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An X-Ray Diffraction Study on the Structure of the Aqua Indium(III) Ion in the Perchlorate Solution

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Synopsis. The structure of the aqua indium(III) ion has been studied in a 3 mol dm^{-3} In(ClO$_4$)$_3$ solution at 25 °C by an X-ray diffraction method. The result showed that the indium(III) ion has six nearest water molecules and the In-OH$_2$ bond distance is 2.15±0.03 Å.

Only a few investigations have been carried out on the structure of indium(III) ion in aqueous solution. Fratiello *et al.*[2] reported from NMR measurements that the indium(III) ion is coordinated by six water molecules in aqueous acetone mixtures. Celeda and Tuck[3] found the $In(OH_2)_6^{3+}$ complex in an aqueous perchlorate solution by densitometry. However, no X-ray analysis has been carried out both for crystal hydrates and solutions, and no datum for the bond length between the indium(III) ion and the coordinated water molecules is available. In the present work, we aimed at determining the bond distance within the aqua indium(III) complex as well as the coordination number of the indium(III) ion in solution.

Experimental Procedure and Treatment of Data

Indium(III) perchlorate was prepared by dissolving indium oxide (99.99% purity) in perchloric acid and recrystallized twice from water. Crystals were dissolved in dilute perchloric acid in order to suppress hydrolysis of the indium(III) ions. The concentration of indium(III) ions in the sample solution was determined gravimetrically by using 8-quinolinol.[4] The concentrations of hydrogen and perchlorate ions were determined as described previously.[5] The atomic composition of the sample solution is listed in Table 1.

TABLE 1. ATOMIC COMPOSITIONS OF THE INDIUM(III) PERCHLORATE SOLUTION (in g-atom dm^{-3})

In	3.023
Cl	9.388
O	71.61
H	68.44

X-Ray scattering data were obtained at 25 °C on a θ-θ diffractometer (JEOL Co., Tokyo) equipped with a Philips Mo-X-ray tube (wavelength λ=0.7107 Å). The measured scattering angles (2θ) ranged from 2 to 140°. Details of measurements and treatments of data are described elsewhere.[5]

Results and Discussion

The radical distribution curve $D(r)$ calculated from the scattered intensities is shown in Fig. 1. Two distinct peaks are seen at around 1.4 and 2.3 Å. The first peak is readily identified to be due to the Cl–O bond within the ClO_4^- ion.[5] The second peak may be ascribed to the In^{3+}–OH_2 bond within the aqua indium(III) ion, because the peak appears at the position as is expected from the sum of the ionic radius of In^{3+} (0.81 Å[6]) and the size of a water molecule ({O–O in water}/2=1.4 Å[7]). This peak contains the contribution from the O–O contact within the tetrahedral ClO_4^- ion ($1.4\,\text{Å}\times\sqrt{8/3}=2.3\,\text{Å}$). The contribution of the Cl–O and O–O contacts within the perchlorate ion (curve b) was subtracted from the radial distribution curve. The bond distances r, temperature factors b, and frequency factors n of the atom pairs are quoted from Ref. 5. The rest is depicted as curve c in Fig. 1.

The bond distance between In^{3+} and the water molecules in the first hydration shell and the number of hydrated water molecules were determined from curve c by the trial-and-error method. The assumption of r=2.15 Å, b=0.004 Å^2, and n=6 led to a smooth background curve (curve e) without an indication of other atom pairs having bond distances less than 2.5 Å. The theoretical peak calculated by using these parameters is drawn as curve d in the same figure. The uncertainty in r is estimated approximately to be ±0.03 Å by the trial-and-error method. We could not find a clear indication for the octahedral structure of the $In(OH_2)_6^{3+}$

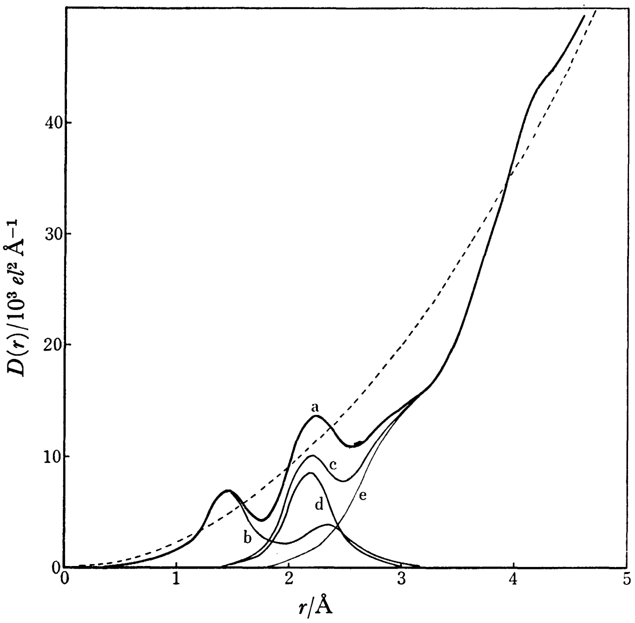

Fig. 1. a: $D(r)$ curve, b: theoretical peak shapes for the Cl-O and O-O contacts within ClO_4^-, c: residual curve ($D(r)$ – curve b), d: theoretical peak shape for the In–OH$_2$ bond within $In(OH_2)_6^{3+}$, e: background curve (curve c – curve d). The broken curve denotes $4\pi r^2\rho_0$.

complex, because the radial distribution curve did not give distinct peaks (although humps are observed) at about 3.04 Å ($=2.15$ Å$\times\sqrt{2}$) and about 4.30 Å ($=2.15$ Å$\times 2$) for the *cis*-O–O and *trans*-O–O contacts, respectively, within the $In(OH_2)_6^{3+}$ ion.

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