

Studies on the Hydrolysis of Metal Ions

XV. Partition Equilibria in the System $^{114}\text{In}/\text{TTA}/\text{benzene}$

F. J. C. ROSSOTTI and HAZEL ROSSOTTI

*Department of Inorganic Chemistry, the Royal Institute of Technology,
Stockholm 70, Sweden **

The mononuclear hydrolysis constants of indium have been determined by studying the distribution of tracer concentrations of the indium-TTA complex, InL_3 , between benzene and aqueous 3M (sodium) perchlorate solutions at 25° C. When allowance was made for TTA complexes in the aqueous phase, the data could be approximately explained in terms of the single hydroxo-complex $\text{In}(\text{OH})_2^+$. However, agreement is improved by also taking into account the first hydrolysis product, InOH^{2+} . The best values of the hydrolysis constants so obtained

$$\begin{aligned} \kappa_1 &= [\text{InOH}^{2+}] [\text{H}^+] / [\text{In}^{3+}] &= 10^{-4.4} \\ \kappa_2 &= [\text{In}(\text{OH})_2^+] [\text{H}^+]^2 / [\text{In}^{3+}] &= 10^{-8.8} \end{aligned}$$

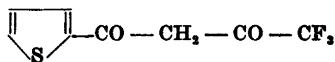
are in very satisfactory agreement with those obtained potentiometrically by Biedermann ⁷.

Although the potentiometric method is the most accurate for studying the hydrolysis of metal ions, it can only be used for total concentrations of metal between 10^{-1} M and 10^{-3} or 10^{-4} M. Since many metal ions form predominantly polynuclear hydrolysis products in this concentration range ^{1,2}, it may be difficult, or even impossible, to obtain reliable values of mononuclear hydrolysis constants from potentiometric measurements.

A number of stability constants have recently been measured by studying the influence of a secondary ligand on the distribution of a metal chelate between an organic and an aqueous phase. Since the partition equilibria may often be followed radiometrically using tracer concentrations of metal, the method would seem to be suitable for the determination of mononuclear hydrolysis constants. Although the effect of hydrogen ion concentration on the partition of *e. g.* 2-thenoyltrifluoroacetone (TTA, I) complexes of zirconium ^{3,4}, thorium ⁵ and neptunium (IV) ⁶ has led to qualitative deductions about the hydrolysis of these ions, no hydrolysis constants were calculated.

* Present address: Department of Chemistry, University of Edinburgh, Scotland.

The possibility of using the method to determine mononuclear hydrolysis constants was therefore tested by studying the $^{114}\text{In} / \text{TTA} / \text{benzene}$ system under the same conditions as were used by Biedermann ⁷ in his potentiometric investigation.



I.

LIST OF SYMBOLS

a	number of hydrogen atoms in the species $\text{H}_a\text{InL}_n^{(3+a-n)+}$, ($n > 1$); negative values refer to hydroxyl groups
\bar{A}	value of a for complex in organic phase
\bar{A}	mean value of A
C_1	initial concentration of TTA in benzene
C_M	initial concentration of indium in aqueous phase
E	measured potential in mV
E_0	$= E - 16.5 h - 59.16 \log h$ (equation 4)
f_p	$= \kappa_p + \sum_{n=1} K_{n-p,n} L^n$ (equation 22)
h	concentration of free hydrogen ions
J	$= \sum_{a \geq 0} \sum_{n=1} K_{a,n} h^a - n L^n$ (equation 17)
k	equilibrium constant for the reaction $\text{H}^+ + \text{L}^- \rightleftharpoons \text{HL}$
$K_{a,n}$	$= \beta_{a,n} k^{-n} (P_{\text{HL}} + 1)^{-n}$ (equation 9)
K_w	ionic product of water
l	concentration of free L^- ions in the aqueous phase
L	sum of concentrations of uncomplexed TTA in both phases (equations 6 and 7)
M	mole/l
n	number of TTA groups in species $\text{H}_a\text{InL}_n^{(3+a-n)+}$ (> 1)
\bar{n}	mean value of n
N	value of n for complex in organic phase
\bar{N}	mean value of N
p	number of hydroxyl groups in species $\text{In}(\text{OH})_p^{(3-p)+}$
$P_{A,N}$	partition coefficient, $[\text{H}_A\text{InL}_N]_o / [\text{H}_A\text{InL}_N]$
P_{HL}	partition coefficient $[\text{HL}]_o / [\text{HL}]$
q	distribution ratio of indium (equations 3 and 5)
R	counting rate of equilibrated aqueous phase
R_i	counting rate of initial aqueous phase
R_o	counting rate of equilibrated organic phase
X	normalised $\log h$, defined by equations (14) and (14a)
y, y_0, y'	defined by equations (12), (13) and (20)
Y	normalised y, y_0 and y' , defined by equations (15) and (15a)
$\beta_{a,n}$	equilibrium constant for the reaction $a\text{H}^+ + \text{In}^{3+} + n\text{L}^- \rightleftharpoons \text{H}_a\text{InL}_n^{(3+a-n)+}$
κ_p	equilibrium constant for the reaction $\text{In}^{3+} + p\text{H}_2\text{O} \rightleftharpoons \text{In}(\text{OH})_p^{(3-p)+} + p\text{H}^+$
K_p	equilibrium constant for the reaction $\text{In}(\text{OH})_{p-1}^{(4-p)+} + \text{OH}^- \rightleftharpoons \text{In}(\text{OH})_p^{(3-p)+}$
A	radiometric absorption ratio (equation 2)
τ	$\kappa_1 \cdot \kappa_2^{-1/2}$ (equation 16) or $f_1 \cdot f_2^{-1/2}$ (equation 16a)
[]	equilibrium concentration in aqueous phase
[] _o	equilibrium concentration in organic phase

All species may be combined with sodium or perchlorate ions, or with molecules of benzene or water. Concentrations and equilibrium constants will be expressed using the molar scale.

METHOD

The variation of the distribution ratio

$$q = \frac{\text{total concentration of indium in organic phase}}{\text{total concentration of indium in aqueous phase}}$$

with the concentration, h , of free hydrogen ions was studied at 25° C for a number of initial concentrations of TTA (C_L) in benzene and of indium (C_M) in the aqueous phase in the range $-2.7 > \log h > -4.5$, $-2.3 > \log C_L > -3.0$ and $-5.24 > \log C_M > -5.65$. The aqueous phase was made 3 M with respect to the perchlorate ion, by the addition of sodium perchlorate. Since the combined concentrations of indium, hydrogen and ligand ions never exceeded 0.1 % of the concentration of perchlorate ions, the activity coefficients of all species in the aqueous phase may be assumed to remain constant⁸. King and Reas⁹ have shown that the activity coefficient of TTA in benzene is effectively constant if $C_L < 10^{-2}$ M. Huffman and Iddings¹⁰ have found that the solubility (and hence the activity coefficient) of the uncharged TTA complex of zirconium in benzene is independent of C_L if $C_L < 0.08$ M, and it is probable that the activity coefficient of the corresponding indium complex in benzene is also constant in the ranges of concentration studied. Thus it may be assumed that there is no variation of activity coefficients in either phase, and that true stoichiometric equilibrium constants may be calculated from the partition measurements.

The distribution ratio, q , was obtained radiometrically, using ¹¹⁴In. Since equal phase volumes were used throughout, and no volume changes occurred on equilibration,

$$q = A R_o / R \quad (1)$$

where R_o and R are the counting rates of the equilibrated organic and aqueous phases, and

$$A = \frac{\text{absorption of } ^{114}\text{In radiation in benzene}}{\text{absorption of } ^{114}\text{In radiation in 3M NaClO}_4}$$

Assuming 100 % mass balance

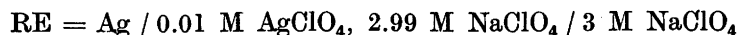
$$A = (R_i - R) / R_o \quad (2)$$

(*cf.* Ref.¹¹) where R_i is the counting rate of the initial aqueous phase, and the initial organic phase is not radioactive. Values of q and A were calculated from the measured values of R_i , R_o and R , using the relationship

$$q = (R_i - R) / R \quad (3)$$

and eqn. (2). The standard deviation in the value of A is a measure of the standard deviation in the overall mass balance (*cf.* p. 783).

The equilibrium hydrogen ion concentration in the aqueous phase was obtained using a glass electrode in combination with the half-cell



For the cell



Table 1. $\log q$ as a function of $\log h$.

$C_L = 10^{-3} \text{ M}$				$C_L = 2 \times 10^{-3} \text{ M},$ $C_M = 4.46 \times 10^{-6} \text{ M}$			$C_L = 3 \times 10^{-3} \text{ M},$ $C_M = 4.46 \times 10^{-6} \text{ M}$			$C_L = 5 \times 10^{-3} \text{ M},$ $C_M = 2.67 \times 10^{-6} \text{ M}$		
$-\log h$	$\log q$	$C_M \times 10^6$	$-y'$	$-\log h$	$\log q$	$-y'$	$-\log h$	$\log q$	$-y'$	$-\log h$	$\log q$	$-y'$
3.090	-2.39	5.34	2.66	2.914	-1.93	2.57	2.880	-1.51	2.58	2.681	-1.46	2.60
3.110	-2.32	2.67	2.64	3.210	-1.13	2.66	3.071	-1.02	2.67	2.830	-1.08	2.66
3.142	-2.13	4.46	2.55	3.412	-0.47	2.61	3.294	-0.34	2.65	3.002	-0.51	2.67
3.280	-1.76	2.67	2.60	3.546	-0.13	2.66	3.440	0.08	2.67	3.022	-0.48	2.64
3.288	-1.64	4.46	2.50	3.673	0.17	2.74	3.580	0.59	2.57	3.059	-0.39	2.66
3.413	-1.36	4.46	2.60	3.758	0.38	2.79	3.734	0.87	2.75	3.085	-0.33	2.67
3.428	-1.30	5.76	2.59	3.903	0.81	2.79	3.781	0.98	2.78	3.254	0.20	2.63
3.489	-1.12	2.67	2.59	4.042	1.09	2.95	3.866	1.29	2.72	3.494	0.86	2.66
3.534	-1.11	4.46	2.71	4.170	1.54	2.84	3.974	1.49	2.71	3.673	1.30	2.71
3.580	-0.80	4.46	2.53	4.386	1.97	3.06	3.979	1.47	2.88	3.846	1.71	2.72
3.660	-0.70	5.76	2.67	4.491	2.14	3.20	4.065	1.61	3.00	3.860	1.71	2.78
3.714	-0.57	4.46	2.70	4.552	2.28	3.23	4.144	1.84	3.00	4.079	2.02	3.06
3.748	-0.50	5.73	2.73				4.232	2.12	2.97	4.084	2.09	2.96
3.756	-0.39	2.67	2.75	$C_L = 4 \times 10^{-3} \text{ M},$ $C_M = 4.46 \times 10^{-6} \text{ M}$			4.336	2.29	3.10	4.324	2.39	2.67
3.800	-0.32	4.46	2.70	$-\log h$	$\log q$	$-y'$				$C_L = 5 \times 10^{-3} \text{ M},$ $C_M = 4.46 \times 10^{-6} \text{ M}$		
3.801	-0.22	5.34	2.60							$-\log h$	$\log q$	$-y'$
3.906	-0.02	2.67	2.72	2.879	-1.11	2.55				2.956	-0.72	2.66
3.969	0.22	4.46	2.66	3.308	0.24	2.56				3.229	0.11	2.66
3.970	0.15	2.67	2.74	3.403	0.41	2.58				3.446	0.74	2.65
4.040	0.18	4.46	2.91	3.874	1.53	2.76				3.702	1.37	2.71
4.119	0.50	2.23	2.82	4.184	2.28	2.75				4.050	1.99	3.00
4.130	0.47	5.76	2.87	4.300	2.42	3.06				4.091	2.12	2.92
4.192	0.58	5.73	2.95							4.268	2.40	2.99
4.232	0.86	2.23	2.89							4.298	2.45	2.98
4.320	0.96	5.73	2.92									

the relationship between the measured potential, E (in mV), and the concentration of free hydrogen ions is given by

$$E = E_0 + 16.5 h + 59.16 \log h \quad (4)$$

where the term E_0 includes the standard potentials of the electrodes and the asymmetry potential of the glass electrode. The term $16.5 h$ represents the liquid junction potential¹². Before each measurement, the glass electrode was immersed in two standard solutions of perchloric acid ($h = 0.231 \text{ M}$ and $h = 0.023 \text{ M}$); the two values of E_0 which were calculated from the measured potentials by means of equation (4) always agreed within 0.1 mV. The distribution experiments were carried out at such low acidities ($h < 0.002 \text{ M}$) that $E_0 \gg 16.5 h$, and $\log h$ could be directly calculated from the expression

$$\log h = (E - E_0) / 59.16 \quad (4a)$$

The partition measurements are given in Table 1, and are plotted in the form $\log q (\log h)_{C_L}$ in Fig. 1.

EXPERIMENTAL DETAILS

Indium perchlorate. Indium-114 (half-life 49 days) was obtained by irradiation of a known weight of "Specpure" indium wire (Johnson Matthey, Ltd.) at A.E.R.E., Harwell. The irradiated wire was dissolved in warm 3M perchloric acid, to which a drop of hydrogen peroxide had been added to prevent the formation of chloride or chlorate ions¹³. The solution was boiled to decompose the excess of hydrogen peroxide, cooled, and diluted to a known volume.

Solutions of *sodium hydroxide, perchloric acid, sodium perchlorate* and *silver perchlorate* were prepared and standardised as described elsewhere^{13,14}.

TTA. The reagent obtained from Dow Chemical Company was not purified further, as the melting point (43.5° C) was the same as that given by Day and Powers⁵. Known weights of the solid were dissolved in benzene (Merck *p. a.*) which had been presaturated with aqueous 3 M perchlorate. This ensured that the equilibrium concentration (~ 10 %) of the keto-hydrate was present¹⁰ and reduced the time required for partition equilibrium. The solutions were stored in the dark, over a small volume of 3 M perchlorate to remove any traces of trifluoroacetic acid formed by decomposition of the TTA.

Apparatus

The radioactivity was assayed using a 20th. Century Electronics Ltd. M6 liquid counter, in conjunction with a Tracerlab scalar.

The hydrogen ion concentrations were measured in a 25 ml beaker, using a Radiometer glass electrode (type G 202 B), which had been tested as described before¹⁴. The reference half-cell, RE, and the valve potentiometer, were the same as used in previous work¹⁴.

Procedure

The equilibrations and measurements were carried out in a room thermostated at $25 \pm 1^\circ \text{C}$. All aqueous solutions were made 3 M with respect to the perchlorate ion by the addition of sodium perchlorate, and were presaturated with benzene.

For each distribution experiment, a known volume of a solution of radioactive indium perchlorate ($\sim 1.6 \times 10^{-5} \text{ M}$) in perchloric acid ($\sim 2 \times 10^{-4} \text{ M}$) was diluted to 25.0 ml, using sufficient perchloric acid ($\sim 1.5 \times 10^{-2} \text{ M}$) or sodium hydroxide ($\sim 2 \times 10^{-4} \text{ M}$) to give the required hydrogen ion concentration. 15.0 ml of this solution, and 15.0 ml of a solution of TTA (concentration C_L) in benzene were pipetted into a 50 ml centrifuge tube. The remaining initial aqueous solution was acidified with one drop of concentrated perchloric acid to prevent adsorption losses on the glass. The centrifuge tube was closed with a ground glass stopper, which was wetted with a solution of collodion in ether and placed firmly in position. The tube was shaken mechanically at 30 revolutions per minute for 16 hours, which had been shown to be sufficient for equilibration, even at the lowest acidities studied ($\log h \sim -4.5$). After centrifugation, the two phases were carefully separated by pipetting.

10 ml portions of the initial aqueous solution, and of the two equilibrated phases, were assayed radiometrically. The counting rates were corrected for the background activity (~ 15 counts min^{-1}). Correction for the paralysis time of the counting assembly was found to be unnecessary at the counting rates used ($\leq 10\,000$ counts min^{-1}) and no correction was needed for the decay of the 49-day indium, as aliquots from any one experiment were assayed consecutively. Whenever possible, the duration of the counting was chosen to give a standard deviation of $\pm 1\%$. The mean value of the absorption ratio, A , was calculated using eqn. (2) and found to be 0.90; the standard deviation in this value, and hence in the overall mass balance (including statistical variations, and fluctuations in the counting efficiency), was $\pm 6.3\%$.

The hydrogen ion concentration in the aqueous phase was determined after the radioactivity of the solution had been measured.

At values of $\log h < -4.5$, or of $\log C_L < -3.0$, low mass balances ($\leq 80\%$, assuming $A = 0.90$) were obtained, and it is possible that some invisible precipitate was present. When $\log h \leq -5$, a visible precipitate collected at the phase boundary.

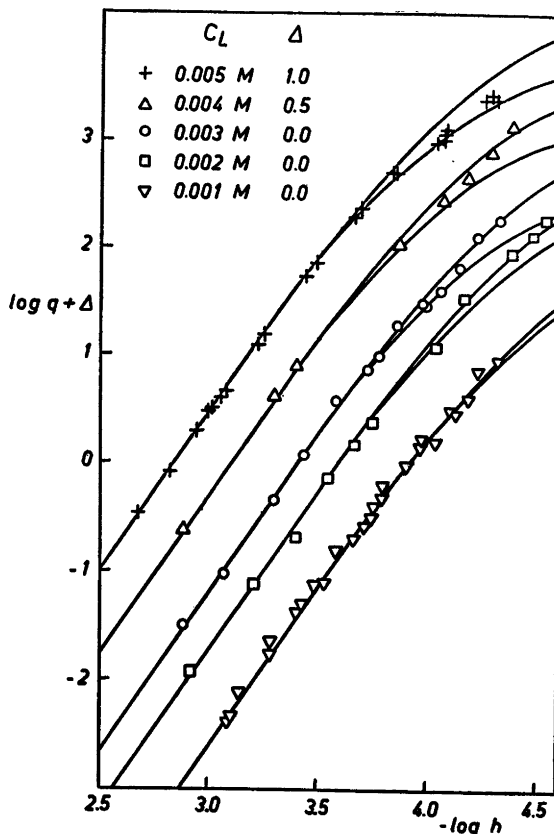


Fig. 1. $\log q$ as a function of $\log h$. +, Δ , \circ , \square and ∇ are experimental points for different initial concentrations, C_L , of TTA; points for different initial concentrations of metal in the range $-5.24 \leq \log C_M \leq -5.65$ are not differentiated. The full curves are calculated for $\log P_{0,2}K_{0,2} = -2.60$, $\log \kappa_1 = -4.4$, $\log \kappa_2 = -8.8$ and $\log K_{0,2} = -3.4$ (upper curves) or -3.0 (lower curves).

INTERPRETATION OF THE DATA

Since the distribution curves shown in Fig. 1 are independent of the total concentration, C_M , of indium, the system is homonuclear; and as $C_M < 6 \times 10^{-6}$ M, it may be assumed that only mononuclear complexes are present in appreciable amounts. If the species $H_A InL_N$ are present in the organic phase

$$\begin{aligned}
 q &= \sum_{A \geq 0} \sum_{N=1} [H_A InL_N]_o / \{ [In] + \sum_{p=1} [In(OH)_p] + \sum_{a \geq 0} \sum_{n=1} [H_a InL_n] \} \\
 &= \sum_{A \geq 0} \sum_{N=1} P_{A,N} \beta_{A,N} h^A l^N / \{ 1 + \sum_{p=1} \kappa_p h^{-p} + \sum_{a \geq 0} \sum_{n=1} \beta_{a,n} h^a l^n \} \quad (5)
 \end{aligned}$$

where charges are omitted, and $[]_o$ and $[]$ refer to concentrations in the organic and aqueous phases respectively; l is the concentration in the aqueous

phase of the anion L derived from TTA (HL), and $P_{A,N}$, κ_p and $\beta_{a,n}$ are defined by

$$P_{A,N} = \frac{[H_A \text{InL}_N]_o}{[H_A \text{InL}_N]^{-1}}$$

$$\kappa_p = \frac{[\text{In}(\text{OH})_p]}{[\text{In}]^{-1}} h^p$$

and

$$\beta_{a,n} = \frac{[H_a \text{InL}_n]}{[\text{In}]^{-1} h^{-a} l^{-n}}$$

Values of a and A will be negative for mixed TTA-hydroxo-complexes.

For equal volumes of the phases at equilibrium, the sum of the concentrations of uncomplexed TTA in both phases is given by

$$L = C_L - \sum_{A \geq 0} \sum_{N=1} N [H_A \text{InL}_N] - \sum_{a \geq 0} \sum_{n=1} n [H_a \text{InL}_n] \quad (6)$$

As the last term is negligible compared with C_L under the experimental conditions used (see p. 788)

$$L = C_L - \bar{N} [H_{\bar{A}} \text{InL}_{\bar{N}}]_o = C_L - \bar{N} C_M q (q + 1)^{-1} \quad (6a)$$

where \bar{A} and \bar{N} are the average numbers of hydrogen and TTA groups attached to each indium ion in the organic phase. In this work, $\bar{N} [H_{\bar{A}} \text{InL}_{\bar{N}}]_o \ll 0.02 C_L$. Now

$$L = [\text{HL}]_o + [\text{HL}] + l = l \{ kh(P_{\text{HL}} + 1) + 1 \} \quad (7)$$

where

$$k = [\text{HL}] h^{-1} l^{-1}$$

and

$$P_{\text{HL}} = \frac{[\text{HL}]_o}{[\text{HL}]^{-1}}$$

If $k \sim 10^6$ (Ref.³) and $P_{\text{HL}} \sim 40$ (Ref.⁹), then $kh(P_{\text{HL}} + 1) \gg 1$ at values of $h > 10^{-5}$ M, and

$$l = L / kh(P_{\text{HL}} + 1) \quad (7a)$$

Combining eqns. (5) and (7a)

$$q = \sum_{A \geq 0} \sum_{N=1} P_{A,N} K_{A,N} h^{A-N} L^N / \{ 1 + \sum_{p=1} \kappa_p h^{-p} + \sum_{a \geq 0} \sum_{n=1} K_{a,n} h^{a-n} L^n \} \quad (8)$$

where

$$K_{a,n} = \beta_{a,n} k^{-n} (P_{\text{HL}} + 1)^{-n} \quad (9)$$

At high acidities, no indium complexes will be formed in the aqueous phase, and moreover, $L \rightarrow C_L$; then^{3,17}

$$\lim_{h \rightarrow \infty} \frac{\partial \log q}{\partial \log h} \Big|_{C_L} = \bar{A} - \bar{N} \quad (10)$$

$$\lim_{h \rightarrow \infty} \frac{\partial \log q}{\partial \log C_L} \Big|_h = \bar{N} \quad (11)$$

From the data $\log q (\log h)_{C_L}$ shown in Fig. 1, it was found that $\bar{A} - \bar{N} = -3.0$. Values of $\log q$ at given values of $\log h$ were interpolated from Fig. 1, and the function $\log q (\log C_L)_h$ is plotted in Fig. 2; whence a value of $\bar{N} = 3.0$ was obtained.

Since $\bar{A} = 0.0$ and $\bar{N} = 3.0$, InL_3 is the sole species extracted, and the function

$$y = \log q - 3 \log L + 3 \log h = \log P_{0,3} K_{0,3} - \log \left\{ 1 + \sum_{p=1} \kappa_p h^{-p} + \sum_{a \geq 0} \sum_{n=1} K_{a,n} h^{a-n} L^n \right\} \quad (12)$$

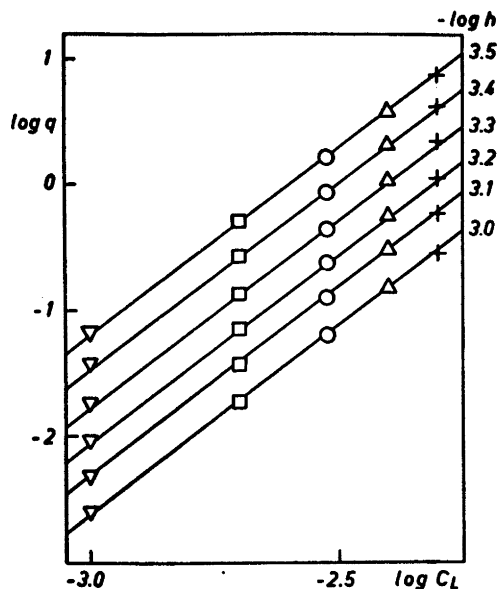


Fig. 2. Interpolated values of $\log q$ as a function of $\log C_L$, for different values of $\log h$, together with the best straight lines of slope 3.0. The symbols are those used in Fig. 1.

derived from eqn. (8) will have a constant value, $\log P_{0,3}K_{0,3}$, if all the metal in the aqueous phase is in the form of free indium ions. If hydroxo-complexes, but no TTA complexes, are present, y will be a function of h only, and independent of L , while if TTA complexes are formed, y will be a function of both h and L .

At hydrogen ion concentrations $> 7 \times 10^{-4}$ M, y is constant (-2.60 ± 0.03) within the experimental error, confirming that InL_3 is the species extracted. At lower acidities, the curves $y(\log h)_{C_L}$ are not coincident, indicating that TTA complexes are formed in the aqueous phase. Approximate values of the hydrolysis constants, κ_p , may be obtained by extrapolating the term y to zero concentration of TTA, and used to calculate preliminary values of the constants $K_{a,n}$; both sets of constants may then be refined by successive approximations, using eqn. (12).

Preliminary values of the hydrolysis constants. Smooth curves were drawn through the points $y(\log h)_{C_L}$ and, for each value of C_L , values of y were interpolated at a number of values of h . Curves $y(C_L)_h$ were then plotted, and extrapolated to $C_L = 0$ to give values of

$$y_0 = \log P_{0,3}K_{0,3} - \log \left\{ 1 + \sum_{p=1} \kappa_p h^{-p} \right\} \quad (13)$$

which are given in Table 2 and Fig. 4. The extrapolated function $y_0(\log h)$ lies only slightly above the points $y(\log h)$ for $C_L = 10^{-3}$ M.

Table 2. Values of y_0 as a function of $\log h$.

$-\log h$	3.50	3.60	3.70	3.80	3.90	4.00	4.10	4.20	4.30	4.40	4.50
$-y_0 \pm 0.04$	2.59	2.63	2.64	2.69	2.74	2.78	2.84	2.89	2.96	3.02	3.13

If the uncharged complex $\text{In}(\text{OH})_3$ is not present in appreciable amounts, preliminary values of the hydrolysis constants κ_1 and κ_2 may conveniently be obtained by superimposing the family of theoretical curves $^{18} Y(X)_\tau$ on the extrapolated function $y_0(\log h)$. The normalised variables X and Y are given by

$$X = \log h - \frac{1}{2} \log \kappa_2 \tag{14}$$

$$Y = y_0 - \log P_{0,3}K_{0,3} = -\log (1 + \tau 10^{-X} + 10^{-2X}) \tag{15}$$

where $\log \tau = \log \kappa_1 - \frac{1}{2} \log \kappa_2$ (16)

The required value of τ is that used to calculate the theoretical curve of the same shape as the experimental function, and the values of $\log P_{0,3}K_{0,3}$ and $\frac{1}{2} \log \kappa_2$ are obtained from the corresponding co-ordinates of the theoretical and experimental curves, in the position of best fit (equations 14 and 15). Within the limits of experimental error, the data $y_0(\log h)$ could be described by the curve $Y(X)$ calculated for $\tau = 1$ (see Fig. 4). Thus there is no evidence for the presence of $\text{In}(\text{OH})_3$, as would be expected from its low solubility 19 . The best fit was obtained with $\log P_{0,3}K_{0,3} = -2.6$ and $\frac{1}{2} \log \kappa_2 = -4.45$; whence $\log \kappa_1 = -4.45$ (eqn. 16) and $\log \kappa_2 = -8.9$.

Final values of the constants. Substituting the preliminary values of $P_{0,3}K_{0,3}$, κ_1 and κ_2 into eqn. (12), values of

$$J = P_{0,3}K_{0,3} \cdot 10^{-\nu} - \{1 + \sum_{p=1} \kappa_p h^{-p}\} = \sum_{a \geq 0} \sum_{n=1} K_{a,n} h^{a-n} L^n \tag{17}$$

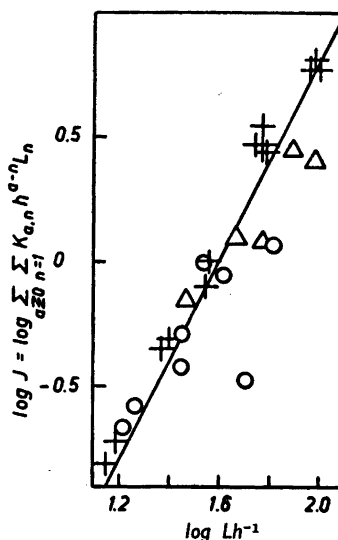


Fig. 3. $\log J = \log \sum_{a \geq 0} \sum_{n=1} K_{a,n} h^{a-n} L^n$ as a function of $\log L h^{-1}$. The symbols are those used in fig. 1 and the straight line is of slope 2.0 and of intercept -3.2 .

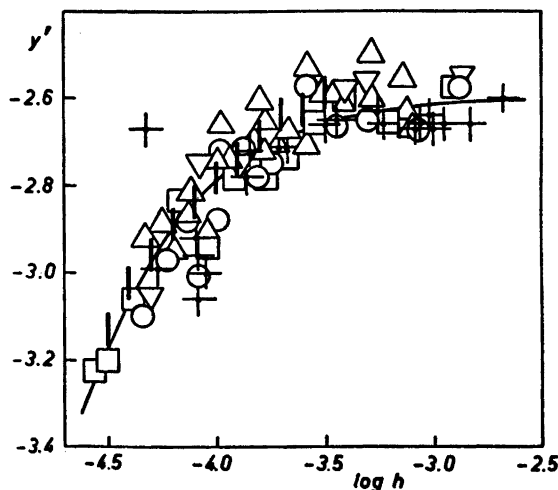


Fig. 4. Values of y' (points) and y_0 (vertical lines) as a function of $\log h$. The symbols are those used in Fig. 1. The full curve is that calculated for $\log \tau = 0$, in the position corresponding to $\log P_{0,3}K_{0,3} = -2.60$ and $\frac{1}{2} \log \kappa_2 = -4.4$.

were calculated for each point $y(h, L)$. If the TTA complexes in the aqueous phase are all of the type InL_n (i.e. $a = 0$), J will be a function of Lh^{-1} only, and

$$d \log J / d \log Lh^{-1} = \bar{n} \quad (18)$$

where \bar{n} is the average number of TTA groups in the complex InL_n ($n > 1$). $\log J$ is plotted as a function of $\log Lh^{-1}$ in Fig. 3; within the limits of experimental error, the points for $C_L > 3 \times 10^{-3}$ M can be represented by the equation

$$\log J = 2 \log Lh^{-1} - 3.2 \pm 0.2 \quad (19)$$

indicating that InL_2^+ is the predominant TTA complex in the aqueous phase in the range $1.2 < \log Lh^{-1} \leq 2.0$, and that $\log K_{0,2} = -3.2 \pm 0.2$. Thus the assumption that $\sum_{a \geq 0} \sum_{n=1} n[\text{H}_a \text{InL}_n] \ll C_L$ (see p. 785) is justified. If

$\log k(P_{\text{HL}} + 1) \sim 7.8$ (refs.^{3,9}), then from eqn. (9) the overall stability constant of InL_2^+ , $\beta_{0,2} \sim 12.4$.

Values of

$$y' = \log \{qh^3L^{-3} - P_{0,3}K_{0,3}K_{0,2}^{-1}h^2L^{-2}\} = \log P_{0,3}K_{0,3} - \log \{1 + \sum_{p=1} \kappa_p h^{-p}\} \quad (20)$$

were calculated for each experimental point $q(h, L)$ using the values of $P_{0,3}K_{0,3}$ and $K_{0,2}$ given above, and are shown in Table 1 and Fig. 4. Within the experimental error (± 0.1 log unit), the function $y'(\log h)$ is independent of L , and is coincident with the function $y_0(\log h)$ obtained by extrapolation to $L = 0$ (eqn. 13). Thus no refinement of the constants is necessary. The limits of error in κ_1 , κ_2 and $P_{0,3}K_{0,3}$ were obtained by curve-fitting using the set of

normalised $Y(X)_\tau$ curves, as described above. Although the data could be approximately explained in terms of the single hydroxo-complex $\text{In}(\text{OH})_2^+$, represented by the curve for $\log \tau = -\infty$ and $\frac{1}{2} \log \kappa_2 = -4.2$, the agreement is more satisfactory if the first hydroxo-complex, InOH^{2+} is also taken into account. The best fit was obtained with $\log \tau = 0.0 \pm 0.1$ and $\log P_{0,3}K_{0,3} = -2.60 \pm 0.03$; for this case, $\frac{1}{2} \log \kappa_2 = -4.4 \pm 0.1$.

The step stability constant of the species $\text{In}(\text{OH})_p$ is given by

$$K_p = [\text{In}(\text{OH})_p][\text{In}(\text{OH})_{p-1}]^{-1} [\text{OH}]^{-1} = \kappa_p / \kappa_{p-1} \cdot K_w \quad (21)$$

Values of K_p were calculated assuming that the ionic product of water, $K_w = 10^{-14.22}$ in a 3 M (sodium) perchlorate medium ²⁰.

Table 3. Equilibrium constants.

	$\log \kappa_1$	$\log \kappa_2$	$\log K_1$	$\log K_2$	$\log P_{0,3}K_{0,3}$
This work	-4.4 ± 0.1	-8.8 ± 0.3	9.8	9.8	-2.60 ± 0.03
Biedermann ⁷	-4.42 ± 0.05	-8.3 ± 0.1	9.80	10.3	—

Curves $\log q(\log h)_{c_\tau}$ were calculated by successive approximations, using eqns. (7) and (12), the values of the equilibrium constants given in Table 3, and the two extreme possible values of $K_{0,2}$. The calculated curves, which are shown in Fig. 1, are in very good agreement with the experimental data.

ALTERNATIVE TREATMENT OF THE DATA

The above interpretation of the data was checked using a method of curve-fitting developed by Sillén ²¹. Eqn. (12) may be rewritten

$$y = \log P_{0,3}K_{0,3} - \log \{1 + (\kappa_1 + K_{0,1}L + K_{1,2}L^2 \dots)h^{-1} + (\kappa_2 + K_{-1,1}L + K_{0,2}L^2 \dots)h^{-2} \dots\}$$

$$= \log P_{0,3}K_{0,3} - \log \{1 + \sum_{p=1} f_p h^{-p}\} \quad (12a)$$

where

$$f_p = \kappa_p + \sum_{n=1} K_{n-p,n} L^n \quad (22)$$

Provided that $p \leq 2$, the parameter $P_{0,3}K_{0,3}$ and the coefficients f_1 and f_2 may be found by comparing the experimental data $y(\log h)_L$ with the family of normalised curves $Y(X)_\tau$. In this case (cf. Ref.¹⁸)

$$X = \log h - \frac{1}{2} \log f_2 \quad (14a)$$

$$Y = y - \log P_{0,3}K_{0,3} \quad (15a)$$

and

$$\log \tau = \log f_1 - \frac{1}{2} \log f_2 \quad (16a)$$

As before, it was found that the value of $\log P_{0,3}K_{0,3}$ (-2.60 ± 0.03) was independent of L , indicating that InL_3 is the extracted species. Since the value of f_1 obtained ($< 10^{-4}$) is independent of L within the experimental error, it may be assumed that this term represents only the first hydrolysis constant

κ_1 . The term f_2 is a function of L , indicating that at least one indium-TTA complex, $H_{n-2}InL_n$, is present in the aqueous phase. If $n < 2$, the function $\log f_2(\log L)$ may also be analysed by curve-fitting¹⁸. Although the presence of appreciable concentrations of $In(OH)L^+$ cannot definitely be excluded, the variation of f_2 with L may best be explained in terms of the two species $In(OH)_2^+$ ($\log \kappa_2 = -8.7 \pm 0.3$) and InL_2^+ ($\log K_{0,2} = -3.2 \pm 0.2$). These conclusions are in satisfactory agreement with those reached above.

DISCUSSION

The hydrolysis constants given in Table 3 may be obtained by extrapolating the experimental data to zero concentration of TTA, and are almost independent of any assumption about the nature of the TTA complexes in the aqueous phase. However, from the variation of extraction with the concentration of reagent, it appears that InL_2^+ ($\log K_{0,2} = -3.2 \pm 0.2$, corresponding to $\log \beta_{0,2} \sim 12.4$) is the predominant TTA complex present under the experimental conditions used. No polynuclear complexes could be detected, as would be expected, since the total concentration of metal in the aqueous phase, $C_M(q+1)^{-1}$, never exceeded 3×10^{-6} M in the range $\log h < -3.5$ in which hydrolysis occurs (*cf.* Ref. 7).

Previous work on the hydrolysis of indium. As the molar fraction of benzene in the aqueous phase was less than 1.8×10^{-3} , the present hydrolysis constants should be strictly comparable with those obtained potentiometrically by Biedermann⁷ (see Table 3). The best value of κ_1 obtained from the partition data is in excellent agreement with Biedermann's value, and the difference between the two values of κ_2 is not surprising in view of the limited accuracy both of the radiometric measurements and of the potentials of indium amalgam electrodes⁷ in solutions of indium $\sim 5 \times 10^{-4}$ M.

Earlier work on the hydrolysis of indium was restricted to measurements of the pH of solutions of indium salts at different concentrations. Hepler and Hugus²² calculated

$$\kappa_1 = \lim_{C_M \rightarrow 0} (C_M - h) h^{-2} \sim 10^{-3.9}$$

from Moeller's data for the indium halides²³, and the same value at infinite dilution may also be obtained from Hattox and De Vries' and Moeller's data^{24, 25} for indium sulphate. Since the measurements were made in the concentration range where indium forms predominantly polynuclear hydrolysis products⁷, this value is probably unreliable. However, a decrease in the hydrolysis constant with increasing ionic strength is in accordance with the extended Debye-Hückel equation, and has also been observed for iron(III)²⁶ and scandium²⁷. The difference in the values of $\log \kappa_1$ at infinite dilution and in a 3 M perchlorate medium is the same (0.5 log unit) for indium as that reported for iron(III)²⁶.

Comparison with other trivalent metals. Mattock² has shown that the stability constants, K_1 , of the hydroxo-complexes often follow the same order as the ratios of the negative heats of hydration, $-\Delta H_{aq}$ of the metal ions, to their characteristic co-ordination numbers, N . The same correlation is valid for the Group III B metals.

	Ga ³⁺	In ³⁺	Tl ³⁺
log K_1 (medium)	11.4 ($\mu = 0$) ^a	9.8 (3 M NaClO ₄)	13.08 (3 M NaClO ₄) ²⁹
$\Delta H_{aq} / N$ ^b	187.3	165.8	246.0
χ ^c	1.6	1.5	1.9

^a Ref.²⁹ and refs. therein^b values taken from Refs. ^{30, 31}^c Ref.³²

The stabilities of the hydroxo-complexes follow the same order (Tl > Ga > In) as Pritchard and Skinner's "best" values, χ , of the electronegativities³².

When $P_{HL} \gg 1$ and $\bar{A} = 0$, $P_{A,N}K_{A,N}$ approximates to the extractability constant³³, $K = [MeL_N]_o [H]^N / [Me][HL_N]$. Although values of K for the extraction of TTA complexes of trivalent metals into benzene have been obtained under different experimental conditions, it seems that indium is extracted less readily than iron(III) and scandium, but more readily than bismuth, aluminium, thallium(III), americium, yttrium, dysprosium, praseodymium, lanthanum and actinium (Ref³⁴. and refs. therein, Refs.³⁵⁻³⁷).

The choice of a chelating ligand for studies of hydrolysis. Although it has been shown that the partition method may be used for quantitative investigation of the hydrolysis of metal ions, the difficulty of obtaining accurate distribution measurements, and the introduction of unknown parameters associated with the extracting reagent, lowers the precision of the hydrolysis constants obtained. Even if a suitable radionuclide is available, the choice of a chelating ligand may be somewhat restricted. In studies of many other types of complexes (*e. g.* if the secondary ligand is the conjugate base of a strong acid, or is an anion which may be added to a strongly acidic solution in the form of the corresponding weak acid) the concentration of the secondary ligand may be varied almost independently of h , and hence of the concentration, l , of chelating ligand; but if the secondary ligand is the hydroxyl ion, its concentration, $K_w h^{-1}$, cannot be varied independently of l (*cf.* eqn. 8). As accurate values of the distribution ratio may only be obtained radiometrically if $2.5 \geq \log q \geq -2.5$, the reagent and solvent should be chosen so that

$$\log P_{A,N}K_{A,N} = (N - A) \log h - N \log C_L \pm 2.5 \quad (23)$$

(assuming $H_A MeL_N$ is the only species extracted, *cf.* eqn. 9). If possible, measurements should be made over the whole range of hydrogen ion concentration in which hydrolysis occurs, and also at somewhat higher acidities, so that a reliable value of $\log P_{A,N}K_{A,N}$ can be obtained. In order to detect, and correct for, the presence of chelate complexes in the aqueous phase, series of experiments should be carried out using different concentrations of reagent (*cf.* eqn. 12). However, even within the limits imposed by eqn. (23), it is not always desirable to vary this quantity over a very wide range; at high values of C_L , the activity coefficient of the reagent in the organic phase may vary with concentration⁹ and at low concentrations such that $C_L < 10 N C_M$, uncertainties in the distribution measurements may result in appreciable uncertainties in the total concentration, L , of the uncomplexed reagent (*cf.* eqn. 7). Thus the TTA / benzene system could not be used to study the polynuclear hydrolysis of indium. A reagent / solvent system for which $\log P_{0,3}K_{0,3} \sim -8$ would be

necessary, since measurements would be required for $C_M < 5 \times 10^{-2}$ M and $h < 10^{-2}$ M (cf. Ref. 7).

We are grateful to Professor Lars Gunnar Sillén for his helpful comments on the manuscript, and to the *Swedish Atomic Energy Commission* and the *Swedish Natural Science Research Council*, for financial assistance.

REFERENCES

1. Sillén, L. G. *Rec. trav. chim.* **75** (1956) 705.
2. Mattock, G. *Acta Chem. Scand.* **8** (1954) 777.
3. Connick, R. E. and McVey, W. H. *J. Am. Chem. Soc.* **71** (1949) 3182.
4. Connick, R. E. and Reas, W. H. *J. Am. Chem. Soc.* **73** (1951) 1171.
5. Zebroski, E. L., Alter, H. W. and Heumann, F. K. *J. Am. Chem. Soc.* **73** (1951) 5646.
6. Sullivan, J. C. and Hindman, J. C. *J. Am. Chem. Soc.* **76** (1954) 5931.
7. Biedermann, G. *Arkiv Kemi* **9** (1956) 271.
8. Biedermann, G. and Sillén, L. G. *Arkiv Kemi* **5** (1953) 425.
9. King, E. L. and Reas, W. H. *J. Am. Chem. Soc.* **73** (1951) 1804.
10. Huffman, E. H. and Iddings, G. M. *U.C.R.L.* 377 (1949).
11. Dyrssen, D. *Svensk Kem. Tidskr.* **65** (1953) 43.
12. Rossotti, F. J. C. and Rossotti, H. S. *Acta Chem. Scand.* **10** (1956) *In the press.*
13. Carleson, B. G. F. and Irving, H. M. *J. Chem. Soc.* **1954** 4390.
14. Rossotti, F. J. C. and Rossotti, H. S. *Acta Chem. Scand.* **9** (1955) 1177.
15. Day, R. A. and Powers, R. M. *J. Am. Chem. Soc.* **76** (1954) 3895.
16. King, E. L. and Reas, W. H. *J. Am. Chem. Soc.* **73** (1951) 1806.
17. Irving, H. M., Rossotti, F. J. C. and Williams, R. J. P. *J. Chem. Soc.* **1955** 1906.
18. Sillén, L. G. *Acta Chem. Scand.* **10** (1956) 186.
19. Moeller, T. *J. Am. Chem. Soc.* **63** (1941) 2625.
20. Frydman, M., Lagerström, G., Sillén, L. G. and Ulfvarson, U. *Unpublished work.*
21. Sillén, L. G. *Acta Chem. Scand.* **10** (1956) 803.
22. Hepler, L. G. and Hugus, Z. Z. *J. Am. Chem. Soc.* **74** (1952) 6115.
23. Moeller, T. *J. Am. Chem. Soc.* **63** (1941) 1206; **64** (1942) 953.
24. Hattox, E. M. and De Vries, T. *J. Am. Chem. Soc.* **58** (1936) 2126.
25. Moeller, T. *J. Phys. Chem.* **45** (1941) 1235.
26. Milburn, R. M. and Vosburgh, W. C. *J. Am. Chem. Soc.* **77** (1955) 1352.
27. Kilpatrick, M. and Pockras, L. *J. Electrochem. Soc.* **101** (1954) 39.
28. Wilson, A. S. and Taube, H. *J. Am. Chem. Soc.* **74** (1952) 3509.
29. Biedermann, G. *Arkiv Kemi* **5** (1953) 441.
30. Quill, L. L. "Chemistry and Metallurgy of Miscellaneous Materials: Thermodynamics", McGraw Hill 1950.
31. Bjerrum, J. *Chem. Revs.* **46** (1950) 381.
32. Pritchard, H. O. and Skinner, H. A. *Chem. Revs.* **55** (1955) 745.
33. Kolthoff, I. M. and Sandell, E. B. *J. Am. Chem. Soc.* **63** (1941) 1906.
34. Keenan, T. K. and Suttle, J. F. *J. Am. Chem. Soc.* **76** (1954) 2184.
35. Hagermann, F. *J. Am. Chem. Soc.* **72** (1950) 768.
36. Cornish, F. W. *A. E. R. E. C/R* 891 (1952).
37. Werner, L. B. *AEC D* 2729 (1948).

Received March 3, 1956.