w; both a and w may be calculated directly from the experimental data. To find the most probable values for the constants, the experimental $\log a$ ($\log w$) data were compared with the normalized form of (14)

$$\log a_1 = \log\,(2 + w_1) = \log a_1\,(\log w_1) \tag{15}$$

where $a_1 = a\,\beta_{22}^{-1}$ and $w_1 = w\, k_{a1}\,\beta_{22}^{-1}$. Superimposing (15) on the experimental data we have calculated from the differences ($\log a_1 - \log a$) and ($\log w_1 - \log w$) in the position of best fit the following values:

$$\log k_{a1} = -6.9_5 \pm 0.1$$
$$\log \beta_{22} = -10.1_5 \pm 0.1$$

which are, as would be expected, slightly lower than those found with the first approximation. Fig. 3 shows the $\log a$ ($\log w$) data. All of them are seen to lie

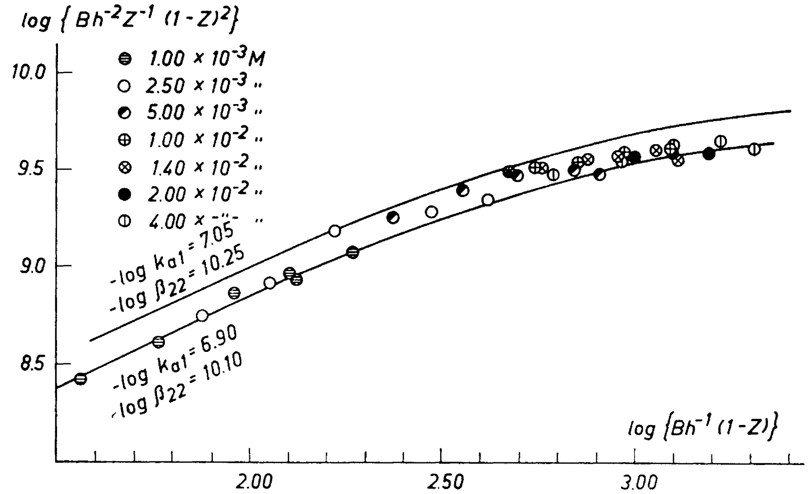

Fig. 3. —log a as a function of —log w, see eqn. (14). The curves are calculated with the log k_{a1} and log β_{22} values given in the figure.

between the curves calculated by taking the upper and lower limits of the calculated log k_{a1} and log β_{22} values.

It should be added that variables as a and w containing the term (1—Z) are to be avoided when Z values near to unity should be considered, because in such a case 1—Z is very sensitive to small experimental errors. In the present case 1—Z is practically equal to 1, therefore this factor has only a slight influence on the accuracy of a and w.

DISCUSSION

The main conclusion of the present work is that the hydrolysis equilibria in 3 M Cl^- can be interpreted in terms of species containing the same number of indium atoms and OH^- groups as those previously found [1] to be present in 3 M ClO_4^-. It seems that the hydrolysis products have a core built up from strongly bound In^{3+} ions and OH^- groups to which water and anions are attached. The absence of the higher members of the series $In(In(OH)_2)_n$ in 3 M Cl^- is understandable. At the very low Z values available the concentrations of complexes with $n >$ 1 might not attain detectable values.

It is difficult to explain quantitatively the magnitude of the differences $k_{a1}(ClO_4^-)$—$k_{a1}(Cl^-)$ and $\beta_{22}(ClO_4^-)$—$\beta_{22}(Cl^-)$ because we are not able to estimate the variation of the activity factors of the reacting species when ClO_4^- is entirely replaced by Cl^-. Nevertheless the following arguments suggest that in 3 M $(Na^+)Cl^-$, Cl^- ions are bound to the main part of the hydrolysis products.

If we neglect the variation of the activity factors, and postulate that In^{3+} and its hydrolysis products do not form complexes with ClO_4^-, then we can write by taking into account the definition of $[In_p(OH)_q]$ given by eqn. (4).

$$\frac{k_{a1}\,(ClO_4^-)}{k_{a1}\,(Cl^-)} = \frac{1 + \Sigma\,\beta_n\,[Cl^-]^n}{1 + \Sigma\,\varkappa_m\,[Cl^-]^m} \tag{16}$$

$$\frac{\beta_{22}\,(ClO_4^-)}{\beta_{22}\,(Cl^-)} = \frac{(1 + \Sigma\,\beta_n\,[Cl^-]^n)^2}{1 + \Sigma\,\varkappa_l'\,[Cl^-]^l} \tag{17}$$

$$\beta_n = [InCl_n]\,[In^{3+}]^{-1}\,[Cl^-]^{-n} \tag{18}$$

$$\varkappa_m = [InOHCl_m]\,[InOH^{2+}]^{-1}\,[Cl]^{-m} \tag{19}$$

$$\varkappa_l' = [In_2(OH)_2\,Cl_l]\,[In_2(OH)_2^{4+}]^{-1}\,[Cl^-]^{-l} \tag{20}$$

and n, m, l may take a series of values.

Minimum values for (16) and (17) may be estimated by considering only β_1 and β_2, *i.e.* by assuming that the unknown β_n $(n > 2)$ are negligible.

The complex formation at 20°C between In^{3+} and Cl^- has been extensively studied in 2 M $NaClO_4$ by Sundén [2] who was able to explain the data obtained at $[Cl^-]_{tot} \leq 0.5$ M in terms of two cationic complexes only with $\log \beta_1 = 2.15$ and $\log \beta_2 = 3.59$. At high $[Cl^-]_{tot}\,[In(III)]^{-1}$ Sundén [2], Carleson and Irving [3], Kraus *et al.* [4] have found evidence also for the presence of $InCl_3$ and $InCl_4^-$. Thus in our solutions where $[Cl^-]_{tot}[In(III)]^{-1}$ was always kept > 75, $\log(1 + \beta_1 [Cl^-] + \beta_2[Cl^-]^2)$ is certainly much smaller than $\log\,(1 + \Sigma\,\beta_n[Cl^-]^n)$. As a consequence, we may estimate, using Sundéns β_1 and β_2 values that

$$\log \frac{k_{a1}\,(ClO_4^-)}{k_{a1}\,(Cl^-)} + \log\,(1 + \Sigma\,\varkappa_m\,[Cl^-]^m) \geq \log\,(1 + 3 \times 10^{2.15} + 9 \times 10^{3.59}) = $$
$$= 4.55 \tag{21}$$

and

$$\log \frac{\beta_{22}\,(ClO_4^-)}{\beta_{22}\,(Cl^-)} + \log\,(1 + \Sigma\,\varkappa'_l\,[Cl^-]^l) \geq 9.1 \tag{22}$$

On the other hand we find from our data

$$\log \frac{k_{a1}\,(ClO_4^-)}{k_{a1}\,(Cl^-)} = 2.5 \pm 0.3 \text{ and } \log \frac{\beta_{22}\,(ClO_4^-)}{\beta_{22}\,(Cl^-)} = 5.0 \pm 0.3 \tag{23}$$

Even if the fundamental assumptions leading to (16) and (17) may be regarded at best as crude approximations the difference between (23) and (21—22) indicates that the Σ terms are of the order of 10^2 to 10^4 so that species of the general composition $InOHCl_m$ and $In_2(OH)_2Cl_l$ would predominate in hydrolysed indium solutions containing 3 M Cl^-.

To determine the composition of the mixed complexes, one would have to study the hydrolysis equilibria in a series of solutions of varying $[Cl^-]_{tot}$, while $[Cl^-]_{tot}$ is to be kept at such low values that the influence of the activity factors may be negligible. Attempts should then be made to measure, besides h, the $[In^{3+}]$ and $[Cl^-]$ also.

Acknowledgements. We are indebted to Professor Lars Gunnar Sillén for his great interest in this work and for his valuable criticism. We would like to thank Dr. Helen S. Dunsmore for assistance in some experiments.

This work was financially supported by *Statens Naturvetenskapliga Forskningsråd (Swedish Natural Science Research Council)*, by the *Air Force Office of Scientific Research of the ARDC, USAF*, through its European Office on contract No AF 61 (052) 162 and by the *U.S. Atomic Energy Commission* through Contract No. AI—(30—1)—1922 with Duquesne University.

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Received November 14, 1960.