The Hydrolysis of Metal Ions. Part 4.[1] Indium(III)

Paul L. Brown and John Ellis
University of Wollongong, P.O.Box 1144, Wollongong, N.S.W. 2500, Australia
Ronald N. Sylva *
Australian Atomic Energy Commission Research Establishment, Lucas Heights, N.S.W. 2232, Australia

The hydrolysis of indium(III) has been investigated by potentiometric titration at 25 °C in 0.10 mol dm^{-3} potassium nitrate. Data treatment by our version of MINIQUAD has shown the 'best' model to be $[\text{In(OH)}]^{2+}$, $[\text{In(OH)}_2]^+$, and $[\text{In}_p(\text{OH})_p]^{2p+}$; the $-\log \beta_{pq}$ values for these species are estimated to be 4.31 (0.003), 9.35 (0.01), and 7.32 (0.006) (p = 4) or 9.12 (0.009) (p = 5) respectively, the estimated standard deviations being given in parentheses.

Although the hydrolysis of metal ions has been studied in detail since the pioneering work of Sillén and co-workers [2,3] the hydrolysis of indium(III) has received little attention. Indeed, the species that form have been poorly characterised and the differences in estimated formation constants are large. Polynuclear speciation, although present, has often been neglected as a result of inadequate or inaccurate data (for example, the use of stoicheiometric salt solutions, or too few data points).[4–9] In an attempt to resolve some of these uncertainties this hydrolytic system has been reinvestigated. This paper details the numerical analysis of, and experimental limitations involved in, the study of the hydrolysis of indium(III).

Experimental

Reagents.—Unless otherwise stated, all reagents were Merck Suprapur and were used without further purification. The source of indium metal was of purity 99.9995% (Balzers'). Potassium hydrogen carbonate (Fluka, Guarantie) was as described by Hedström.[10]

Procedure.—The previously described procedures [1,11,12] were followed using an automated potentiometric technique.[13] The value of λ in the expression $[\text{H}^+] = 10^{-\text{pH}}/\lambda$ was found to be 0.866. Because of the low pH range, the ionization reaction of water could be ignored. All titrations were carried out at 25.0 ± 0.1 °C using 0.10 mol dm^{-3} KNO_3 as the ionic medium. A summary of the titrations is given in Table 1; full details are available on request.

Results

The stoicheiometric equilibrium constants for reactions (1), as defined in equation (2), are in accord with the convention previously adopted.[1,11,12] Each species is represented by either a (p,q) pair or its formula.

$$p\text{In}^{3+} + q\text{H}_2\text{O} \rightleftharpoons [\text{In}_p(\text{OH})_q]^{(3p-q)+} + q\text{H}^+ \tag{1}$$

$$\beta_{pq} = [\{\text{In}_p(\text{OH})_q\}^{(3p-q)+}][\text{H}^+]^q/[\text{In}^{3+}]^p \tag{2}$$

Our version [12] of MINIQUAD [14,15] was used to examine a large number of models. The initial estimates of the formation constants were obtained from the generalised form of the Sylva–Davidson empirical relationship.[1]

The existence of the monomers $[\text{In(OH)}]^{2+}$ and $[\text{In(OH)}_2]^+$ has been documented by all previous workers.[8,16–19] These two species were, therefore, used in an attempt to explain the data, but both the estimated standard deviations and error square sum were too high for this to be considered a 'best' model.[1,12] It was thus assumed that one or more polynuclear species were present, and the approach adopted by Baes and Mesmer [20] was used to determine the missing species. The result of the addition of a polynuclear species to the mononuclear base model is summarised in Table 2. The Table shows that the 'best' model for each value of p is obtained when $q = p$, *i.e.* $[\text{In(OH)}]^{2+}$, $[\text{In(OH)}_2]^+$, and $[\text{In}_p(\text{OH})_p]^{2p+}$, all of which meet the acceptance criteria.[1,11,12] Of these, the model containing the (4,4) species shows the best fit. It is not necessary, therefore, to attempt to explain the data by assuming more than three hydrolysis products.[21]

Table 3 gives a comparison of what is here regarded as the global minimum (*i.e.* the 'best' model, model 3; the R factor [12] is 0.001 003) and some closely situated minima. Although model 3 is the 'best' model, models 1—5 all meet the above criteria. As was the case with lead(II),[1] the variations in the $-\log \beta_{pq}$ values and their standard deviations are quite small.

For this system, given the experimental pH range, the proton mass-balance equation is of comparable importance to the metal ion mass-balance equation. This allows λ to be sensibly refined, and the variation of the other parameters with λ is quite large. The variation of the error square sum with respect to λ is similar to that of uranium(VI).[12] The

Table 1. Summary of titrations of indium(III) at 25 °C in 0.1 mol dm^{-3} KNO_3

Total initial In concentration (10^{-3} mol dm^{-3})	pH Range	Number of points
2.008	2.921—3.737	98
1.004	3.000—3.899	139
0.502	3.041—3.986	217
0.201	3.338—4.161	261

Table 2. Error square sum ($\times 10^{10}$) for various hydrolysis models [a]

Stoicheiometric coefficients	$q = p - 1$	$q = p$	$q = p + 1$
2	130.7	31.3	fails [b]
3	48.0	20.5	47.0
4	22.6	17.9	32.2
5	fails [b]	18.2	29.3
6	fails [b]	20.3	29.6

[a] Model: $[\text{In(OH)}]^{2+}$, $[\text{In(OH)}_2]^+$, $[\text{In}_p(\text{OH})_q]^{(3p-q)+}$. [b] The model fails due to species rejection (β_{pq} becomes negative).

Table 3. Comparison of some models of indium(III) hydrolysis

Model number	Model	$-\log \beta_{pq}$	Estimated standard deviation of $-\log \beta_{pq}$	Estimated relative standard deviation (%) of β_{pq}	10^{10} × error square sum
1	(1,1)	4.53	0.008	1.9	31.3
	(1,2)	9.34	0.02	4.1	
	(2,2)	5.48	0.007	1.6	
2	(1,1)	4.38	0.004	0.8	20.5
	(1,2)	9.33	0.01	3.3	
	(3,3)	6.46	0.006	1.3	
3	(1,1)	4.30	0.003	0.6	17.9
	(1,2)	9.35	0.01	3.3	
	(4,4)	7.32	0.006	1.4	
4	(1,1)	4.26	0.004	1.0	18.2
	(1,2)	9.36	0.02	3.5	
	(5,5)	9.12	0.009	2.1	
5	(1,1)	4.25	0.002	0.5	20.3
	(1,2)	9.37	0.02	3.7	
	(6,6)	8.85	0.008	1.8	
6	(1,1)	4.18	0.003	0.7	215.2
7	(1,1)	4.23	0.007	1.5	198.2
	(1,2)	9.39	0.06	12.7	
8	(1,1)	4.23	0.007	1.5	40.3
	(4,4)	7.32	0.01	3.2	
9	(1,1)	4.30	0.003	0.9	47.0
	(1,2)	10.34	0.24	56.1	
	(3,4)	10.35	0.009	2.2	
10	(1,1)	4.50	0.01	3.2	31.0
	(1,2)	9.39	0.03	6.6	
	(2,2)	5.53	0.02	5.1	
	(3,4)	11.27	0.17	38.5	

experimentally determined value of 0.866 is also very similar to that determined for uranium(VI), namely 0.850.

Each titration was commenced at a pH value at which approximately 5% hydrolysis had occurred. The conclusion of the titrations, *i.e.* the point of incipient precipitation, was readily ascertained since at this point the change in pH after each addition of titrant rapidly slowed down and soon became negative (see Discussion section).

Discussion

A survey of some previous potentiometric studies of the hydrolysis of indium(III) at 25 °C is given in Table 4. Early studies which are based on the pH of stoicheiometric salt solutions have been omitted owing to the inadequacy of this procedure, as previously mentioned.[4–7]

In the concentration ranges studied, the (1,1) monomer is the most important species. Only at high concentrations of both indium(III) and hydrogen ion does the polymer become of equal importance. The (1,2) species is a minor species at all concentrations. The relative percentage formation of each species at the highest metal concentration is given in Figure 1.

Biedermann's [8] potentiometric study of 1956 was limited by precipitation reactions. Numerical analysis of these data allowed identification of the mononuclear species $[In(OH)]^{2+}$ and $[In(OH)_2]^+$; however, only an estimate of the polynuclear species present could be made and the 'core-plus-links' species were suggested to explain the data. Baes and Mesmer [20] attributed this inconclusiveness to the ratio, average hydroxide ion : metal ion ($\bar{n}$), being too low before precipitation reactions begin. This view is partly correct, but the main reason is the limited resolvability of the species in the accessible concentration ranges. That is, the species are not well enough defined in the experimental regions to allow their contribution to the data to be uniquely resolved. Neither the calculations of Biedermann [8] nor later recalculations by Sillén,[22] and by Ferri,[23] were able to solve this problem.

Table 4. Survey of potentiometric investigations of the hydrolysis of indium(III) at 25 °C

Medium	Total indium concentration range (10^{-3} mol dm^{-3})	Model	$-\log \beta_{pq}$	Ref.
3 mol dm^{-3} $NaClO_4$	0.5—100	(1,1)	4.42	8
		(1,2)	8.3	
		$(n + 1,2n)$[a]	$0.52 + 4.69n$[a]	
3 mol dm^{-3} NaCl	1—40	(1,1)	6.95	16
		(2,2)	10.15	
3 mol dm^{-3} $LiClO_4$	1.04	(1,1)	4.42	17
		(1,2)	7.14	
3 mol dm^{-3} $LiClO_4$[b]	1—50	(1,1)	3.18	18
		(1,2)	6.34	
		(2,2)	4.37	
3 mol dm^{-3} $NaClO_4$	(2.24—5.75) × 10^{-3}	(1,1)	4.4	19
		(1,2)	8.8	
0.1 mol dm^{-3} KNO_3	0.2—2.008	(1,1)	4.31	This work
		(1,2)	9.35	
		(4,4)	7.32	

[a] n is an integer constant $\geqslant 1$. [b] In 0.064 mol equivalent of acetonitrile.

Because the present investigation has more data points than that of Biedermann [8] (715 compared with 104), it might be expected to allow for a better determination of the species and their formation constants due to the greater density of data points in the accessible regions where each species is important. However, the limited formation and resolvability of the species before precipitation is an inherent characteristic of this

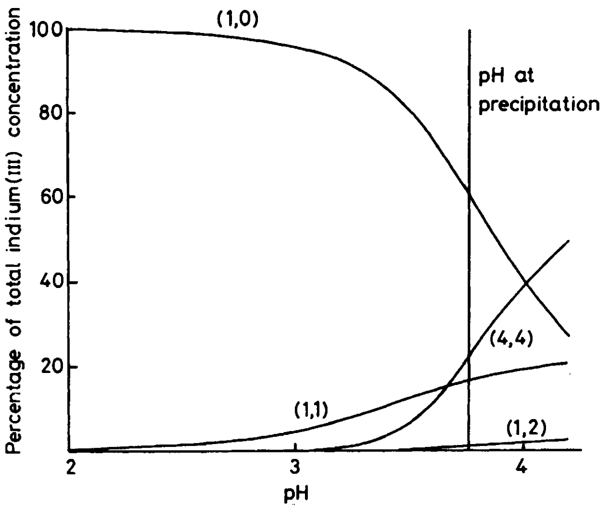

Figure 1. Percentage distribution of indium(III) hydrolysis products at total $[In^{3+}] = 2 \times 10^{-3}$ mol dm^{-3}, assuming $[H^+] = 10^{-pH}$ ($\lambda = 1$)

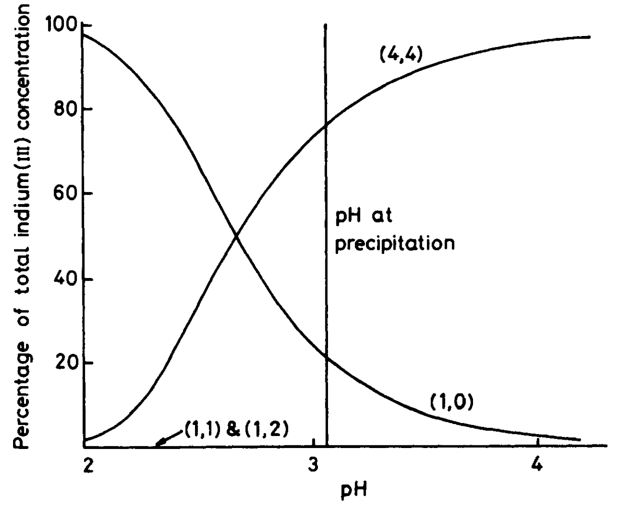

Figure 2. Percentage distribution using constants of this work (model 3), at total $[In^{3+}] = 0.1$ mol dm^{-3} and end-point approximation given by extrapolation using equation (3)

particular system. Thus, an increase in the number of data points may not necessarily allow for a better determination of the system to be made. This is illustrated in Figures 2 and 3 in which the results for the high total metal concentration of 0.1 mol dm^{-3} obtained using Biedermann's [8] speciation scheme are compared with ours. In Figure 2, the pH of incipient precipitation (' end-point ' of titration) can be approximated by an extrapolation of data obtained from the titrations using equation (3) where subscript sp means solubility product.[24]

$$pH = pK_w + \tfrac{1}{3}(pIn^{3+} - pK_{sp}) \qquad (3)$$

The model used in Figure 3 is the base model determined by Sillén.[22] Clearly, there is no experimentally accessible range of either pH or total metal whereby resolution can be achieved. The analysis of the present work is consistent with this explanation, in that eight models meet our acceptance criteria.

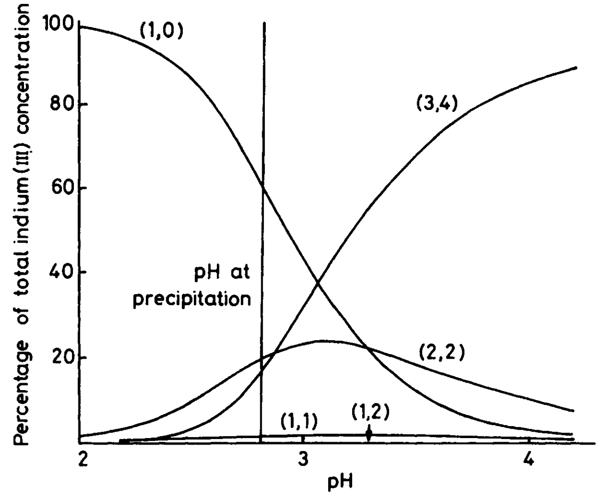

Figure 3. Percentage distribution using the constants of Biedermann [8] at total $[In^{3+}] = 0.1$ mol dm^{-3} with end-point as determined in ref. 8

Although the stated model of (1,1), (1,2), and (4,4) gives the lowest sum of squares for the data, it is not unique. This result is similar to that found by Collados *et al.*[25] for the hydrolysis of cobalt(II), a system where resolvability is also a problem.

Each titration has an interesting feature at a point just before precipitation. As more base is added the pH becomes more acidic rather than more basic. This phenomenon has been observed in the hydrolysis of manganese(II),[26] copper(II),[27] and uranium(VI).[27] At incipient precipitation, all species present are presumably involved in reactions tending towards the formation of the species, $In(OH)_3$ (solid). This process requires a very rapid transition from low $\bar{n}$ values (*ca.* 0.7) to high values ($\leqslant 3$), thus leading to the generation of hydrogen ions, which is not fully offset by the base addition. Thus a decrease in pH is observed.

A comparison of the results of the present work with those of Biedermann [8] shows that for the monomers, reasonable agreement exists when the difference in ionic strength used is considered. Resolvability problems, which are an intrinsic characteristic of the indium(III) hydrolysis system, however, prevent a definitive description.

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