On the Structure of Highly Hydrolyzed Thorium Salt Solutions

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The structure of highly hydrolyzed thorium salt solutions has been investigated by large and small-angle X-ray scattering techniques. It is shown that the hydrolysis complexes formed at room temperature contain a small number of Th atoms probably situated at the corners of slightly distorted face-sharing tetrahedra. Hydrolysis at higher temperatures leads to the formation of small crystallites (~ 40 Å), which have the ThO_2 structure. The arrangement of Th atoms in the hydrolysis complexes formed at room temperature differs from that found in ThO_2 , although the Th atoms in both of the structures are joined by double oxygen bridges and form tetrahedral arrangements with Th–Th distances of 4.0 Å.

The hydrolytic reactions of the Th(IV) ion have been extensively investigated.^{1–6} The hydrolysis leads to the formation of polynuclear complexes probably containing from two up to about six thorium atoms. X-Ray diffraction investigations of crystalline basic thorium salts⁷ and of hydrolyzed thorium salt solutions⁸ have clarified the structure of the dinuclear complex which is first formed. The two thorium atoms which are situated 4.0 Å apart are held together by two bridging oxygen atoms. Although the previously reported solution X-ray scattering data⁹ did not result in unambiguous structure determinations of the complexes containing more than two Th atoms, they indicated that the structures are based on tetrahedral arrangements of the Th atoms within the complexes.

The hydrolysis of the solutions investigated previously was carried out by addition of HO^- to a thorium salt solution or by dissolving aqueous thorium oxide in the solutions. A maximum number of about 3 HO^- per Th^{4+} ion can be introduced in this way without

the formation of a permanent precipitate. In the present paper results are reported from investigations of thorium nitrate solutions hydrolyzed by the extraction of HNO_3 with a primary amine. By combining this with heat treatment of the solution the hydroxide number, n_{HO} can be increased beyond 3 HO^- per Th^{4+} . This is a procedure which is commonly used in CNEN hydrometallurgical processes for the transformation of solutions containing Th, U, or Pu into gel microspheres, which are then used for the preparation of ceramic oxides for nuclear fuels.⁹ Because of these technological applications the structures of the metal ion complexes in the strongly hydrolyzed solutions are of interest.

EXPERIMENTAL

Preparation and analysis of the solutions. An acidic thorium nitrate solution (solution A) was prepared by dissolving a weighed amount of $\text{Th}(\text{NO}_3)_4$ (Carlo Erba reagent grade) in 1 M nitric acid. A hydrolyzed solution was prepared from a 1 M thorium nitrate solution by extracting HNO_3 into an organic phase by means of a primary amine RNH_2 .¹⁰ The formation of the amine salt, RNH_2NO_3 , is strongly favoured, which allows the preparation of solutions of a known average hydroxyl number, n_{HO} , by using known amounts of amine in the starting solution. The organic phase was prepared by dissolving a long chain primary amine (Primene JMT by General Mills Inc.) in Solvesso 100 (aromatic diluent manufactured by Esso-Chemical).

A solution B with $n_{\text{HO}} \approx 2.9$ was prepared in this way. An aliquot of solution B was refluxed for about 1 h at 80–90°C and a new solution, B', with the same value of n_{HO} , was obtained. By further extraction of HNO_3 with Primene at 40–50°C from the solution

Fig. 1. Reduced intensity functions $i(s)$ in electron units e.u., multiplied by s , for solution B' measured with CuK α and MoK α radiation. The ThO $_2$ powder pattern is indicated by vertical lines. The height of each line is proportional to the relative intensity of the reflection (ASTM-card No. 4-0556).

B' a more hydrolyzed solution, having $n_{\text{HO}} \approx 3.6$ was prepared (solution C).

These three hydrolyzed solutions (B, B' and C) were filtered through an ultrafine filter (Jena-Glass G5) with a pore size of about 1 μm . In contrast to solution B, which was clear, the two solutions B' and C were opaque but seemed to be stable for an indefinite period of time. This is shown by the essentially identical scattering curves in Fig. 1 which were obtained for the same solution B' with a time interval of about one year.

The solutions were analyzed by titrating Th $^{4+}$ with standard EDTA using pyrocatechol

violet as indicator.¹¹ The hydrolyzed solutions were first depolymerized by boiling with concentrated nitric acid.

The nitrate content was determined by amperometric titration using iron(II) ammonium sulfate solution in a concentrated sulfuric acid medium.¹¹ The densities were determined both by a pycnometer and a digital precision densimeter (Anton Paar K.G.). The compositions of the four solutions are given in Table 1.

X-Ray scattering measurements. For the large-angle X-ray scattering measurements two different diffractometers were used. Both use the Bragg-Brentano semifocusing arrange-

Table 1. Compositions of the four solutions A, B, B' and C.

Solution	A (acid)	B ($n_{\text{HO}}=2.88$)		B' ($n_{\text{HO}}=2.88$)		C ($n_{\text{HO}}=3.57$)		
Concentration	mol/l	atoms/V	mol/l	atoms/V	mol/l	atoms/V	mol/l	atoms/V
Th	0.888	1	1.023	1	1.127	1	1.298	1
O	62.75	70.66	58.58	57.20	58.74	52.12	57.41	44.23
N	4.04	4.54	1.151	1.12	1.269	1.12	0.56	0.43
H	101.5	114.3	110.2	107.7	109.8	97.4	111.5	85.9
Stoichiometric volume $V/\text{\AA}^3$	1869.7		1622.9		1473.2		1279.1	
Absorption coeffi- cient μ/cm^{-1} (CuK α)	80.4		89.5		97.3		109.8	

ment with a focusing monochromator in the diffracted beam and with the X-ray tube and the scintillation counter moving in opposite directions around the stationary sample. The first one, which has been described in a previous paper,¹² was used with MoK α radiation ($\lambda=0.7107$ Å), mainly for measurements on the solution B'. The second one, manufactured by Rich. Seifert & Co., was used with CuK α radiation ($\lambda=1.5418$ Å) for measurements on all the solutions. The θ range covered (2θ = the scattering angle) was from 2 to 70 degrees corresponding to an s range ($s=(4\pi/\lambda)\sin\theta$) of about 0.3 to 7.7 (CuK α) or 0.6 to 16.6 Å⁻¹ (MoK α). Measurements were performed at discrete points with intervals of 0.2° for CuK α and 0.25° ($\theta < 25^\circ$) or 0.5° for MoK α . Three combinations of opening, receiving and scatter slits were used to cover the complete θ -range. The data were recalculated to a common slit width using the measurements in overlapping regions. The fraction of incoherent radiation reaching the counter was estimated from the spectrum of the X-ray tube and the resolving power of the monochromator.

For the *small-angle measurements*, a commercial Kratky camera with Ni-filtered CuK α radiation was used. The sample-detector distance, L , was 219.3 mm. A source slit of 0.08 mm and a detector slit of 0.15 mm were used for all measurements. The solutions were contained in thin-walled Lindemann-type glass capillaries with diameters of 0.5 mm. Of the four solutions A, B, B' and C, only B' and C gave appreciable intensities in the observable small-angle region. In order to estimate the influence of interparticle interference and of instrumental effects for these highly absorbing solutions (see Table 1), two more solutions were studied. These were prepared by diluting solution C with water to 1/2 and 1/10 of its original concentration and they will here be denoted C/2 and C/10, respectively.

DATA TREATMENT

Large-angle scattering. The observed intensity values, corrected for background radiation and for polarization in the solution and in the monochromator, were normalized to a stoichiometric unit of volume, V , containing one Th atom (Table 1). The normalization was done by comparing the corrected intensities in the high angle region, with the sum of the independent coherent scattering ($\sum n_i f_i^2$) and

the incoherent scattering. The normalization was also done by an integration method.^{13,14} The scattering factors given by Cromer and Waber¹⁵ for neutral Th, O, and N atoms were used. For H they were taken from the

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Fig. 2. Reduced intensity functions $i(s)$ in e.u., multiplied by s , for the four solutions A, B, B' and C, obtained by CuK α radiation.

International Tables.¹⁶ Anomalous dispersion corrections were applied to thorium.¹⁷ The incoherent intensity for Th, O and N was obtained from Cromer¹⁸ or Cromer and Mann¹⁹ and for H from Compton and Allison.²⁰ Corrections were made for the Breit-Dirac²¹⁻²³ effect. The normalized intensities, I'_{obs} , were corrected for the incoherent part of the radiation, and the reduced intensity function, $i(s)$, was calculated from the resulting values, I_{obs} , according to the expression: $i(s) = I_{\text{obs}} - \sum n_i f_i^2$.

Figs. 1 and 2 show the intensity data for the solutions investigated.

The radial distribution functions, $D(r)$, were calculated by a Fourier transformation of the diffraction data according to the expression:

$$D(r) = 4\pi r^2 \rho_0 + (2r/\pi) \int_0^s \sin(rs) i(s) M(s) ds$$

where ρ_0 is calculated as $[\sum n_i f_i(0)]^2/V$, and $M(s)$

is a modification function of the form $M(s) = [f_{\text{Th}}(0)/f_{\text{Th}}(s)]^2 \exp(-Ks^2)$, where $\exp(-Ks^2)$ is a damping factor. The K values of 0.02 and

Fig. 3. Radial distribution functions, $D(r)$ (continuous lines), and the corresponding $4\pi r^2 \rho_0$ functions (dashed lines), for A, B, B' and C with $\text{CuK}\alpha$ radiation.

0.01 were used for $\text{CuK}\alpha$ and $\text{MoK}\alpha$ radiations, respectively; the larger value for $\text{CuK}\alpha$ was chosen to reduce the greater truncation errors.

The experimental intensity values were extrapolated to $s=0$. The $D(r)$ curves were corrected for spurious peaks below 1 Å.²⁴ Fig. 3 shows the distribution functions obtained for the four solutions A, B, B' and C.

All calculations were carried out by means of computer programs which have been described in a previous paper.²⁵

Line-broadening measurements. The pronounced peaks in the scattering curves for the solutions B' and C indicate the presence of small crystalline particles of ThO_2 (see Fig. 1). The average size of these was estimated by comparing the widths of two well-separated peaks ($\{111\}$ and $\{220\}$) with those obtained for a standard specimen consisting of a crystalline powder UO_2 , as shown in Fig. 4a. The estimate was made using the formula for spherical particles²⁶

$$D = 0.92\lambda / [\Delta(2\theta) \cos \theta]$$

D is the average diameter of the crystallites, λ is the wavelength and 2θ is the scattering angle. The half-maximum line width, $\Delta(2\theta)$ in radians, was corrected for instrumental broadening by means of the expression²⁷

$$\Delta(2\theta) = (B - b)^{1/2} (B^2 - b^2)^{1/4}$$

Fig. 4. (a) The $\{111\}$ and $\{220\}$ peaks of solution C and corresponding peaks from a crystalline powder of a UO_2 standard specimen. (b) Correction for the diffuse scattering for solution C/2. The background scattering from a non-polymerized solution of the same Th concentration (continuous line with crosses) is subtracted from the experimental peak (continuous line with dots). The B value is obtained from the resulting corrected peak (continuous line).

Table 2. Average diameters, D , of the crystallites estimated by line broadening measurements for solutions C, C/2, C/10 and B' for the two wavelengths used. All B and b values correspond to $\Delta(2\theta)$ -values measured in degrees.

Wave-length	$2\theta/\text{deg.}$	$\{hkl\}$	Sol. C/10 B	$D/\text{\AA}$	Sol. C/2 B	$D/\text{\AA}$	Sol. C B	$D/\text{\AA}$	Sol. B' B	$D/\text{\AA}$
MoK α	12.4	{111}	0.90	43.8	0.96	41.0	1.04	37.6	1.20	32.5
($b=0.08$)	20.3	{220}	1.04	38.2	1.00	39.8	0.96	41.4	1.20	32.8
CuK α	27.0	{111}					1.90	44.7	2.20	38.5
($b=0.06$)	45.0	{220}					2.00	44.7	2.40	37.1

Here B is the measured line width for the particles in the solution and b is the corresponding value for the standard substance. Correction for the α -doublet separation on the observed B values was found to have a negligible effect.

For the diluted solutions C/2 and C/10 a correction for the diffuse scattering from the solution was found to be necessary in order to obtain symmetrical peak shapes. The scattering from a non-polymerized acidic Th solution of the same Th concentration, was subtracted from the experimental intensity curves as shown in Fig. 4b for solution C/2. The results obtained for the four solutions are given in Table 2.

Small-angle scattering. The purpose of the small-angle X-ray scattering (SAXS) investigation was to compare the actual size of the particles in solution with the average size of the crystallites found from the line broadening and large-angle scattering measurements. The following approximate analysis of the data was then considered to be sufficient.

The measured intensities were corrected for parasitic scattering by subtracting intensity values, obtained by the same measuring procedure, for a non-polymerized solution having the same Th concentration. Slit-height corrections were not applied. As shown by Neilson²⁸ this should not affect to any great extent the results obtained. The scattering curves are shown in Fig. 5a.

For the analysis of the SAXS data the particles were assumed to be spherical. The Guinier approximation for spherical particles of uniform size and scattering density²⁹ can be written as $I(s) = I(0) \exp [-(sR)^2/5]$, where R is the actual radius of the particles. The intensity values $I(s)$, are in arbitrary units and $s = (4\pi/\lambda) \sin \theta \approx (2\pi x)/(\lambda L)$, where x is

the vertical distance from the primary beam as measured on the instrument scale. The Guinier plots, which are shown in Fig. 5b, indicate a non-uniform size distribution for the particles in the solutions. An approximate analysis was made by selecting two different regions of the curves from which a "largest" value (R) and a "smallest" value (r) for the

Fig. 5. (a) Experimental small-angle intensities (in arbitrary units a.u.) as a function of the vertical distance x on the instrument scale for solutions C, C/2, C/10 and B'. (b) Guinier plots ($\log I$ versus x^2) for the same solutions. The lines represent the best fit obtained in the two selected regions. (The intensity values for the solution B' have been plotted on a different arbitrary scale than that used for the solutions C).

Table 3. Actual particle radii obtained by the Guinier approximation (R and r) and by the Hosemann treatment (r_H). Errors have been estimated by a least squares method (R and r) or by a graphical evaluation (r_H).

Solution	$R/\text{\AA}$	$r/\text{\AA}$	$r_H/\text{\AA}$
C/10	82.9(8)	22.2(6)	62(3)
C/2	83.0(2)	24.0(1)	66(3)
C	81.5(7)	23.8(6)	58(3)
B'	83.7(8)	19.0(6)	64(3)

particle radii were calculated. These values are given in Table 3.

An attempt to determine the particle size distribution by the Hosemann method²² was also made. In this method the distribution of the radii of gyration of the particles is represented by a Maxwellian distribution of the form

$$F(R_0) = 2R_0^n \exp(-R_0^2/r_0^2) / [r_0^{(n+1)} \Gamma(n/2 + 1/2)]$$

where Γ is the gamma function. The two parameters n and r_0 defining the Maxwellian distribution were calculated from the expressions $(s_0'/2s_m' - 1) = \frac{1}{2}(n+1)^{-1/2}$ and $r_0 = \frac{3}{\pi s'}$, $(n+2)^{-1/2}$ after a graphical evaluation (Fig. 6a) of s_0' and s_m' ($s' = (2/\lambda) \sin \theta$).

The arithmetic mean of the actual radii assuming spherulic particles of uniform scatter-

ing density calculated from $r_H = (5/3)^{1/2} r_0 \times \Gamma(n/2 + 1)/\Gamma(n/2 + 1/2)$ is given in Table 3. All of the four values obtained are within 6%, which does not exceed the precision to be expected from this determination. A Maxwellian distribution curve valid for all four solutions, could then be calculated from the average s_0' and s_m' values, and is given in Fig. 6 b.

INTERPRETATION OF THE DATA

Large-angle scattering. The reduced intensities and the radial distribution curves (RDF) for the four solutions investigated are shown in Figs. 1–3.

The acidic solution, A, and the solution hydrolyzed at room temperature, B, give scattering curves typical of true solutions. For solution B', which has nearly the same stoichiometric composition as B (Table 1), from which it was obtained by heat treatment, the scattering curve is radically different. Sharp peaks similar to those of a powder pattern occur at the positions expected from the cubic ThO_2 structure (Fig. 1). This change is further accentuated in solution C.

The scattering data were analyzed by comparing peaks in the RDF's with peak shapes calculated for assumed interatomic interactions.²⁵ The results obtained for solutions A and B are given in Table 4.

Fig. 6. (a) Values of $(s')^2 I$ versus the $s' = (2/\lambda) \sin \theta$ for solutions C/2, C/10 and B'. The value s_m' corresponds to the maximum of the curve. The s_0' value is given by the intersection with the s' -axis of the tangent to the curve at the inflection point. (b) The Maxwellian distribution curve, $F(R_0)$, versus the radius of gyration R_0 . In the $F(R_0)$ function the gyration radii from the Guinier plots, R_G , and r_G are indicated for comparison.

Table 4. Results of the comparison of calculated peak shapes with the experimental distribution curves for solutions A and B; r_{nm} is the interatomic distance, n_d is the number of distances per Th atom, and b_{nm} is one-half of the mean square variation of the distance.

Interaction	Sol. A (acid)			Sol. B ($n_{\text{HO}}=2.88$)		
	$r_{nm}/\text{\AA}$	n_d	$b_{nm}/\text{\AA}^2$	$r_{nm}/\text{\AA}$	n_d	$b_{nm}/\text{\AA}^2$
1st Th—O	2.55	5.5	0.01	2.55	7.0	0.01
Th—NO ₃ { Th—N Th—O	3.10	3.5	0.01	3.10	1.1 _s	0.01
	2.70	7.0	0.01	2.70	2.3	0.01
Th—Th	—	—	—	3.96	4.3	0.008
Coordination number of Th	5.5 + 7.0 = 12.5			7.0 + 2.3 = 9.3		

For the non-hydrolyzed solution A the analysis leads to the same conclusions as those reported previously.⁸ The thorium ion is coordinated to about twelve water and nitrate oxygens, with the nitrate group bonded as a bidentate ligand. In the hydrolyzed solution B ($n_{\text{HO}} \approx 2.9$) the coordination number has decreased to a value of about nine, which reflects the decreased coordination of nitrate groups. As shown previously⁸ the large peak at 4.0 Å in the RDF can be related to the shortest Th—Th distance within the polynuclear hydrolysis complexes. Each Th atom has an average of about 4 Th neighbours at this distance (Table 4). Two more peaks in the distribution curves — at about 6.5 and 7.5 Å — probably contain major contributions from Th—Th and Th—O interactions within the polynuclear complexes. However, these are much less pronounced than the peak at 4.0 Å.

In the crystal structures of basic thorium salts⁷ and in thorium dioxide, which has the cubic fluorite structure³⁰ the shortest Th—Th distance is close to 4.0 Å, as is also found in the solutions, and occurs between Th atoms joined by two bridging oxygens. In the ThO₂ structure (Fig. 7a) each Th atom is surrounded by 12 other Th atoms at this distance. Eight oxygen atoms arranged at the corners of a cube are coordinated to each thorium. Since heating of solution B leads to the formation of particles, which have the ThO₂ structure, as shown by the scattering curve for solution B', it would seem reasonable to expect similarities also between the structures of the hydrolysis complexes formed at room temperature in solution B and the structure of ThO₂. However,

the long distances at 6.5 and 7.5 Å, indicated in the RDF for the solution B, do not seem to be consistent with distances found in the ThO₂ structure.

The large average number (≥ 4) of Th atoms joined at 4.0 Å to each Th atom in the hydrolysis complexes in solution B (Table 4) and the absence in its RDF of peaks between 4.0 and 6.5 Å, which can reasonably be related to Th—Th interactions, leads to the conclusion that the basic unit in the structure contains a tetrahedron of Th atoms.⁸ Since the number of neighbours in a tetrahedron is only three, further Th atoms must be attached to this unit.

In the ThO₂ structure, tetrahedra of Th atoms can be distinguished and the structure may be described as being built up from tetrahedra sharing Th—Th edges or Th corners (Fig. 7a). In such fragments of the structure the longer Th—Th distances occur at 5.60, 6.86, and 7.95 Å, which are inconsistent with those found for the hydrolysis complexes even if we allow for Th—O interactions and for possible distortions from the regular arrangement in the ThO₂ structure. It seems, therefore, that the bonding of further Th atoms to the basic tetrahedral unit in the hydrolysis complexes differs from that in the ThO₂ structure.

Face-sharing between the tetrahedra would be a conceivable arrangement, but does not occur in the ThO₂ structure. It has, however, been found in hydrolysis complexes of lead(II)^{31,32} and tin(IV).³³ In Pb₂O(OH)₂ the lead atoms are linked by double oxygen bridges and the complex is built up from three slightly distorted tetrahedra of lead atoms sharing faces. If we use the same model for the thorium

Fig. 7. (a) Fragments of the ThO₂ structure, showing Th tetrahedra sharing corners or edges. (b) The Th₄O₇ complex (analogous to the Pb₄O(OH)₆ complex) consisting of three face-sharing tetrahedra of Th atoms.

complexes (Fig. 7b), slightly enlarged to give an average of the short Th–Th distances of 3.96 Å, and calculate the corresponding peak shapes for this complex, we find their positions to be consistent with the peaks in the observed RDF for solution B (Fig. 8). It is possible, therefore, that the hydrolysis complexes formed at room temperature are built up from tetrahedra sharing faces.

Each tetrahedron in the ThO₂ structure contains an oxygen atom at its center. In a structure built up from face-sharing tetrahedra two neighbouring tetrahedra cannot both contain an oxygen. If the double oxygen bridges between the Th atoms are to be re-

tained, as indicated by the short Th–Th distance of 4.0 Å, it can easily be shown that an addition of further face-sharing tetrahedra can occur only in one direction, leading to linear complexes. In an infinite complex of this type the average number of Th neighbours around each Th atom is 6. In a complex containing only three tetrahedra this number is 4 (Fig. 7b). These values, when compared with the value of about 4.3 found from the RDF for solution B, indicate a very limited number of face-sharing tetrahedra in the hydrolysis complexes. This is supported by the absence of pronounced peaks at larger r values in the RDF.

Fig. 8. Comparison between the RDF for solution B (full-drawn line) and the peak shapes (dotted line) calculated for the complex Th₄O₇ in Fig. 7b.

For solutions B' and C, obtained from B by heat treatment, the scattering data show the presence of large fragments of the ThO_2 structure in the solutions. An analysis of the data, analogous to that carried out for solutions A and B, shows the average number of nearest Th neighbours around each Th atom to be about 7.5 for solution B' and about 9.6 for solution C, compared to the value of 12 for the "infinite" ThO_2 structure. Without knowledge of the possible presence of non-crystalline material in the solutions these values cannot be directly used to estimate the size of the particles. However, if the crystallites are sufficiently small, the longer of the inter-atomic distances occurring in the ThO_2 structure should fall outside a crystallite relatively more frequently than the shorter distances and this can be used to make a rough estimate of the size of the particles. For a distance, d , in the ThO_2 structure the variation of its frequency, n_d , with the size of the crystallite, measured as the number of unit cells along an edge of a cubically shaped particle, is shown in Fig. 9. The ratios $n_d/n(\infty)$, where $n(\infty)$ represents the frequency of the distance in the infinite structure and n_d is estimated from the RDF for solution C, are also shown in Fig. 9. The ratios are seen to decrease approximately as expected for a crystallite size corresponding to 4.5 unit cell edges. As there are no significant differences between the relative sizes of the peaks for B' and C the same result is obtained for solution B'.

The crystallite size corresponding to 4.5 unit cells is marked by a vertical line in Fig. 9. The corresponding n_d values for the various distances are in agreement with the values determined from the RDF for solution C. It would seem, therefore, that in solution C, but not in solution B', all thorium is present as ThO_2 . In Fig. 10 a comparison is given between the RDF for solution C and peak shapes calculated for all Th-Th and Th-O interactions using different assumptions for the size of the crystallites.

The large-angle scattering data thus indicate that the crystallites in solutions B' and C have an average size of around 28 Å, which is equivalent to a diameter of about 35 Å for a spherical particle. Although, in this derivation, the very probable occurrence of a distribu-

Fig. 9. Variation of the number of neighbours per Th atom, n_d , for distances, d , occurring in the ThO_2 -structure as a function of the size of a cube-shaped crystallite measured as the number of unit cells along the crystallite edge. Full and dashed-dotted lines, identified by different symbols, give the n_d values for the first Th-Th and Th-O distances respectively; the limiting values, $n(\infty)$, correspond to the "infinite" ThO_2 structure. The vertical dashed line corresponds to an edge length of 4.5 unit cells. The inset shows the ratio $n_d/n(\infty)$ for the Th-Th distances. The line gives calculated values for a size corresponding to 4.5 unit cells, the dots give the experimental values with the estimated errors for solution C.

tion of particle sizes and shapes has not been taken into account, calculations based on reasonable assumptions about such distributions show that this will not be critical and the conclusions will still be approximately valid for the average size of the crystallites.

Line-broadening measurements. The results are given in Table 2. The diameters found for the crystallites all fall in the range 32 to 45 Å, and thus are of the same order of magnitude as those derived from the large-angle scattering data.

Small-angle measurements. Although solutions B' and C are stable for a long period of

Fig. 10. $D(r)$ -curve (full-drawn line) and calculated peak shapes (dots) for solution C ($\lambda = \text{CuK}\alpha$). The peak shapes are calculated assuming all the Th atoms to be present as cube-shaped crystallites of ThO_2 with an edge length corresponding to 4.5 unit cells; the dashed line, a, represents the difference curve $D(r) - \text{peak shapes}$. Two other difference curves are shown: b, peak shapes calculated assuming 93 % of all Th atoms to occur as cube-shaped crystals of ThO_2 with an edge length of 6 unit cells and c, assuming 80 % of all Th atoms to occur as "infinite" crystals of ThO_2 .

time they are strongly opaque and it seems likely that the actual size of the particles in solution is larger than that determined for the crystallites. This is confirmed by the small-angle scattering measurements, which indicate that a range of particle sizes, generally larger than that determined for the crystallites, occurs in the solutions (see Table 3). Thus, each such particle must contain a number of crystallites joined together without any orientational relationship. The parameters s_m' and s_0' defining the distribution of particle sizes, are almost the same for all the solutions investigated (Fig. 8a) which implies that neither further hydrolysis nor dilution affect the particle sizes. The results for the diluted solutions also show that concentration-dependent scattering effects such as interparticle scattering are negligible.

CONCLUSIONS

The X-ray scattering data show that the method used in the present work for the hydrolysis of a thorium nitrate solution, *i.e.* the extraction of HNO_3 from the thorium solution by means of a primary amine, leads to the for-

mation of the same hydrolysis complexes as those obtained by peptization, *i.e.* by dissolving aqueous thorium oxide in the solution. When the hydrolysis is carried out at room temperature the structures of the hydrolysis complexes formed are based on tetrahedral arrangements of Th atoms in which a Th atom shares two oxygens with each of its neighbors. Similar tetrahedra of thorium atoms with the same Th-Th distance can be distinguished in the ThO_2 structure but the linking of these tetrahedra in the hydrolysis complexes seems to be different from that found in the ThO_2 structure. In ThO_2 the tetrahedra are joined by common corners or edges. In the hydrolysis complexes the scattering data can be interpreted as indicating face-sharing between the tetrahedra. The structure of the hydrolysis complexes formed at room temperature cannot, therefore, be described merely as fragments of the ThO_2 structure, although the basic units in the structures are the same.

The heat treatment leads to the formation of crystallites which have the ThO_2 structure. The combination of large-angle and small-angle measurements has made it possible to distinguish between the actual size of the particles in the solution and the size of the crystallites. It is found that the crystallites have an average size of about 30–40 Å and can be joined together, without any orientational relationship, into larger particles.

The structural differences between the hydrolysis complexes formed at room temperature and thorium dioxide may explain the observation that precipitates from solutions hydrolyzed at increased temperature can be sintered into the ThO_2 microspheres used for the preparation of nuclear fuels at considerably lower temperatures ($\sim 1100^\circ\text{C}$) than those required for precipitates obtained at room temperature ($\sim 1600^\circ\text{C}$).⁹

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