

On the Structures of Polynuclear Hydrolysis Complexes of Indium(III) in Aqueous Solution

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Large angle X-ray scattering measurements on hydrolyzed indium(III) nitrate solutions showed the presence of polynuclear hydrolysis complexes with In–In distances of 3.89 Å, indicating single hydroxo bridges between the In atoms. The data are consistent with a dominant four-nuclear complex, $\text{In}_4(\text{OH})_6^{6+}$, built up from InO_6 octahedra sharing corners, with the In atoms arranged at the corners of a regular tetrahedron.

In an early potentiometric investigation¹ of the hydrolysis of the indium(III) ion in aqueous perchlorate solution, the data were explained by the formation of the mononuclear complexes InOH^{2+} and $\text{In}(\text{OH})_2^+$ and an infinite series of polynuclear complexes, $\text{In}[(\text{OH})_2\text{In}]_n^{(3+n)+}$, in accordance with Sillén's "core+links" hypothesis. Later recalculation of the same data with the use of least-squares methods, seemed to indicate that some complexes in the series were favored in comparison with others.²

From large angle X-ray scattering measurements on concentrated hydrolyzed indium perchlorate and nitrate solutions the In–In distances within the polynuclear complexes were determined to be about 4.0 Å.³ This distance would be expected for In atoms joined by single hydroxo bridges and seemed inconsistent with the "link" part of the suggested formula, $[\text{In}(\text{OH})_2]$, or its equivalent, $[\text{InO}]$. In a new emf investigation of hydrolyzed indium perchlorate solutions⁴ extending to higher indium concentrations, Biedermann and Ferri concluded that the data could be well explained by assuming, in addition to the mononuclear InOH^{2+} and $\text{In}(\text{OH})_2^+$, only two polynuclear complexes, $\text{In}_2(\text{OH})_2^{4+}$ and $\text{In}_4(\text{OH})_6^{6+}$,

both members of the original "core+links" series.

Comparison between X-ray scattering curves for hydrolyzed and unhydrolyzed solutions is capable of giving information not only on the In–In distances in the polynuclear hydrolysis complexes, but also on their frequency and on possible coordination changes for the indium ion. It also offers a possibility of identifying other prominent distances within the complexes which could be useful for the derivation of plausible models for their structures. In the present work, we have chosen indium nitrate for such a comparison because of its high solubility and because the hydrolysis can be carried farther before precipitation of hydroxide than is possible for perchlorate solutions. The same complexes are formed in both solutions as shown by results from previous potentiometric measurements on indium hydrolysis in NaNO_3 medium,⁵ which do not differ from those obtained in perchlorate medium.

Experimental

Preparation of solutions

Indium metal (Carl Roth KG. Indium, 99.95 %) was dissolved in an excess of nitric acid to give a nearly saturated slightly acid solution in which hydrolysis was negligible. The hydrolyzed solu-

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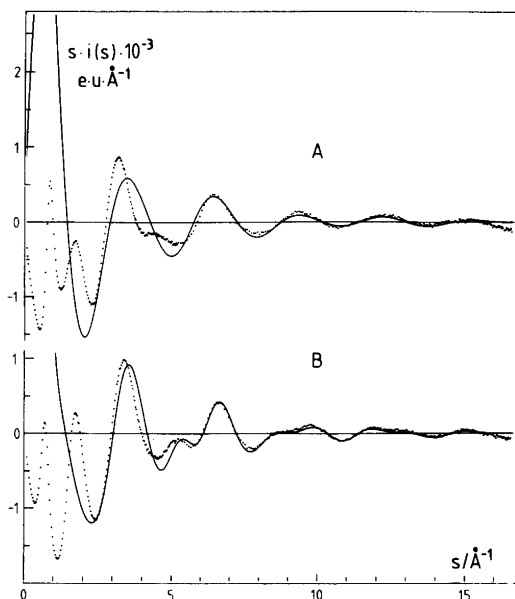


Fig. 1. Observed $s \cdot i(s)$ values (dots) as a function of $s = 4\pi\lambda^{-1}\sin\theta$ for the unhydrolyzed (A) and the hydrolyzed (B) indium nitrate solution. Theoretical $s \cdot i(s)$ values calculated with parameter values in Table 2, are given by the solid lines.

tion was prepared by evaporation of nitric acid from the $\text{In}(\text{NO}_3)_3$ solution under a heating lamp. In a very concentrated solution, a white solid – probably a mixture of $\text{In}(\text{NO}_3)_3$ and hydrolysis complexes – formed, which was freshly soluble in water. After filtration, the solution was clear and apparently stable with no observable precipitation of hydroxide.

The solutions were analyzed for In^{3+} by an EDTA titration and for NO_3^- by ion exchange. The analysis showed a deficiency in the hydrolyzed solution of about 0.75 protons for each hydrated In^{3+} ion (Table 1). The density of each solution was determined with an Anton Paar digital densimeter DMA35. The compositions of the solutions are given in Table 1.

X-ray measurements

The X-ray scattering was measured in a Rigaku Theta-Theta diffractometer using a graphite monochromator. Four different opening slits ($1/6^\circ$, $1/2^\circ$, 1° , and 2°) were used to cover the accessible θ range, $1^\circ < \theta < 70^\circ$, where 2θ is the

scattering angle. Intensities were measured at discrete points at intervals in θ of 0.1° for $\theta < 20^\circ$, and 0.25° for $\theta > 20^\circ$. For each point, 10^5 counts were collected and each θ range was scanned twice.

Data treatment

All calculations were performed with the KURVLR program as described in previous papers.⁶ Corrections were made for background radiation, for polarization in the sample and in the monochromator and for incoherent scattering reaching the counter. No absorption correction was needed ($\mu > 15 \text{ cm}^{-1}$). The data were normalized to the chosen stoichiometric unit of volume by comparing observed intensities in the high angle region of the intensity curves with the calculated sum of coherent and incoherent scattering. From the normalized intensity values, I_{obs} , corrected for incoherent radiation, the reduced intensities, $i(s)$, were obtained as $i(s) = I_{\text{obs}}(s) - \sum n_i f_i(s)^2$. Here $s = 4\pi\sin\theta/\lambda$, $f_i(s)$ = scattering factors⁷ corrected for anomalous dispersion, n_i = number of atoms “i” in the stoichiometric unit of volume V (Table 1).

Radial distribution functions (RDF) were obtained by the Fourier transformation (1) shown below.

$$D(r) = 4\pi r^2 \rho_0 + 2\pi r^{-1} \int_0^{s_{\text{max}}} s \cdot i(s) \cdot \sin(rs) \cdot M(s) \cdot ds \quad (1)$$

For both solutions, the same upper integration limit $s_{\text{max}} = 15.6 \text{ \AA}^{-1}$ and the same modification function $M(s) = f_{\text{In}}^2(0) \cdot f_{\text{In}}^2(s) \cdot \exp(-k \cdot s^2)$ were

Table 1. Composition of solutions. Concentrations are given as mol l^{-1} (upper figures) and as number of atoms in the stoichiometric unit of volume, $V/\text{\AA}^3$ (lower figures). H = the hydrogen ion excess.

| Solution | In^{3+} | NO_3^- | H_2O | H | density | $V/\text{\AA}^3$ |
|------------|------------------|-----------------|----------------------|-------|---------|------------------|
| A. (acid) | 3.96 | 12.59 | 35.7 | 0.71 | 1.879 | |
| | 1 | 3.18 | 9.0 | 0.18 | | 419.3 |
| | 0.821 | 2.61 | 7.40 | 0.15 | | 344.4 |
| B. (hydr.) | 4.81 | 10.81 | 40.9 | -3.62 | 1.955 | |
| | 1 | 2.25 | 8.49 | -0.75 | | 345.2 |

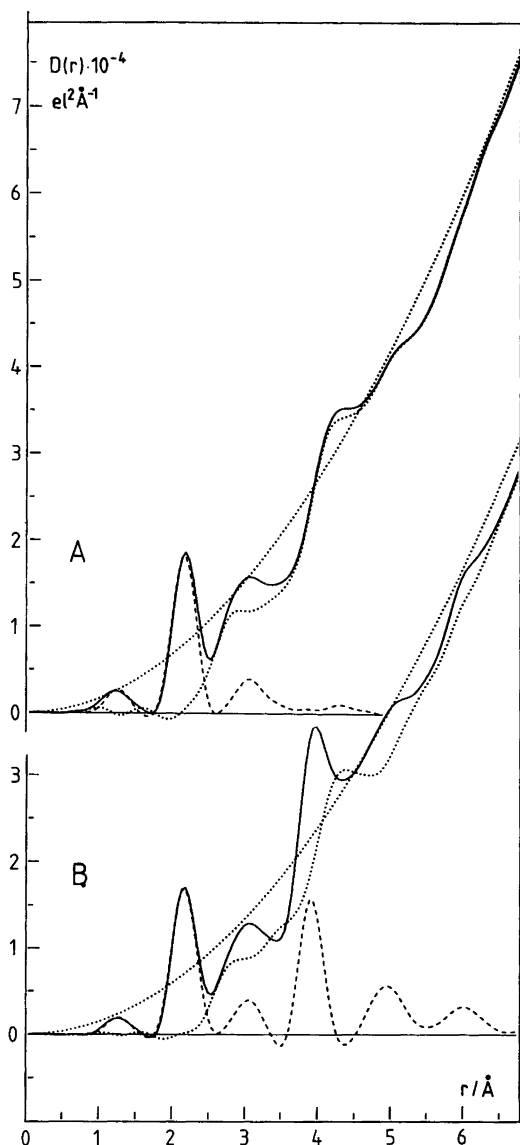


Fig. 2. The $D(r)$ functions (solid lines), theoretical peaks (dashed lines) calculated with parameters given in Table 2, and the corresponding difference curves (dotted lines) for the solutions A and B. The $4\pi r^2 \rho_0$ functions are also given as dotted lines.

used. For the RDFs (Figs. 2 and 3), a value of $k = 0.01$ was used, but for the difference curves in Fig. 4 the value was 0.00. Theoretical values for pair interactions were calculated from the Debye expression (2) shown below. Here r_{pq} is the

$$i(s) = \sum f_p f_q \cdot [\sin(r_{pq}s)] \cdot (r_{pq}s)^{-1} \cdot \exp(-1/2 \cdot l_{pq}^2 \cdot s^2) \quad (2)$$

distance between the two atoms involved and l_{pq} is the assumed rms variation in the distance. Theoretical peak shapes were calculated from these $i(s)$ values in the same way as used for the experimental values, with the same s_{\max} and the same $M(s)$ function.

Results and discussion

The reduced intensity functions, $s \cdot i(s)$, for the two solutions are shown in Fig. 1. The radial distribution functions $D(r)$ and $D(r) - 4\pi r^2 \rho_0$, are compared in Figs. 2 and 3. The first peak, at 1.2 Å, in the RDFs (Figs. 2 and 3) corresponds to N–O distances within the nitrate group. The second peak, at 2.2 Å, contains contributions from In–H₂O distances within the first coordination sphere of the In³⁺ ion and also from O–O distances within the NO₃⁻ ions. The peak at about 3 Å is probably caused mainly by H₂O–H₂O interactions but may also contain contributions from distances within possible indium-nitrate complexes. A sharp peak at 3.9 Å in the hydrolyzed solution, which corresponds to the In–In interactions within the polynuclear hydrolysis complexes, had no correspondence in the acid solution. That applies also to the less pronounced peak at about 6.0 Å. A peak at about 4.2 Å occurred in the acid solutions and is probably due, at least in part, to a second coordination sphere around the indium ion.⁸ A corresponding peak was indicated in the hydrolyzed solution but was overlapped by the In–In interaction at 3.9 Å.

The differences between the RDFs for the acid and the hydrolyzed solutions are best brought out by a difference curve, $D(r)_{\text{hydr}} - D(r)_{\text{acid}}$, which can also be used to derive more precise values for the

Table 2. Parameter values: d = distance in Å; n = frequency (referred to one In atom); l = root mean square variation in Å.

| | d | l | n |
|---------------------|------|-------|------|
| In–H ₂ O | 2.17 | 0.11 | 6.0 |
| In–In | 3.89 | 0.12 | 0.65 |
| N–O | 1.25 | 0.063 | 3 |

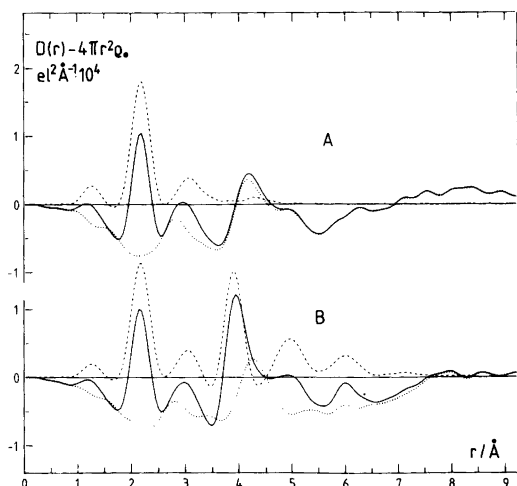


Fig. 3. The $D(r) - 4\pi r^2 Q_0$ functions (solid lines) compared with theoretical curves (dashed lines) calculated with parameter values in Table 2. The corresponding difference curves are given by dotted lines.

number of In–In interactions contained in the peak at 3.9 Å. This peak was partly overlapped by the 4.2 Å peak, which presumably contains contributions from both indium-light atom and light atom-light atom interactions. If the former were dominant, the comparison between the two RDFs would best be made by choosing stoichiometric units of volume for the two solutions which contain equal numbers of In atoms. If the light atom interactions were dominant, equal numbers of oxygen atoms would be the preferable choice. Both calculations were made and the results are shown in Figs. 4b and a, respectively. After subtraction of the extrapolated background curves, the remaining peaks are almost identical. They are compared in Figs. 4c and d with a theoretical In–In peak calculated from parameter values given in Table 2.

Besides the In–In peak at 3.9 Å the only remaining significant peak in the difference curve occurred at 6.0 Å. The peak at 2.2 Å in Fig. 4a results from the unequal numbers of In atoms in the stoichiometric units of volume chosen (Table 1). No significant peaks remain at 2.2 Å in Fig. 4b, which shows that the In coordination is not changed in the hydrolysis process.

The In–H₂O distance of 2.17 Å does not differ significantly from corresponding distances found

for octahedrally coordinated indium(III) in crystal structures: 2.16 Å in $\text{In}(\text{OH})\text{SO}_4(\text{H}_2\text{O})_2$;⁹ 2.17 Å in $\text{In}(\text{OH})_3$;¹⁰ 2.08 Å in InOHF_2 ;¹¹ and 2.16 Å in $\text{InH}(\text{SO}_4)_2 \cdot 5\text{H}_2\text{O}$.¹² A theoretical peak calculated for six In–H₂O interactions (Table 2) is in close agreement with the observed peak (Figs. 2 and 3). The In³⁺ ions are thus octahedrally coordinated in the solutions and no significant differences between the hydrolyzed and the acid solutions are observed.

The sharp peak at 3.89 Å in the hydrolyzed solution is close to distances found in crystal structures between In atoms which are joined by a single hydroxo bridge: 3.95 Å in $\text{In}(\text{OH})\text{SO}_4(\text{H}_2\text{O})_2$;⁹ 3.96 Å in $\text{In}(\text{OH})_3$.¹¹ This leads to the conclusion that the hydrolysis complexes in solution are built by the same type of bridging between the In atoms.

The analysis of the difference curves in Fig. 4 gave a value of 0.65 for the In–In frequency (Table 2) with an estimated uncertainty of less than 0.05. If only dinuclear complexes were formed, the frequency could not be larger than 0.5; therefore, the average number of In atoms in the polynuclear complexes must have exceeded two.

Pronounced peaks which are associated with longer In–In distances were not observed in the RDF for the hydrolyzed solution, with the possible exception of the 6 Å peak. Complexes with a nuclearity larger than two or three, but with only one In–In distance, must be based on a regular triangular or tetrahedral arrangement of the In atoms. Corner sharing InO_6 octahedra with In–In distances of 3.90 Å can easily be arranged into such complexes (Fig. 5) with only small deviations (2.10–2.20 Å) of the In–O distances from the average value of 2.17 Å.

A complex with four In atoms tetrahedrally arranged and joined by single hydroxo bridges has the formula $\text{In}_4(\text{OH})_6^{6+}$ and is shown in Fig. 5. With 43% of the indium ions in solution engaged in this complex, assuming the remaining In atoms to occur as unhydrolyzed $\text{In}(\text{H}_2\text{O})_6^{3+}$ ions, the number of In–In distances per In atom would be 0.65, in agreement with the value determined (Table 2). The sum of the corresponding peak shapes is compared in Figs. 2 and 3 with the RDF for the hydrolyzed solution. The agreement with the observed peaks at 2.17 Å and 3.90 Å follows from the derivation of the structure, but, in addition, the long In–O and O–O distances within

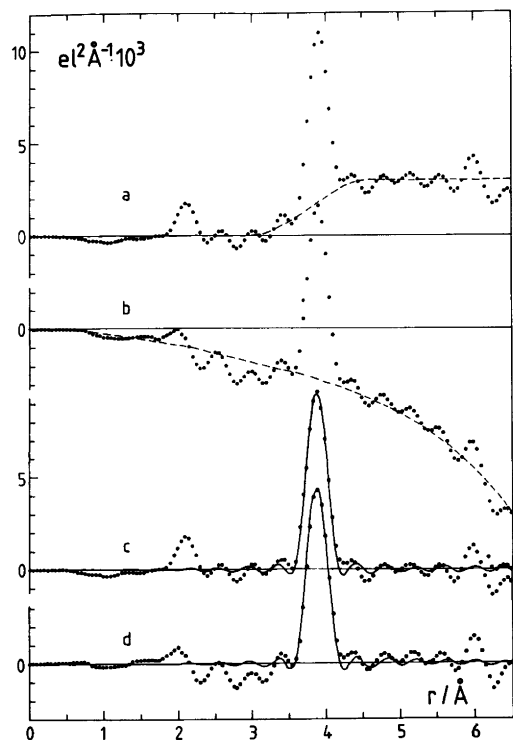


Fig. 4. Differences between the $D(r)$ functions for the hydrolyzed (B) and the unhydrolyzed (A) solutions. The curves "a" and "b" correspond to different choices for the stoichiometric units of volume (Table 1). Subtraction of the background curve (dashed line) in "a" and "b" leads to the peaks in "c" and "d", respectively. They are compared with a theoretical In-In peak (solid lines) calculated with the parameters given in Table 2.

the tetrahedral complex closely reproduce the 6 Å peak and also the 5.0 Å peak. This gives additional support for the model suggested. In the difference curve in Fig. 3, the 4.2 Å peak now appears as a separate peak analogous to the one in the acid solution.

A triangular complex obtained by removing one of the InO_6 octahedra from the tetrahedral structure in Fig. 5 is also a conceivable model. With 65% of the In^{3+} ions engaged in a triangular complex, the In-In frequency would have the required value of 0.65. The sum of the corresponding theoretical peaks differs only slightly from that for the tetrahedral one. The same applies to any combination of 2-, 3-, and 4-nuclear com-

plexes based on the structure in Fig. 5 and having an In-In frequency of 0.65. The scattering data, therefore, cannot be used to distinguish between them.

Biedermann and Ferri⁴ concluded from their emf measurements that only $\text{In}_4(\text{OH})_6^{6+}$ and $\text{In}_2(\text{OH})_2^{4+}$ are formed in hydrolyzed solution in addition to the mononuclear complexes InOH^{2+} and $\text{In}(\text{OH})_2^+$. If their stability constants are used for the much more concentrated nitrate solution investigated here, about 42% of In^{3+} should occur as $\text{In}_4(\text{OH})_6^{6+}$, 12% as $\text{In}_2(\text{OH})_2^{4+}$ and the rest as mononuclear complexes. This would correspond to an In-In frequency of about 0.69, which is close to the value found from the scattering data. The combined evidence from the emf measurements and the scattering data thus points to the formation of polynuclear hydrolysis complexes, $\text{In}_4(\text{OH})_6^{6+}$, having the structure shown in Fig. 5.

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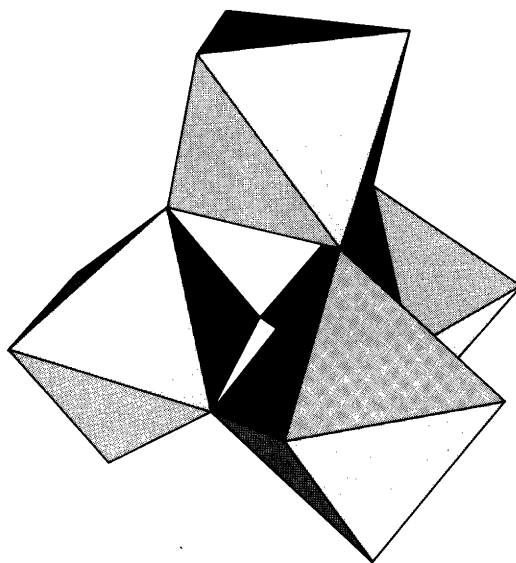


Fig. 5. Suggested model for the $\text{In}_4(\text{OH})_6^{6+}$ complex consisting of four corner sharing InO_6 octahedra with the In atoms arranged at the corners of a regular tetrahedron.

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