On the Polynuclear Hydrolysis of the Indium Ion; In^{3+}

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The hydrolysis has been studied in the indium concentration range 0.2 to 0.75 M, by measuring the hydrogen ion concentration, h, in coulometrically alkalified (and reacidified) solutions at 25 °C, with liquid junction-free cells containing a glass electrode. The h data so obtained, as well as the indium amalgam measurements in dilute (5×10^{-4} to 0.1 M) indium solutions reported previously, which were confirmed and refined, may be explained by assuming that only two polynuclear ions are formed: In$_2$(OH)$_2^{4+}$ and In$_4$(OH)$_6^{6+}$. Their formation constants in the inert 3 M NaClO$_4$ and in the various In(ClO$_4$)$_3$ – NaClO$_4$ media of 3 M [ClO$_4^-$] level are summarized in Tables 1 and 2. No evidence was found for the formation of hydrolysis products with a higher degree of polymerization.

The indium ion represents an acid of considerable strength, and several mono- and polynuclear bases are formed by its protolysis.[1] The most suitable method to study these equilibria and the interpretation of the data has been the matter of some controversy.[2,3]

A rather comprehensive investigation on this subject was carried out by one of us in 1955.[1] The potentiometric measurements have given clear evidence that for [In(III)] < 1 mM the mononuclear ions InOH^{2+} and In(OH)$_2^+$ are the predominating products of the hydrolysis, while the binuclear species In$_2$(OH)$_2^{4+}$ and other polynuclear ions of the general composition In(In(OH)$_2$)$_t^{(3+t)+}$ become increasingly important as the solutions get more concentrated for In(III); t was assumed to represent an integer growing without limit.

This model was criticized[2,3] and the same emf data were subjected to reinterpretation by applying the computerized error square sum minimization techniques developed meanwhile.[4] No definite conclusions could, however, be drawn.[2,3]

One of us (D.F.) has therefore undertaken a new potentiometric study of the hydrolysis. These new amalgam data of a precision of around 0.03 mV have been found to agree with the previous set of emf measurements[1] to within a few tenths of a mV. Thus the steep part of the formation curves which were considered in great detail in the least square calculations[2,3] correspond to homogeneous equilibria.

A new series of systematic computations has been carried out with these recent, precise amalgam data. We preferred especially comparison with normalized model functions, a method originated by Sillén[5] which does not require to guess the magnitude of the formation constant of the species to be tested.

Moreover, we extended the hydrolysis measurements to the indium concentration range 0.2 to 0.75 M, where the highly polymerised species represent the most important hydrolysis products.

These two topics form the main subject of parts I and II of this article. In the light of the present results the hydrolysis equilibria of groups 3a and 3b cations are shortly surveyed in the last, third part.

Notation.

H = proton excess =
   $[ClO_4^-] - 3[In(III)] - [Na^+] - [Ag^+] - 2[Pb^{2+}]$.

h = hydrogen ion concentration at equilibrium.

B = stoichiometric concentration of indium ions
   = [In(III)].

b = concentration of In^{3+}.

η = log (B/b).

w = mol of electrons introduced cathodically or removed by anodic oxidation.

$^*K_1 = [InOH^{2+}]hb^{-1}$.

$^*K_2 = [In(OH)_2^+]h[InOH^{2+}]^{-1}$.

$^*\beta_{qp} = [In_p(OH)_q^{(3p-q)+}]h^q b^{-p}$.

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In accordance with the nomenclature of the Stability Constants, asterisks are employed to emphasize that H_2O and not OH^- is regarded as the reagent.

I. THE POLYNUCLEAR HYDROLYSIS IN DILUTE INDIUM SOLUTIONS

Interpretation of the amalgam electrode data.

We sought to explain the great number of $\eta(\log h)_B$ data * comprising the B range 0.5 to 100 mM, which are illustrated in Fig. 1, in several stages. In each, a more general and comprehensive model function was introduced based on the results of the preceding step.

Our guiding principle has been to separate, as far as possible, the determination of the composition of the reaction products from the evaluation of the magnitudes of the corresponding formation constants.

(a) Functional analysis at constant acidity levels

We considered first data sets interpolated at a series of *constant* hydrogen ion concentration values, lying in the vicinity of $\log h = -3$. In this region a vertical drawn from the $\log h$ axis is seen from Fig. 1 to cut several $\eta (\log h)_B$ curves.

Along a vertical, a *single variable b* remains, and an analysis of the $\eta(B)_h$ sets thus obtained should therefore provide straightforward information concerning the number of indium atoms present in the hydrolysis products.

Let's first assume that in addition to $In_2(OH)_2^{4+}$ only another polynuclear ion, $In_P(OH)_Q$, is formed. Then, the ratio of the concentration of indium atoms present as polynuclear species, $\sum\limits_{p \ge 2} p[In_p(OH)_q]$, to b^2 takes the simple form (1), where C_1 and C_2 represent conditional constants depending on the acidity.

$$R_{h,2} = \frac{B - b(1 + {}^*K_1 h^{-1} + {}^*\beta_2 h^{-2})}{b^2} =$$

$$2{}^*\beta_{2,2}h^{-2} + P{}^*\beta_{QP}h^{-Q}b^{(P-2)} = C_1 + C_2 b^{P-2} \quad (1)$$

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*The complete set of primary data, considered in this article, is available on request from the authors.
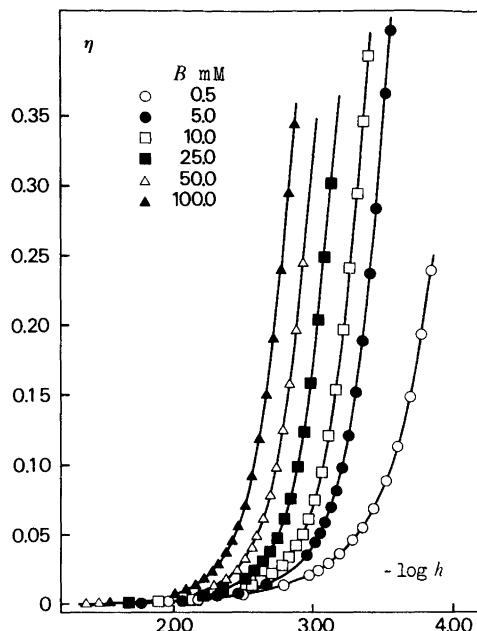

Fig. 1. The hydrolysis of the indium ion in the concentration range 0.5 to 100 mM, $\log(B/b)_B$ as a function of $-\log h$. Symbols represent the amalgam data. For the sake of clarity, about each third point is shown only. The curves have been constructed with the formation constant values summarized in the last column of Table 1.

In eqn. (1) ${}^*K_1$ is the symbol for the formation constant of $InOH^{2+}$ and ${}^*\beta_2 = {}^*K_1{}^*K_2$ that for its protolysis product $In(OH)_2^+$. Both the new and the old [1] $\eta(\log h)_{5.10^{-4}}$ measurements, that agree to within a few tenths of a mV, were used to evaluate these constants which are needed to calculate the mononuclear correction terms in eqn. (1) and many other formulas which follow.

Comparison of the amalgam data with a normalized model function led to the estimates (2). These values deviate considerably from the previous

$$\log {}^*K_1 = -4.3 \pm 0.1 \text{ and } \log {}^*K_1^*K_2 = -8.6 \pm 0.1$$

$$(2)$$

results [1] ($p{}^*K_1 = 4.4_2$ and $p{}^*K_1^*K_2 = 8.3$). The difference is due to the improved method of data treatment not requiring a linearization.

A series of plots $R_{h,2}$ *versus* b^N, $N = P - 2$, were constructed at each acidity level; for the correct
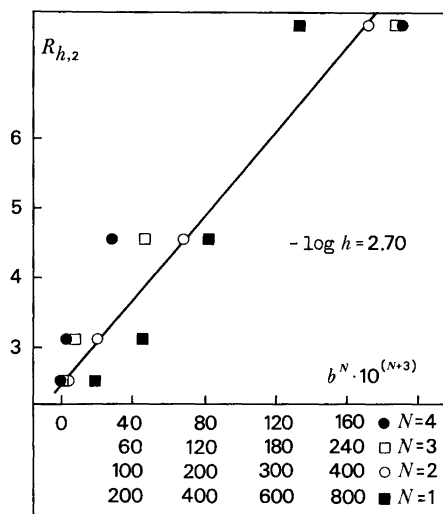
Fig. 2. Determination of the nuclearity in the most polymerized hydrolysis products, $R_{h,2}$ as a function of b^N, *cf.* eqn. (1). The ordinate is common, but for each choice of $N = P\text{-}2$ a special abscissa scale has been taken. The line represents the equation $R_{h,2} = 2.46 + 1.21.10^3 b^2$.

choice of N the plots should, according to (1), be approximable with a straight line.

Typical results are shown in Fig. 2. This affords clear evidence that the additional hydrolysis product is *tetranuclear* as only the $R_{h,2}$ *versus* b^2 data

give rise to a plot which is describable with a straight line.

Similar results were obtained in all the other plots covering the $\log h$ range -2.4 to -3.0. We know on the basis of the 1955 work, and it was fully corroborated by our recent data, that all the hydrolysis products have the general composition $In_{t+1}(OH)_{2t}$. Hence, the tetranuclear species is likely to be the ion $In_4(OH)_6^{6+}$ as t equals 3.

To test whether the amalgam data are sufficiently accurate to afford an unequivocal reaction mechanism, plots of $R_{h,3}$ against $b^{(P-3)}$ were also made. All of them led to a set of points exhibiting a great curvature.

(b) Comparison with normalized functions

To corroborate these preliminary conclusions further arguments are needed. To this end, *all* the amalgam measurements belonging to the B range 10 to 100 mM have been recalculated to the form (3)

$$\alpha = \log[\{Bb^{-1} - (1 + {}^*K_1 h^{-1} + {}^*\beta_2 h^{-2})\} h^2 b^{-1}]$$

versus $\log(bh^{-2})$ (3)

and they were compared with the normalized model functions

$$Y_P = Y_P(\log x) = \log(2 + Px^{P-2}) = \alpha - \log {}^*\beta_{2,2} \quad (4)$$
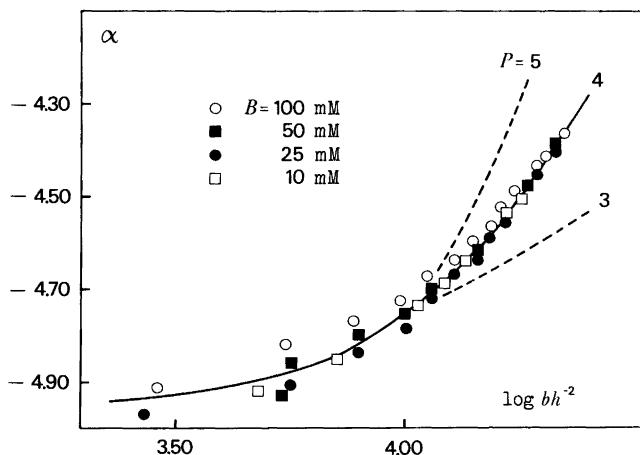
where

Fig. 3. Determination of the composition of the most polymerized hydrolysis product. Symbols: Data α *versus* $\log(bh^{-2})$, *cf.* eqn. (3). The curves represent the functions $Y_P(\log x)$, eqn. (4), in the position of best fit. For Y_4 this criterion corresponds to $-\log {}^*\beta_{2,2} = 5.25$ and $-\log {}^*\beta_{6,4} = 13.75$. About each third point is included.

$$\log x = \log(bh^{-2}) + \frac{1}{P-2}\left(\log\frac{*\beta_{2(P-1),P}}{*\beta_{2,2}}\right) \qquad (4a)$$

Our results are graphically represented in Fig. 3. This shows that only Y_4 corresponding to the formation of $In_4(OH)_6^{4+}$ fits the data. We get a first estimate for $\log*\beta_{2,2}$ by reading off the ordinate difference, and a first approximation for $\log*\beta_{6,4}$ on the basis of the abscissa difference $\log(bh^{-2}) - \log x$, *cf.* Table 1. Hence this approach is in complete agreement with our preceding conclusions.

(c) Comparison with projection maps. Final estimate of the formation constants

In is seen from eqn. (3) that the magnitudes of the mononuclear formation constants must be known for the calculations. We turned therefore back to the primary data themselves, visualized in Fig. 1, and calculated by interpolation sets of data pairs $(B,h)\eta$ at a series of η levels. These sets were then recalculated to the form $\log(Bh^{-2})$ *versus* $\log(h)_\eta$ and they were compared with a projection map representing the hypothesis that the hydrolysis proceeds through the species $InOH^{2+}$, $In_2(OH)_2^{4+}$ and $In_4(OH)_6^{6+}$.

The map, $\log Y(\log v(u))_{l,\eta}$, was constructed with eqn. (6), where $u = *K_1 h^{-1}$, v represents $*\beta_{2,2}bh^{-2}$, while l denotes $*\beta_{6,4}*\beta_{2,2}^{-3}$.

$$\log Y = \log\{v(1+u+2v+4lv^3)\} = \log(Bh^{-2}) + \log*\beta_{2,2} \qquad (6)$$

An optimal fit was found with $\log l = 2.1$ and by superposition the formation constant values summarized in Table 1 have been deduced.

(d) Least square calculations

We undertook also several series of computations to find the minimum value for the sum

$$U = \sum_{i=1}^{n} (E_i - E_{c,i})^2,$$

where E_i stands for a certain emf value measured with the amalgam cell (I) (see below), and $E_{c,i}$ is its value calculated on the basis of a specified hypothesis. The index i runs to n representing in most cases the total number of amalgam potentials, remeasured in the present work, about 130.

First we wanted to check the visual fit obtained in the preceding sections. By taking as starting values the results of the projection map (*cf.* Table 1), we obtained the formation constants listed under alternative I in the same table. These, corresponding to an average deviation of ± 0.07 mV, show only negligible differences from the graphical calculations.
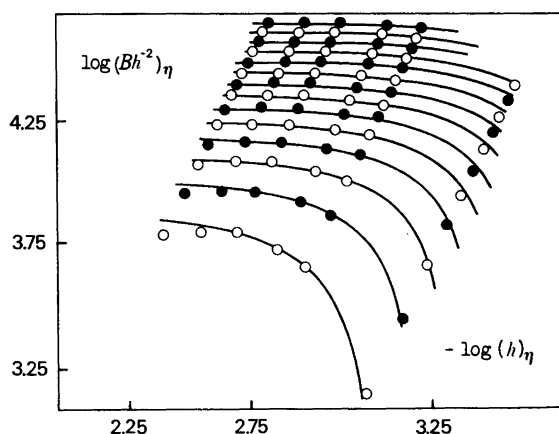
Fig. 4. Comparison of the amalgam measurements with a projection map representing the hypothesis that the hydrolysis proceeds through the formation of the species $InOH^{2+}$, $In_2(OH)_2^{4+}$ and $In_4(OH)_6^{6+}$. Each curve represents an η level that increases in steps of 0.02 units from 0.04 to 0.30 from the lower edge to the top. The curves have been calculated with the formation constants shown in the third column of Table 1.

Next, we started a systematic search for the *minor species* which could have been easily overlooked in our simple graphical treatment. We introduced first as additional reaction product the ion $In_3(OH)_4^{5+}$, which was postulated by Biedermann in 1955 [1] and later by other authors.[2,3]

With this ion the error square sum U could be made to diminish by 3 % but the formation constant $*\beta_{4,3}$ was found to possess an uncertainty equalling its mean value. The magnitudes for the other hydrolysis constants remained practically unchanged as well as the average deviation from the amalgam cell data. Hence this trinuclear ion is not formed in an amount which can be detected with measurements of the present precision.

Then we tested the higher members of the series $In(In(OH)_2)_t$ by taking in each case a starting value for the formation constant on the basis of Biedermanns [1] hypothesis of an unlimited series of hydrolysis products.

Calculations were made up to $t = 24$ but no significant improvement in U could be achieved. Thus it appears that no other mechanism consisting of four steps may explain the data better than the simple scheme proposed in the preceding stages of calculations.

Finally we took up the problem of *systematic experimental errors*. The indium concentration values, b, were measured with the cell (I), where

$$(Pt),In - Hg|In(III) \; B, \; H^+ \; H, \; Na^+$$
$$(0.01\%)$$
$$(3.00 \; M - 3B - H), \; ClO_4^- \; 3.00 \; M|RHC + \qquad (I)$$
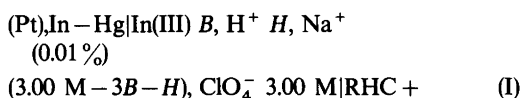
RHC:|3.00 M $NaClO_4$|2.99 M $NaClO_4$, 0.0100 M $AgClO_4$|Ag. The emf of this cell at 25 °C can be set equal to eqn. (7), where E_j stands for the small liquid junction potential correction, while E_0 represents the sum of the concentration independent terms.

$$E_{am} = E_o - 19.72 \log[In^{3+}] + E_j(h) \qquad (7)$$

With more concentrated amalgams the overpotential was not sufficient to hinder the dissolution of indium.

Our experiments lasted usually ten to twenty hours and in its course trace amounts of redox impurities (as air or substances dissolved from the stopcock grease) might have easily contaminated the test solution and changed the amalgam concentration. Hence, an average value for E_o reflecting the effect of the contamination, is more correct to use than a value derived by a short series of measurements carried out at the start of the experiment.

Consequently we minimized each series of measurements individually, and we let also E_o represent an adjustable parameter in addition to the equilibrium constants.

The final results, denoted in Table 1 as alternative II, were derived in this way.

The E_o corrections never exceeded 0.13 mV. We attained, however, a great decrease in the error square sum, about 20%. Moreover the average deviation could be suppressed to ± 0.05 mV.

II. THE STUDY OF CONCENTRATED INDIUM SOLUTIONS

Interpretation of the glass electrode measurements.

(a) Method

The hydrolysis in the indium concentration range 0.2 to 0.75 M has been studied with test solutions of the general composition

$$In(III) \; B, \; H^+ \; H, \; Ag^+ \; A_1, \; Pb^{2+} \; A_2, \; Na^+$$
$$(3.00 \; M - 3B - H - A_1 - 2A_2), \; ClO_4^- \; 3.00 \; M$$
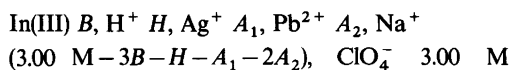
which in the following discussion will be abbreviated by TS.

Table 1. The hydrolysis constants derived by the methods of Part I valid in 3 M $(Na^+)ClO_4^-$ medium.

	Eqn. (1)	Eqn. (3)	Projection map	Letagrop I	Letagrop II [a]
$-\log *K_1$	—	—	4.26 ± 0.05	4.29 ± 0.03	4.23 ± 0.07
$-\log *\beta_{2,2}$	5.3	5.25	5.30 ± 0.05	5.3 ± 0.1	5.27 ± 0.06
$-\log *\beta_{6,4}$	13.7	13.75	13.8 ± 0.1	13.86 ± 0.1	13.79 ± 0.03

[a] Minimization with the adjustment of E_o, cf. eqn. (7).

Two *auxiliary ions* Ag$^+$ and Pb^{2+} are seen to be introduced, both of them represent so weak acids [6,7] that their protolysis can be entirely neglected in the high hydrogen ion concentration range here in question. For reasons which will emerge in the following discussion, their concentrations were kept always at around 0.1 M.

The auxiliary ion Ag$^+$ was chosen primarily as the reference in the cell (II), which served for the determination of the hydrogen ion concentration in hydrolyzed indium solutions.

glass electrode|TS|Ag +   (II)

$$E_{Ag} = E_{o,Ag} + 59.16 \; \log \left([Ag^+]/h \right) \qquad (8)$$

The emf of cell (II) may at 25 °C be put into the simple form (8), where the sum of the concentration independent terms is denoted by $E_{o,Ag}$. Its actual value must be determined in each experiment by measuring E_{Ag} at such high acidities ($\log h \geq -1$) where the indium hydrolysis becomes negligible and consequently h can be set equal to the proton excess, H.

Although the hydrogen ion concentrations of the four stock solutions that were needed to prepare TS were known with some precision, small volumetric errors rendered the starting H value, calculated on the basis of the mixing ratio, rather uncertain. Hence they had to be determined together with $E_{o,Ag}$ by constructing a Gran-diagram.[8] In each case $E_{o,Ag}$ could in this way be evaluated to within ± 0.05 mV, while the starting value for the proton excess could be estimated with an uncertainty of a few tenths of a percent.

In another research project now being carried out in this laboratory [9] evidence was obtained that replacement of the cations of the medium at a constant $[ClO_4^-]$ does not affect the activity factor ratio of the Ag$^+$ and H$^+$ ions to an appreciable extent when they are present in the solution at low concentrations. Hence the activity factor ratio term is incorporated into the constant $E_{o,Ag}$ of eqn. (8).

The lead ions were introduced to enable us to vary reversibly the hydrogen ion concentration in TS by coulometric methods. For this purpose we immersed two additional electrodes into TS giving rise to the electrolysis circuit (III), which was connected to a constant current supply.

(Pt)Ag|TS|PbO$_2$(s),(Pt)   (III)

Although the test solution now contains two redox couples Ag$^+$ − Ag and PbO$_2$ − Pb^{2+}, no spontaneous reaction occurs as the oxidized form of the stronger couple, PbO$_2$, is kept completely separated from the reduced form of the weaker, Ag, both being solids adhering to a platinum net support. The solubility of PbO$_2$ is quite negligible in acid solutions. Indeed, the emf of cell (II), E_{Ag}, has always been found (even up to 100 °C) to remain unchanged to within 0.1 − 0.2 mV for several days.

A great number of experiments were made to find the conditions for ensuring theoretical current efficiencies in both directions for the electrode reactions (9) and (10).

$$Ag^+ + e \rightleftharpoons Ag(s) \qquad (9)$$

$$PbO_2(s) + 4H^+ + 2e \rightleftharpoons Pb^{2+} + 2H_2O \qquad (10)$$
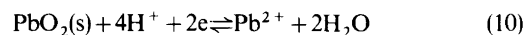
The current efficiency was studied first by neutralizing with the cathodic reduction of PbO$_2$ and then reacidifying with the anodic oxidation of Pb^{2+} a standardized sample of HClO$_4$. The coulometric analysis was always found to agree to within 0.1 − 0.2 % with the value obtained by titration with NaOH.

A similar degree of agreement was obtained when the hydrogen ion concentration in concentrated AgClO$_4$ solutions was determined using a PbO$_2$ cathode and it was measured by titrating with NaOH.

Many experiments were carried out with cell (II) and the electrolysis circuit (III) to determine the hydrogen ion concentration of Pb(ClO$_4$)$_2$ − AgClO$_4$ mixtures which had been also analyzed in divided cells with a glass electrode. The two methods never differed more than 0.2 %.

The reversibility of the electrolysis reactions (9) and (10) was checked by acidification − realkalification cycles. The corresponding E_{Ag} values often agreed to within 0.01 mV. Further, in experiments of this kind we also calculated the $E_{o,Ag}$ values ensuing each step of electrolysis by assuming a theoretical current efficiency, eqn. (11). In this

$$E_{o,Ag} = E_{Ag} + 59.16 \; \log \frac{w^o_{H^+} \pm 2w}{w^o_{Ag^+} \mp w} \qquad (11)$$

equation w is the symbol for the number of mol of electrons passed through the test solution, $w^o_{H^+}$ stands for the mol of hydrogen ions present at the start of the experiment, and $w^o_{Ag^+}$ for the initial mol

of Ag^+ ions, We usually obtained $E_{o,Ag}$ values agreeing better than 0.1 mV, when w was varied in both directions by large amounts.

In another experiment we introduced two PbO_2 electrodes, and measured E_{Ag} while current was passed for many hours between them, its strength sometimes was increased to 64 mA. No change in E_{Ag}, exceeding 0.1 mV, could be detected. The same results were obtained when the electrolysis was carried out instead between two silver electrodes immersed into TS.

On the basis of this evidence we concluded, that provided the current density does not exceed 5 mA/cm^2, both electrode reactions (9) and (10) may be considered to proceed with a theoretical current efficiency in both directions. Hence the proton excess could simply be calculated by the equation $H = (w^o_{H^+} \pm 2w)/V$ and the actual concentration of silver ions by $(w^o_{Ag^+} \mp w)/V$ where the upper sign refers to acidification and the lower to alkalification. The test solution volume is denoted by V. For the small number of coulombs passed through in a series of measurements, no serious error may arise by assuming V to remain unchanged.

(b) R e s u l t s

This coulometric approach was primarily chosen to avoid premature precipitation of indium hydroxide due to a local excess of hydroxide ions. Only experiments in which direct evidence could be obtained for the reversibility by the agreement of the alkalification and the reacidification measurements have been considered in the following discussion. A typical experiment satisfying this condition, within the limits of the present precision, is illustrated in Fig. 5.

Our hydrogen ion concentration measurements with cell (II), comprising more than twenty series, are graphically represented in Fig. 6. This shows the average number of hydrogen ions set free per indium ion, Z, eqn. (12), as a function of the

$$Z = \frac{h-H}{B} = Z(\log h)_B \qquad (12)$$

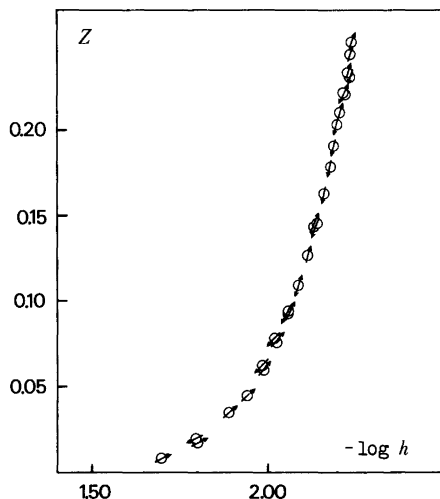logarithm of the hydrogen ion concentration at the three indium concentration levels 200, 500 and 752

Fig. 5. Reversibility test. The average number of hydrogen ions set free per indium, Z, as a function of $\log h$ at the indium concentration level 0.4967 M. Circles with an upward arrow represent alkalification, with a downward arrow acidification experiments.
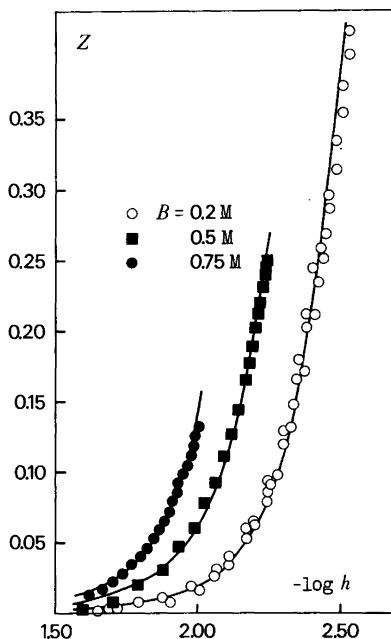

Fig. 6. The hydrolysis of indium(III) in concentrated solutions; $Z = Z(\log h)_B$ at 0.2 (circles), 0.5 (filled squares) and 0.75 M (dots) levels. The curves have been calculated with the $*\beta_{2,2}$ and $*\beta_{6,4}$ values summarized in Table 2. About each third experimental point is shown.

mM. For the sake of clarity, about each third of the data is shown only and no distinction is made between alkalification and acidification experiments.
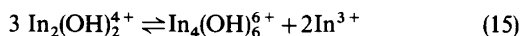
As the replacement of a large portion of the solvent sodium ion with the reacting indium ion influences the activity factors of the reacting species, each B level was interpreted separately.

The sets of $Z(\log h)_B$ data were treated in two stages. First, a comparison was made with model functions representing the hypothesis that only two reaction products are formed in appreciable concentrations: $In_2(OH)_2^{4+}$ and $In_4(OH)_6^{6+}$. On the basis of the results presented in Part I one may easily see that the mononuclear species become quite negligible in the concentrated indium solutions here considered.

We first recalculated the data to the form $Z(\log Bh^{-2})$, and compared each set with the model function (13), where $u = *\beta_{2,2}bh^{-2}$ and x is the symbol for the normalized variant of Bh^{-2}; eqn. (14).

$$Y = \frac{2u + 6lu^3}{1 + 2u + 4lu^3} = Y(\log x)_l \tag{13}$$

$$\log x = \log(Bh^{-2}) + \log *\beta_{2,2} =$$
$$\log\{u(1 + 2u + 4lu^3)\} \tag{14}$$

$$3\,In_2(OH)_2^{4+} \rightleftharpoons In_4(OH)_6^{6+} + 2In^{3+} \tag{15}$$

The parameter $l = *\beta_{6,4}*\beta_{2,2}^{-3}$ stands for the equilibrium constant of the redistribution reaction (15). By choosing for $\log l$ the value of 2.15, a satisfactory agreement could be obtained at all three B levels. Superimposition of $Y_{2.15}$ yielded in the position of best fit, cf. Fig. 6, the $\log *\beta_{2,2}$ and $\log *\beta_{6,4}$ values summarized in Table 2. These results served as the starting point for the least square adjustment.

At each B level we calculated, by employing the recent version of the Letagrop program,[4] the $*\beta_{2,2}$ and $*\beta_{6,4}$ values providing a minimum for the sum

$$\sum_{i=1}^{n} (Z_i - Z_C)^2,$$

where Z_i denotes an experimental datum and $Z_C = Z_C(*\beta_{2,2}, *\beta_{6,4})$ a calculated value for the average number of hydrogen ions set free per indium at a certain B level.

Table 2 demonstrates that the two methods of data interpretation afford practically coinciding results. The Letagrop approach enabled us to analyze the fit in more details. At each series of measurements the number of positive and negative deviations was found to differ less than 10%; hence our hypothesis concerning polynuclear hydrolysis may be regarded as a close approximation. The average percentage deviation in Z, $\Delta Z/Z$, varied between 5 and 10%. This is quite reasonable as a large part of the measurements corresponds to a small difference between the hydrogen ion concentration at equilibrium and the proton excess.

We may see by comparing Tables 1 and 2 that the magnitude of $\log *\beta_{2,2}$ is but little influenced by the replacement of a large part of the Na^+ ions with In^{3+} and its hydrolysis products. This result is in accord with the specific interaction theory[10] which yields for the medium effect of the equilibrium constant of this reaction the relationship (16), where

$$\log \frac{*\beta_{2,2}(I)}{*\beta_{2,2}(3)} = 2\log \frac{a_{H_2O}(I)}{a_{H_2O}(3)} \tag{16}$$

I denotes the ionic strength in an $In(ClO_4)_3$ $- NaClO_4$ solution and 3 stands for the ionic strength of the inert $NaClO_4$ medium. The water activity is denoted by a_{H_2O}. Its value is not known in indium perchlorate solution.

Table 2. The polynuclear hydrolysis constants in concentrated indium solutions.

Medium	$-\log *\beta_{2,2}$ Eqn. (13)	Letagrop	$-\log *\beta_{6,4}$ Eqn. (13)	Letagrop
0.2 M In(III), 2.4 M $(Na^+ + H^+)$	$5.3_2 \pm 0.05$	5.32 ± 0.08	13.8 ± 0.1	$13.6_5 \pm 0.15$
0.5 M In(III), 1.5 M $(Na^+ + H^+)$	5.25 ± 0.05	5.25 ± 0.08	13.7 ± 0.1	13.7 ± 0.1
0.752 M In(III), 0.74 M $(Na^+ + H^+)$	5.2 ± 0.1	5.23 ± 0.05	13.4 ± 0.1	13.3 ± 0.1

On the other hand, the osmotic coeffient of gallium perchlorate has been carefully studied in a wide concentration range.[11] As the effect of water activity change is small, no serious error is likely to be made by assuming that the water activities in 1 m $Ga(ClO_4)_3$ and 1 m $In(ClO_4)_3$ are equal. Thus we may estimate, with the osmotic coefficient reported in 3.5 m $NaClO_4$[12] as the upper limit for the medium effect, eqn. (16), $2(-0.052+0.053)=0.002$ which is of course far below our experimental precision.

For the medium effect of the tetranuclear species the theory predicts eqn. (17), where $D=D(I)$

$$\log\frac{^{*}\beta_{6,4}(I)}{^{*}\beta_{6,4}(3)}=$$

$$6\{D(I)-D(3)\}+6\log\frac{a_{H_2O}(I)}{a_{H_2O}(3)} \qquad (17)$$

represents the Debye-Hückel function, equalling at 25 °C $0.5107\sqrt{I}/(1+1.5\sqrt{I})$. We thus obtain that $\log {^{*}\beta_{6,4}}$ should increase, compared with its value in the inert medium, by 0.04 at $B=0.2$ M, by 0.08 at 0.5 M and by 0.11 units at 0.75 M.

These estimates are seen from Table 2 to be in approximate agreement with our results in the 0.2 and 0.5 M indium perchlorate solutions. However, the increase of 0.3, as we pass to the highest B level, is much larger than expected by the theory.

This discrepancy may in part be ascribed to the experimental uncertainty of our $^{*}\beta_{6,4}$ (0.75 M) value. It arises from the fact that at this B level precipitation occurs already at $Z\sim0.15$, where $[In_4(OH)_6^{6+}]$ is still below $[In_2(OH)_2^{4+}]$. In the more dilute solutions, the tetranuclear species represents the predominant product of hydrolysis in a large part of the accessible acidity range.

Another reason may be that for the correct estimate of the activity factor of the tetranuclear ion, one should make a realistic estimate of the charge distribution, instead of regarding it as a large sphere with uniform charge density.

We checked, however, on the basis of the emf[13,14] and vapor pressure[14] measurements in $LaCl_3$ − HCl, $AlCl_3$ − HCl and $LaCl_3$ − NaCl[12] mixtures that the specific interaction theory may be safely employed as a useful first approximation in 3 M media containing simple singly and triply charged ions.

DISCUSSION

The main result of the present work is that the polynuclear hydrolysis is explainable by the formation of only two species $In_2(OH)_2^{4+}$ and $In_4(OH)_6^{6+}$ that link the simple ions In^{3+}, $InOH^{2+}$ and $In(OH)_2^{+}$ with the final reaction product, colloidal indium hydroxide. This hypothesis receives additional support by the preliminary result of an X-ray diffraction study of multimolar indium nitrate and perchlorate solutions. Dr. Georg Johansson with the collaboration of fil.kand. Anita Persson has undertaken in this laboratory this investigation at about the same time as our potentiometric work was started.

The diffraction data at the highest degree of hydrolysis ($Z\sim0.8$) afford evidence for the presence of tetranuclear ions. Moreover, the radial distribution curves hitherto obtained may be explained by assuming that the four octahedrally coordinated indium ions occupy the corners of a tetrahedron and are bound by single hydroxo bridges located at the centers of the six edges.

The question is now arising which types of forces are responsible for the preferential formation of certain hydrolysis products while others, at the first sight equally probable, as $In_3(OH)_4^{5+}$, do not appear to be present in detectable amounts.

The formation constants of the hydrolysis products[15] of the general composition $MeOH^{2+}$ are summarized below together with the electronegativities, χ, of the Me^{3+} ions. The values have been taken from Allred's comprehensive study.[16] For reasons to emerge later, the Fe^{3+} ion is included as well.

$p^{*}K_1$, χ: Group 3a. Sc^{3+}: 5.1, 1.3_6; Y^{3+}: 9.1, 1.2_2; La^{3+}: 10.1, 1.1_0.

Group 3b. Al^{3+} ~5, 1.6_1; Ga^{3+} ~4, 1.8_1; In^{3+}: 4.30, 1.7_8; Tl^{3+}: 1.14, 2.0_4; Fe^{3+}: 2.9, 1.9_6.

A clear correlation is seen to exist between the strength of the aquo acidity and electronegativity within each group.

Based on Allred's arguments and results[16] we may regard the difference in electronegativity within the same group, including cations of the same charge and of the same coordination number, to provide the difference in the extent of the electron transfer from the ligand oxygen to the central ion.

Oxygen is, of course, more electronegative than hydrogen and therefore a drainage of charge will ensue in the direction hydrogen to oxygen, giving rise to a positive charge density on the periphery of the hydrated ion. The greater the charge density

thus established, the less work needed to remove a proton and transfer it to a water molecule. In other articles to be published soon from this laboratory, evidence will be presented that also within the group 2b and for the lanthanoids the trends in $*K_1$ and in the electronegativity are parallel.

Hence, this model of a hydrated cation, suggested by Pauling,[17] provides an explanation for the trend of the aquo acidity.

Further, it is in accordance with this picture that the solubility in alkalies in group 3b runs opposite to the strength of the aquo acidity. Accumulation of negative charge on the hydroxo complex will promote the solubility, because the degree of hydration increases. For the same reason, strong cation acids, like Fe^{3+} and Bi^{3+}, cannot generally be dissolved in alkali hydroxides.

One may also argue[18] — as a paraphrase — that in a stable complex species the charge on the central cation becomes entirely neutralized by the electrons donated from the ligands. The greater the electronegativity of the central cation, the more negative charge will be transferred from a hydroxide ion, and hence neutralization occurs with a smaller number of ligands. As a consequence, as many as four hydroxide ions will be bound most readily to Al^{3+}.

For In^{3+}, Tl^{3+} and Sc^{3+} even the second step of the mononuclear hydrolysis could be studied. In each case the acid strength of the ion $MeOH^{2+}$ was found[15] to be near to that of the unhydrolyzed species. This somewhat unusual result is probably due to the presence of two coordinated water molecules in antipodal position. The condition $p*K_1 \sim p*K_2$ thus seems to imply a high coordination number. Indeed, the tetracoordinated Be^{2+} ion has been found[19] to be an acid of much higher strength ($p*K_1 = 5.7$) than the $BeOH^+$ ion[20] ($p*K_2 = 8.0$).

Finally, we would like to recall that no evidence could be found either in group 3a or 3b for the formation of the uncharged species $Me(OH)_3$. This is, of course, easy to understand on the basis of an electrostatic model.

It is practical to approach the problem of polynuclear hydrolysis by considering it as polymerization of the mononuclear species.

The polynuclear hydrolysis of the three ions Sc^{3+}, Y^{3+} and In^{3+} has been studied comprehensively, and we may with some confidence use these results as a basis for a general discussion.

Independently of temperature and ionic medium,

the main product of the polynuclear hydrolysis for these ions has been found to be the dimer $Me_2(OH)_2^{4+}$. The following table lists the values for the dimerization constant

$$2\ MeOH^{2+} \rightleftharpoons Me_2(OH)_2^{4+}; K_{2,2} = *\beta_{2,2}(*K_1)^{-2}$$
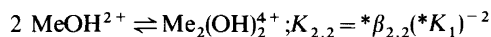
at 25 °C in 1 and 3 M media:

|	$p*K_1$	$p*\beta_{2,2}$	$\log K_{2,2}$
Y^{3+}	9.1	14.3	3.9
In^{3+} (3M NaCl)	6.9_5	10.1_5	3.7_5
Sc^{3+}	5.1	6.1	4.1
In^{3+} (this work)	4.3_0	5.2_7	3.3_3

We may see from this presentation, that although the aquo acidity is greatly increasing as we pass from Y^{3+} to In^{3+}, the $\log K_{2,2}$ values show no trend.

The spread of around ± 0.4 units from the mean, 3.7_5, is only slightly greater than the uncertainty of our $\log K_{2,2}$ calculations which may be estimated to ± 0.3 units.

The Fe^{3+} and Cr^{3+} ions are also of some interest, because the main product of their polynuclear hydrolysis has also been found to be[15] the ion $Me_2(OH)_2^{4+}$. Hedström's precise measurements[15] at 25 °C lead to the $\log K_{2,2}$ estimate of 3.2 for the polymerization of $FeOH^{2+}$. Bjerrums classical investigation[15] of the hydrolysis in dilute chromium (III) chloride solutions yields at 75 °C $\log K_{2,2} = 3.3$ and at 100 °C 3.1. These values are reasonably near to our average 3.7_5.

It appears from this short survey that the extent of dimerization is primarily a property of the oxygen atom and the hydroxide ion. A hydroxide ion bound to a hexahydrated triply charged cation obtains an electrostatic bond strength of 1.5 as defined by Pauling, instead of 2.0 which corresponds to a stable species. When the hydroxide ion joins another coordination sphere, it receives the 0.5 units of electrostatic bond strength needed for stability.

A comparison of the formation constants for the dimerization with a single hydroxo bridge
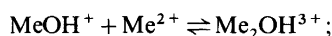
$$MeOH^+ + Me^{2+} \rightleftharpoons Me_2OH^{3+};$$

$$K_{1,2} = [Me_2OH^{3+}]/([Me^{2+}][MeOH^+])$$

within the group 2b, where the aquo acidity is increased by six logarithmic units from Zn^{2+} to Hg^{2+}, while $K_{1,2}$ remains practically unaffected,

lends further support to our hypothesis. The data will be presented in another publication.

We would also like to mention that polynuclear complex formation has been predominantly found to occur with the ligands of the group 6b elements when they are associated with other atoms of a lower electronegativity, as hydrogen.

Except for indium, too little is known on the more hydrolyzed species, in yttrium and scandium solutions only hydrogen ion concentration data are available. On the other hand, one would like to understand the reason for the preferential formation of $In_4(OH)_6^{6+}$.

In this tetrahedral species, according to Johansson and Persson, the indium ions are bound by single hydroxo bridges, and consequently the average distance between the positive charges is rather long.

The simplest model for the ion $In_3(OH)_4^{5+}$ seems to be an indium coordination octahedron joined to two other indium octahedra by two double hydroxo bridges. Such a configuration involves a shorter distance between the positive charges (distributed as discussed previously), because edges are shared and not corners. As a consequence the formation of this ion would require a greater effort against the electrostatic forces and thus it would less likely be formed. The role of electrostatic forces in polynuclear complex formation will form the subject of a subsequent communication.

EXPERIMENTAL

The *amalgam cell measurements* discussed in Part I were carried out by the technique that has been described in some details by Ferri.[21]

Materials and analysis. The indium, silver and sodium perchlorate solutions, which were employed in Part II for the study of concentrated indium solutions, were prepared and analyzed as usual in this laboratory.[21]

Lead perchlorate solutions were made from lead nitrate preparations of *pro analysi* quality. The nitrate was first recrystallized from 0.1 M HNO_3 and then it was decomposed to PbO at 800 °C. Next the PbO was added in a slight excess to concentrated ($\sim 2M$) $HClO_4$ of commercial quality, and the pH of the resulting suspension was adjusted to 6. As a consequence, the heavy metal ion contaminants, originating from the perchloric acid, precipitated slowly as hydroxides or silicates. The excess of PbO was finally removed by filtration through a platinum pad and the filtrate was acidified

with dilute $HClO_4$ until pH became 3. This minimum buffer capacity is needed to avoid absorption of CO_2 and reaction with the glass container while the solution is being preserved.

The Pb(II) content of these iron- and chloride-free stock solutions were determined either by titration with an EDTA reagent solution or by precipitating PbO_2 anodically.[22] As the hydrolysis of Pb^{2+} is negligible for pH < 4, the proton excess of the solutions could be determined potentiometrically with a glass electrode using a 10 mM NaOH solution.
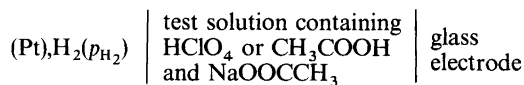
Electrodes. These lead perchlorate stock solutions, made first 1 M for $HClO_4$, served also for the preparation of the PbO_2 electrodes of the coulometric circuit. The PbO_2 crystals were precipitated anodically onto a large platinum net, using a current density not exceeding 0.5 mA/cm². A slow stream of oxygen was introduced in the vicinity of the platinum cathode to avoid the loss of Pb^{2+} ions.

The silver electrodes, used for the measurement of the silver ion concentration as well as for the electrolysis, were prepared by cathodic reduction from a solution of $KAg(CN)_2$, purified by recrystallization. The silver layers on the platinum net were washed with concentrated ammonia to dissolve AgCN and they were soaked for several days with water.

When several silver electrodes were immersed into a test solution, they never differed more than 0.02 mV from each other or from the silver electrode of the coulometric circuit.

Glass electrodes manufactured by the Beckman Co. and by the Jenaer Glasswerk, Schott & Gen, were employed.

In a series of special experiments we found that the emf of the cell

$$(Pt),H_2(p_{H_2}) \quad \left| \begin{array}{c} \text{test solution containing} \\ HClO_4 \text{ or } CH_3COOH \\ \text{and } NaOOCCH_3 \end{array} \right| \quad \begin{array}{c} \text{glass} \\ \text{electrode} \end{array}$$

remained unchanged to within 0.02 mV or better as the log h value of the test solution was varied from -1 to -5. Thus, these glass electrodes may under the present experimental conditions be regarded to be equivalent with the hydrogen half-cell.

At the end and start of each potentiometric series of measurements the emf of the glass electrode $-$ silver cell was monitored for several hours. The drift was usually less than 0.01 mV/h and it could therefore be neglected.

Technique of the coulometric experiments. All the emf measurements were carried out in a silicone $-$ oil thermostat kept at 25.00 ± 0.01 °C.

The recurrent sequence of operations: stepwise change of hydrogen ion concentration by coulometry, determination of the emf and measurement of the bath temperature, was performed with the automatic data acquisition system constructed in this laboratory. The program (current levels, direction of electrolysis and current passage period, duration of waiting time *etc.*) was based on the experience gathered in preliminary experiments. The number of coulombs passed through the test solution could in this way be determined with an uncertainty of $0.01-0.02\%$, while we sought to establish the emf values to within ± 0.02 mV.

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