drolysis of hydroxylamine-N-sulfonate to hydroxylamine and sulfate, attributed a deviation from the acid stoichiometry at pH greater than 2 to the reaction reported here. They did not, however, identify the products. At pH 3.5 and 75°, for example, they reported only a 6% yield of hydroxylamine; and, if the remaining material were to decompose to hyponitrite, the corresponding rate of the side reaction would have to be 9.5×10^{-7} sec^{-1}. The rate law we have reported here would only provide a reaction some eight powers of ten slower than that. Consequently, the mechanism proposed here cannot account for their side reaction.

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CONTRIBUTION FROM THE CHEMISTRY DIVISION,
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Equilibrium Ultracentrifugation of Hydrolyzed Thorium(IV) Solutions[1]

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The hydrolytic aggregation of Th(IV) in 1 *M* total perchlorate media has been investigated by equilibrium ultracentrifugation (interference optics) from hydroxyl number $\mathbf{n}$ (hydroxyls bound per thorium) of 0–3. Concentrations of Th(IV) were 0.025–0.1 *M* over most of the range. The solutions appeared essentially to reach chemical equilibrium up through $\mathbf{n} = 2.5$. All hydrolyzed solutions contained polymeric species, and the weight-average degree of polymerization, N_w, increased with degree of hydrolysis. Comparison of centrifugations at the same $\mathbf{n}$ but different thorium(IV) concentrations indicated that the charge per monomer unit z' on the polymeric species was not the maximum, $4 - \mathbf{n}$, *i.e.*, that there was some complexing of perchlorate ions by the polymers. At $\mathbf{n} = 2$, for example, N_w was about 3.6 and z' appeared to be about 1.3, instead of the maximum 2. For $\mathbf{n} = 3$, chemical equilibrium was not attained, and molecular weights were much higher and increased with time. Hydrolyzed thorium(IV) chloride solutions did not reach chemical equilibrium and, if aged for a few weeks, contained much more highly aggregated species than perchlorate solutions of the same degree of hydrolysis. Volumes and refractive index increments of hydrolyzed thorium(IV) perchlorate solutes are presented. Approximate molecular weight determinations of some highly aggregated Th(IV) dispersions are described.

For over a decade,[3,4] people in the field have realized that polymeric species are formed when Th(IV) hydrolyzes. Probably the most cited evidence has been the dependence of the acidity of solutions having a given hydroxyl number on thorium concentration. (The hydroxyl number $\mathbf{n}$ is defined as the average number of hydroxides bound per thorium and is determined by the stoichiometric moles of base per mole of Th(IV) in the solution, with a correction for the free acid.) Number-[4] and weight-average[5] molecular weight determinations have also indicated aggregation, however. (Some results of ultracentrifugation studies preliminary to the present have been quoted previously.[6,7])

There has been widespread disagreement concerning the species formed. Since the literature was reviewed not long ago,[5] we shall stress only work from two laboratories which have published on the subject recently. The Stockholm group, on the basis of emf measurements,[8] postulated a continuous series of "core-link" species, $\mathrm{Th[Th(OH)_3]_{\mathit{l}}^{(4+\mathit{l})+}}$; in a recent publication,[9] they appear to have abandoned this interpretation and now postulate a series $\mathrm{Th}_N\mathrm{(OH)}_{nN}{}^{(4N-nN)+}$ having (N,nN) of (1,2), (2,1), (2,2), (2,3), (6,14), and (6,15). Their earlier measurements were in perchlorate media, and their more recent study in chloride. Baes, Meyer, and Roberts[10] report emf measurements of thorium(IV) perchlorate hydrolysis at 0 and 95° and an interpretation of their data, as well as a reinterpretation of 25° measurements of Kraus and Holmberg.[7] Several schemes were tried; the best two both involved (1,1), (1,2), (2,2), and (6,15) and one other species, (4,8) being slightly preferred over (3,6).

Kraus and Holmberg[7] were able to fit acidity data for the early stages of hydrolysis ($\mathbf{n} < 0.2$) by postulating (1,2) and (2,2) species; these species appear in the other schemes mentioned, along with some others, *e.g.*, (1,1) and (2,1), which should have their greatest importance at the same Th(IV) concentrations and acidities. We report here results of an ultracentrifugation study of Th(IV) hydrolysis in perchlorate media for $\mathbf{n} = 1$ and above, a range overlapped by the Kraus and Holmberg measurements, though outside the range of their interpretation. The degrees of polymerization obtained are similar to those reported on the basis

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[2] Oak Ridge Institute of Nuclear Studies Summer Participant, 1965.

[3] R. Schaal and J. Faucherre, *Bull. Soc. Chim. France*, **14**, 927 (1947).

[4] P. Souchay, *ibid.*, **15**, 143 (1948).

[5] F. C. Hentz, Jr., and S. Y. Tyree, Jr., *Inorg. Chem.*, **4**, 873 (1965).

[6] K. A. Kraus, *Proc. Intern. Conf. Peaceful Uses At. Energy, Geneva, 1955*, 7, 245 (1956).

[7] K. A. Kraus and R. W. Holmberg, *J. Phys. Chem.*, **58**, 325 (1954).

[8] S. Hietanen, *Acta Chem. Scand.*, **8**, 1626 (1954).

[9] S. Hietanen and L. G. Sillén, *ibid.*, **18**, 1018 (1964). See also L. G. Sillén, *ibid.*, **16**, 1051 (1962).

[10] C. F. Baes, N. J. Meyer, and C. E. Roberts, *Inorg. Chem.*, **4**, 518 (1965).

of light-scattering measurements[5] and thus confirm the incompleteness or incorrectness of many proposals in the literature. They do not, however, allow a clear decision between some other postulated schemes. We also present some ultracentrifugation observations of Th(IV) hydrolysis in chloride media and of non-equilibrium species of high hydroxyl number.

Experimental Section

1. **Ultracentrifugation.**—Centrifugations were carried out with a Spinco Model E ultracentrifuge. The procedures were, for the most part, similar to those previously reported.[11,12] Sedimentation was followed by interference optics (546 mμ). Solutions were usually contained in 12-mm double-sector cells with pure epoxy centerpieces, the centrifugations being carried out in a five-cell rotor; a few solutions were centrifuged in 12- or 30-mm interference cells with a two-place rotor. The temperature of the experiments was 25°.

In analysis of results, unless otherwise indicated, allowance was made for effect of charge (degree of ionization) of the solute of interest.[11] Briefly, the equation used for computation of degree of polymerization, N_w, is

$$N_w = \frac{d \ln c_2'/d(x^2)}{A_2' - (z'/2)\, d \ln[(1 + \eta)/(1 - \eta)]/d(x^2)} \qquad (1)$$

where subscript 2 indicates the Th(IV) component; 3, the supporting electrolyte; primes, quantities expressed in terms of monomer units; c, concentration in moles per liter; x, radius; z', charge per monomer unit of the thorium polymer (which, because of perchlorate complexing, may not be the maximum possible); $\eta = z'c_2'/2c_3$; $A_2' = M_2'(1 - \bar{v}_2\rho)\omega^2/2RT$; M, molecular weight; $\bar{v}$, partial specific volume; ρ, solution density; ω, angular velocity; R, gas constant; and T, absolute temperature. The definition of the (primed) polymeric component 2, $Th(OH)_n(ClO_4)_{4-n}$–$(z'/2)NaClO_4$, is that proposed by Scatchard[13] and reflects the charge.

The reported values of N_w were evaluated for the radius at which the intial concentration of Th(IV) occurs at centrifugation equilibrium. The procedure for obtaining c_2' from interference patterns is complicated by the effect of charge and the consequent use of the Scatchard definition of components; it is described in detail elsewhere.[11] Computations were carried out with a version of the basic Fortran program described previously.[14,15]

Some centrifugations were carried out with a schlieren optical system, with which sedimentation is followed by the displacement, Z, of a wire shadow proportional at a given point to the gradient of refractive index with radius. In most of these, our primary interest was in a comparison of degrees of polymerization under different conditions, and no correction for charge was made. The equation[16] used for computation was

$$N_{Z,z'=0} = \frac{d \ln (Z^*/x)/d(x)^2}{M_2'(1 - \bar{v}_2\rho)\omega^2/2RT} \qquad (2)$$

N_Z being the Z-average degree of polymerization

$$N_Z = \frac{\sum_i M_i^2 w_i}{M_2' \sum_i M_i w_i} \qquad (3)$$

which is obtained most directly with schlieren optics and which emphasizes heavier species more than a weight average. In these equations, Z^* represents the difference in schlieren displacement between the solution in question and a background of the same composition except for absence of the solute of interest, here Th(IV); M_i is the molecular weight of species i of the solute of interest and w_i its concentration in grams in a given volume of solution, and M_2' is here the monomeric molecular weight for z' assumed 0.

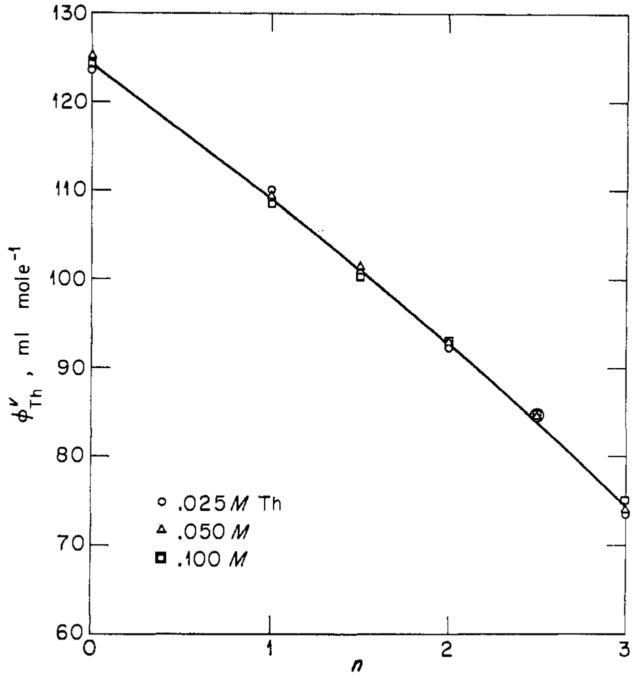

Figure 1.—Apparent molal volume of thorium solute as a function of hydroxyl number. Total perchlorate, 1 M. Thorium component, $Th(OH)_n(ClO_4)_{4-n}$.

2. **Materials.**—A thorium perchlorate stock was prepared from thorium nitrate by fuming in perchloric acid until a diphenylamine[17] test for nitrate was negative. After dilution, the stock was analyzed gravimetrically for Th(IV) and for perchlorate by removal of thorium with a cation-exchange column in the hydrogen form, followed by titration with base of the effluent perchloric acid. One gram of the stock solution contained about 0.4 mmole of $Th(ClO_4)_4$ and 0.2 mmole of excess $HClO_4$.

A concentrated $NaClO_4$ stock (about 5 mmoles/g of solution) was prepared by addition of NaOH pellets to $HClO_4$ solution, bubbling thorugh N_2 while still slightly acid to remove CO_2, and adjusting the pH to about 4.5. The stock was analyzed by evaporation and drying to constant weight at 110°.

Solutions (*ca.* 1 M in total perchlorate) having the desired Th(IV) concentration and hydroxyl number were prepared by weight from these and from analyzed NaOH and $NaClO_4$ stocks. The acidities of solutions containing hydrolyzed thorium were obtained from the emf of a glass electrode *vs.* a silver–silver chloride electrode, separated from the solution by a junction; the emf was measured with a vibrating-reed electrometer.[18] Approximate values of the hydroxyl number **n** given by stoichiometry were then corrected for free acidity.

3. **Densities and Refractive Indices.**—Densities were measured with a ~24-ml pycnometer and refractive indices (546 mμ) with a Brice–Phoenix differential refractometer. Data obtained by others were used for the volumes[19] and refractive index[20] increments of supporting electrolytes.

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[11] J. S. Johnson, G. Scatchard, and K. A. Kraus, *J. Phys. Chem.*, **63**, 787 (1959).

[12] R. M. Rush, J. S. Johnson, and K. A. Kraus, *Inorg. Chem.*, **1**, 378 (1962).

[13] G. Scatchard, *J. Am. Chem. Soc.*, **68**, 2315 (1946).

[14] O. E. Esval, Thesis, University of North Carolina, 1962.

[15] O. E. Esval and J. S. Johnson, Jr., *J. Phys. Chem.*, **69**, 959 (1965).

[16] (a) W. D. Lansing and E. O. Kraemer, *J. Am. Chem. Soc.*, **57**, 1369 (1935); (b) J. S. Johnson and K. A. Kraus, *ibid.*, **78**, 3937 (1956).

[17] F. Feigl, "Spot Tests," Vol. I, Elsevier Publishing Co., New York, N. Y., 1954, p 299.

[18] K. A. Kraus, R. W. Holmberg, and C. J. Borowski, *Anal. Chem.*, **22**, 341 (1950).

[19] H. E. Wirth and F. N. Collier, *J. Am. Chem. Soc.*, **72**, 5292 (1950); T. F. Young and M. B. Smith, *J. Phys. Chem.*, **58**, 716 (1954).

[20] Refractive indices: $NaClO_4$ solutions, H. Kohner, *Z. Physik. Chem.*, **B1**, 427 (1928); $HClO_4$, R. M. Rush, unpublished results.

Results and Discussion

1. Volumes and Refractive Index Increments.—The volumes of solutes are necessary for the so-called buoyancy correction in the interpretation of ultracentrifugation results, and refractive index increments ($n_{\mathrm{Th\ solution}} - n_{\mathrm{bg}})/c$ (where n is refractive index, bg indicates a background solution of the same composition except that Th(IV) is absent, and c is thorium concentration in moles/liter) are necessary to relate interference patterns to concentration distributions.

The apparent molal volumes ϕ^{V} of hydrolyzed thorium perchlorate (component taken as $\mathrm{Th(OH)_n(ClO_4)_{4-n}}$) are given in Figure 1. These values were computed from the stoichiometries and densities of the solutions prepared for centrifugation; volumes for 0.01 M Th(IV) solutions were omitted because of low precision. The volume of hydrolyzed thorium perchlorate decreases with increasing degree of hydrolysis, approximately linearly. It is of interest, though probably more fortuitous than significant, that, if the decrease is taken to be linear and extrapolated to $\mathbf{n} = 4$, a value of about 59 ml is obtained for $\mathrm{Th(OH)_4}$; from the density of $\mathrm{ThO_2}$ (about 10) plus 36 ml for 2 moles of water, one estimates 62 ml/mole of $\mathrm{Th(OH)_4}$.

For present purposes, there appears to be no significant dependence of ϕ^{V} on Th(IV) concentration, and the apparent molal volumes obtained from the curve through the points in Figure 1 were therefore used for the partial molal volumes in the interpretation of ultracentrifugation results. Uncertainties in computed degrees of polymerization N_{w} from uncertainties in volume are small; at $\mathbf{n} = 2$, for example, a volume error of about 3.5 ml corresponds to an error of 1% in N_{w}.

In analysis of results for chloride solutions, we have used for the partial molal volumes of hydrolyzed thorium chloride those of the perchlorate solutions of the same hydroxyl number plus $(4 - \mathbf{n})(\bar{V}_{\mathrm{NaCl}} - \bar{V}_{\mathrm{NaClO_4}})$, the partial molal volumes of NaCl and $\mathrm{NaClO_4}$ being taken for 1 M solutions.[19] A few measurements of volumes of hydrolyzed thorium(IV) chloride solutions indicated that errors introduced by this procedure are unimportant.

Refractive index increments of hydrolyzed thorium(IV) perchlorate measured on the solutions centrifuged are summarized in Figure 2; the 0.01 M Th(IV) solutions are omitted here also, because of the low precision obtained at this concentration. There appears to be no significant dependence of refractive index on Th(IV) concentration for a given hydroxyl number, and values used in computation of results were taken from the line in Figure 2 drawn through the points. Very approximately, the percentage uncertainty in computed N_{w} stemming from refractive index increment is the same as the percentage uncertainty in the increment; the small scatter of the values in Figure 2 indicates the uncertainty introduced from this source is small.

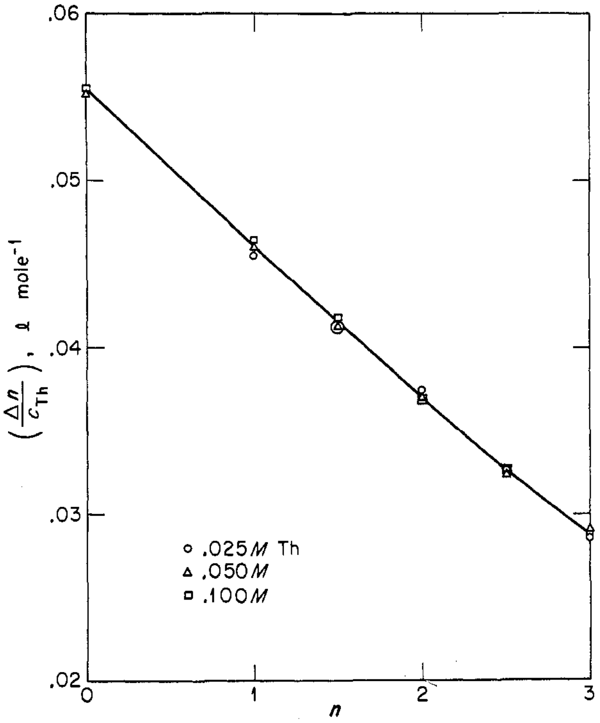

Figure 2.—Refractive index increment of thorium (546 mμ) as a function of hydroxyl number. Total perchlorate, 1 M. Thorium component, $\mathrm{Th(OH)_n(ClO_4)_{4-n}}$.

2. Ultracentrifugation of Thorium(IV) Perchlorate Solutions.—We have centrifuged solutions of hydroxyl numbers 0, 1, 1.5, 2, 2.5, and 3.0. Thorium concentrations were about 0.025, 0.05, and 0.1 M and, in a few cases, 0.01 M. The unhydrolyzed solutions ($\mathbf{n} = 0$) contained 0.1 M $\mathrm{HClO_4}$, and sodium perchlorate supporting electrolyte was present in all solutions in sufficient quantity to make the total perchlorate concentration 1 M. Results are summarized in Figures 3–7 as curves of $1/N_{\mathrm{w}}$ for individual centrifugations computed as a function of assumed charge per monomer unit, z'. (Since chemical equilibrium was obviously not attained at $\mathbf{n} = 3$, results for this hydroxyl number are not reported graphically.) The best value of N_{w} for a given hydroxyl number (other than $\mathbf{n} = 0$, where $N_{\mathrm{w}} = 1$) is presumably given by the intersection or closest approach of the curves for individual centrifugations. Before dealing with these results, we wish to discuss briefly some approximations in the analysis.

a. Influence of Polydispersity.—With solutions of hydrolyzed metal cations, one usually deals with a mixture of species of varying degrees of hydrolysis and aggregation; occasionally a species predominant over a range of conditions is encountered, for example, as with Bi(III)[11] and probably with Zr(IV) and Hf(IV).[16b,21] With the present system, most hydrolysis schemes which have been advanced involve mixtures of species. With such polydisperse systems, the present methods of analysis of centrifugation results involve approximations beyond the usual assumption of constancy of species activity coefficients. The various species will likely have different refractive index increments, volumes, charges per monomer unit, and molecular weights of the monomer units.

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[21] J. S. Johnson, K. A. Kraus, and R. W. Holmberg, *J. Am Chem. Soc.*, **78**, 26 (1956).

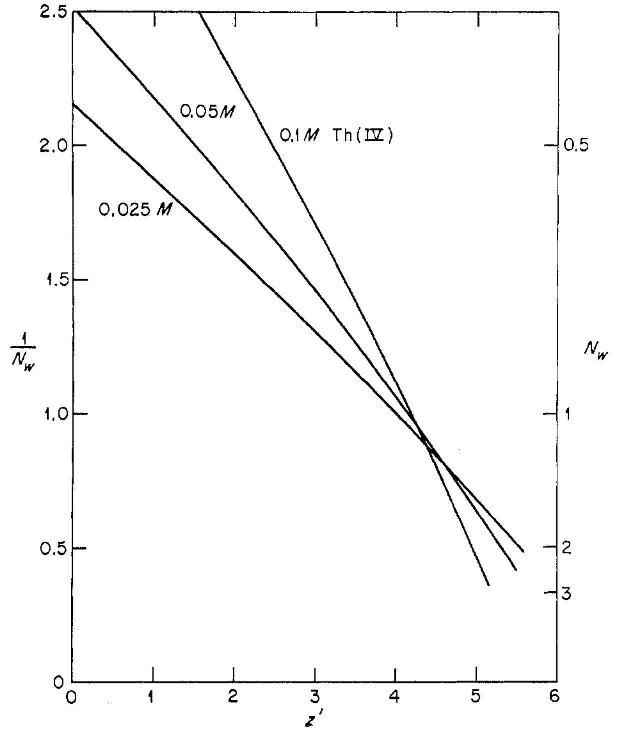

Figure 3.—Degree of polymerization of unhydrolyzed thorium perchlorate (**n** = 0) computed as a function of assumed charge, z'. Supporting electrolyte, $HClO_4$ (0.1 *M*) and $NaClO_4$, solution 1 *M* in total perchlorate. 17,975 rpm.

The influences of polydispersity are minimized by comparing centrifugations of solutions having the same hydroxyl number, since these solutions should have more nearly the same ratios of the various species than solutions of different values of **n**. The effects are by no means eliminated, however, since for a constant acidity (a condition closely approximated as a function of radius in a single centrifugation) **n** varies with Th(IV) concentration[7,8] and will not be constant at all radii. The various gradients of functions of concentration with radius (eq 1), on which analysis of results depends,[11] will therefore be affected. In addition, since the pressure in the cells varies with radius, and, in general, volumes of the various species in equilibrium cannot be assumed to be the same, the equilibria will be shifted somewhat; the magnitude of the effect will be small, however. For example, we can estimate from Figure 1 that a reaction to produce a polymeric species of **n** = 2 and 2 moles of $HClO_4$/mole of Th(IV) from N moles of $Th(ClO_4)_4$ and $2N$ moles of H_2O would involve a change in volume of less than 15 ml/mole of Th(IV). Since the maximum pressure attained in any of these experiments is about 40 atm, the change in the log of the equilibrium quotient should be only about 0.01 per Th(IV) involved, or unimportant for present purposes.

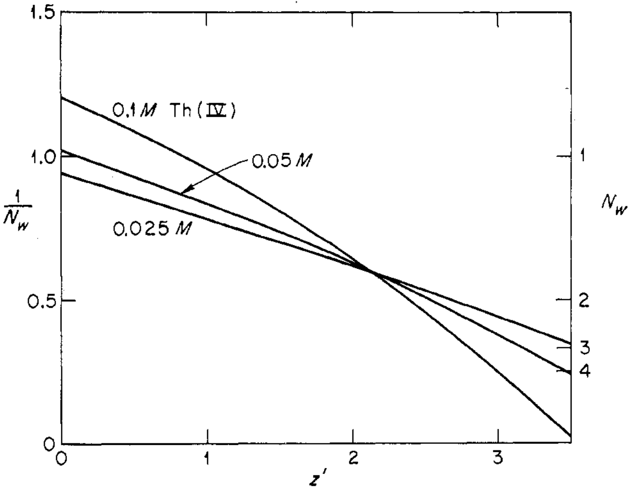

Figure 4.—Degree of polymerization of hydrolyzed thorium perchlorate (**n** = 1.0) computed as a function of assumed charge, z'. Supporting electrolyte, $NaClO_4$, solution 1 *M* in total perchlorate. 15,218 rpm for 0.1 *M*; 17,975 for others.

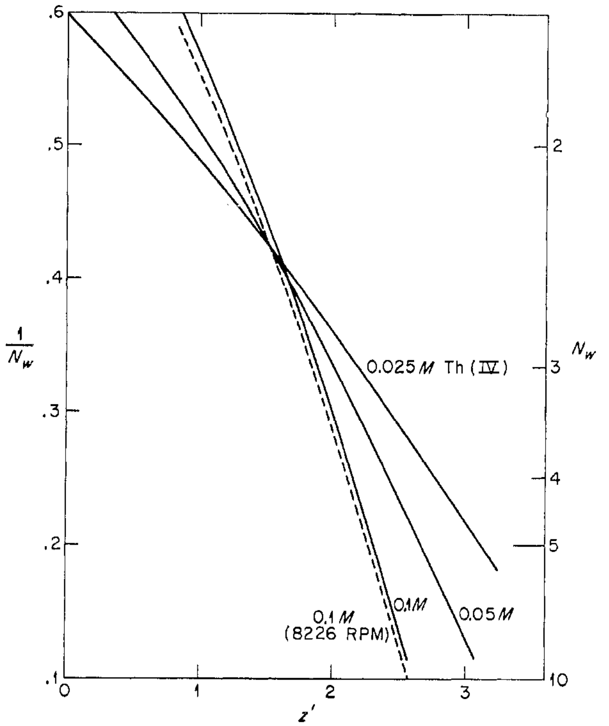

Figure 5.—Degree of polymerization of hydrolyzed thorium perchlorate (**n** = 1.5) computed as a function of assumed charge, z'. Supporting electrolyte, $NaClO_4$, solution 1 *M* in total perchlorate. 15,218 rpm unless otherwise noted.

A crude indication of the degree of polydispersity is obtained from departures from linearity of ln n^* *vs.* x^2, n^* being $n_{\text{solution}} - n_{\text{bg}}$. In the present case, these graphs were either flat or concave downward (the direction indicating effect of charge) for **n** up through 2. Only for **n** = 2.5 and 3.0 were the plots clearly concave upward, the direction indicating polydispersity. Although this by no means justifies a conclusion that the Th(IV) solute is essentially monodisperse at **n** = 1.0, 1.5, and 2.0, it does indicate that the values of N_w obtained from ultracentrifugation should be fair approximations to the weight-average degree of polymerization. In Figures 3–7, N_w was evaluated for the radius at which the Th(IV) concentration originally introduced into the cell occurs at centrifugation equilibrium.

b. Chemical Equilibrium.—Normally, at least 1

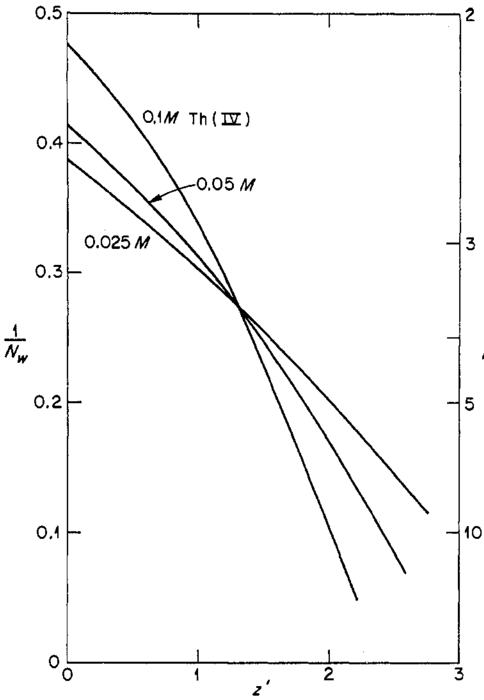

Figure 6.—Degree of polymerization of hydrolyzed thorium perchlorate (n = 2.0) computed as a function of assumed charge, z'. Supporting electrolyte, $NaClO_4$, solution 1 M in total perchlorate. 11,273 rpm.

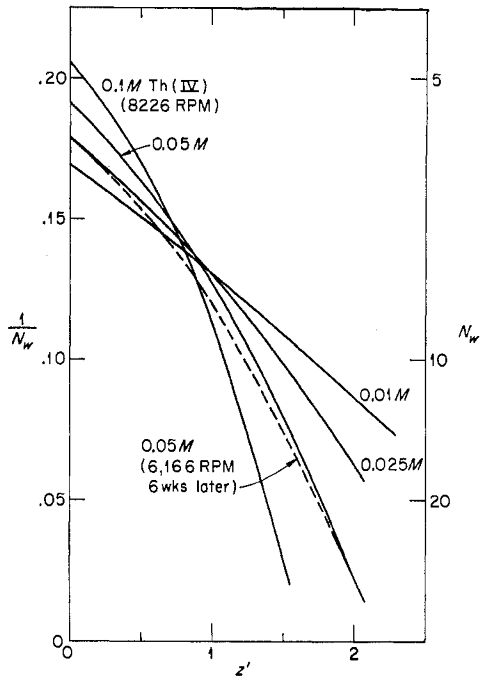

Figure 7.—Degree of polymerization of hydrolyzed thorium perchlorate (n = 2.5) computed as a function of assumed charge, z'. Supporting electrolyte, $NaClO_4$, solution 1 M in total perchlorate. 11,273 rpm unless noted otherwise.

week elapsed between preparation of solutions and attainment of centrifugation equilibrium. In the hydrolysis of metal ions, however, slow reactions frequently occur, and the question as to whether or not the results reported are for solutions at chemical equilibrium is always pertinent. In the present case, this is particularly so, since in preliminary studies several years ago, slow, but definite, drifts in the interference patterns, in a direction indicating increase of molecular weight, were noted from day to day for $\mathbf{n} \geq 1.5$ (see also schlieren results (perchlorate) displayed in Figure 10). Such drifts were not encountered in the present study up through $\mathbf{n} = 2.5$; with $\mathbf{n} = 3$, there was clearly a rapid increase in molecular weight from day to day. Centrifugations at two velocities for 0.1 M Th(IV), $\mathbf{n} = 1.5$ (Figure 5), reached equilibrium about 1 week apart, and the results are in essential agreement. At $\mathbf{n} = 2.5$, a solution recentrifuged 6 weeks later gave a value of N_w about 5% higher than for the first equilibrium (Figure 7). The difference may not be real, however, since at this $\mathbf{n}$ the solute was clearly polydisperse, and the two runs were at different speeds. In this connection, it is of interest that N_w computed for the initial concentration, the procedure used for the figures, was for practical purposes the same as N_w computed by integration across the cell[22] (the procedure is only approximately applicable here, since different species are in chemical equilibrium) for $\mathbf{n} = 0$ through 2, but not for $\mathbf{n} = 2.5$. Here, the difference between the value of N_w obtained by the two methods of analysis was at the point of intersection of the various curves (z' about 0.8) comparable to the difference between the values of N_w obtained 6 weeks apart.

Measurements 4 weeks apart of acidity of the $\mathbf{n} = 2.5$ solutions at 0.1 and 0.05 M Th(IV) indicated a decrease in pH (about 3.5) of 0.02, barely if at all significant, and no significant change at $\mathbf{n} = 2.0$ (pH $\sim$3.1). We conclude that our results in perchlorate media are affected little if at all by slow chemical reactions. The drifts noted in the earlier centrifugations may result from presence of traces of chloride, an ion which may catalyze irreversible transitions to species of high molecular weight (see below). Precautions were taken to exclude chloride in preparation of solutions.

c. Results.—Since complexing of perchlorate by Th^{4+} ions is not expected, the difference of experimental N_w from 1 for unhydrolyzed thorium(IV) perchlorate (Figure 3) at $z' = 4$ should give an indication of the influence of activity coefficient variations. For 0.1 M $Th(ClO_4)_4$, the value was 0.90; for 0.05 M, 0.95; and for 0.025 M, 0.99; the deviations, incidentally, are in the direction opposite to that expected from perchlorate complexing. It is likely that with hydrolyzed solutions, the effect of activity coefficient variations will be less, since in a given centrifugal field the heavier thorium species will be more sedimented than the unhydrolyzed thorium, relative to the supporting electrolyte.

The curves for the various concentrations of hydrolyzed Th(IV) in Figures 4–7 intersect in a narrow range of N_w and z'. The degrees of polymerization increase with $\mathbf{n}$ with no indication of a plateau. In all cases, the value of z' is less than $4 - \mathbf{n}$, a fact indicating

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[22] E. O. Kraemer in "The Ultracentrifuge," T. Svedberg and K. O. Pedersen, Ed., Oxford University Press, London, 1940, p 344.

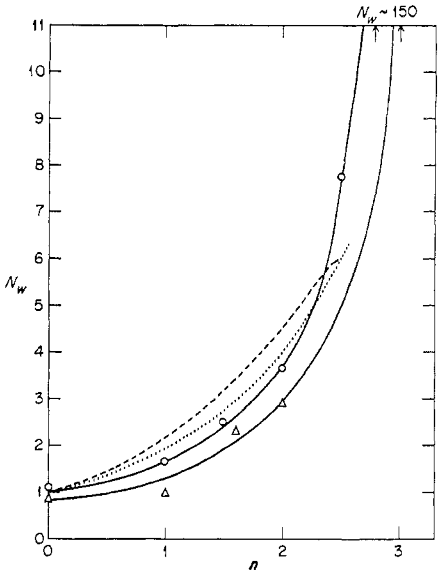

Figure 8.—Weight-average degree of polymerization of hydrolyzed Th(IV) solutions as a function of hydroxyl number (25°): —O— equilibrium ultracentrifugation and —△— light scattering (Hentz and Tyree), both in 1 *M* perchlorate. Interpretation of acidity measurements in terms of species $Th_N(OH)_{nN}$: ...... Baes, *et al.*, 1 *M* perchlorate, (*N*,*nN*) of (1,1), (1,2), (2,2), (4,8), (6,15); ---- Hietenan and Sillén, 3 *M* chloride, (*N*,*nN*) of (1,2), (2,1), (2,2), (2,3), (6,14), (6,15).

that there is some complexing of perchlorate ions by the hydrolyzed polymers.

At **n** = 3, rapid increases in the number of fringes from day to day clearly indicated that further aggregation was occurring. No estimate of charge was possible, but if z' is assumed to be at least half the maximum, 1, the value of N_w, when the centrifugations were terminated, appeared to be greater than 100.

The values of N_w obtained from the intersection of curves for different Th(IV) concentrations are summarized in Figure 8.

3. Comparison of Th(IV) Aggregation in Chloride and Perchlorate Media.—In chloride solutions (or in perchlorate solutions containing a small amount of chloride (see paragraph 5)), we found that hydrolytic polymers of Th(IV) were not stable against further aggregation. An illustration is given in Figure 9: two solutions, both 0.05 *M* in Th(IV) and of **n** = 1.5, but one in 1 *M* sodium chloride and the other in 1 *M* sodium perchlorate supporting electrolyte, were centrifuged simultaneously in a two-place rotor, the solutions having been prepared from unhydrolyzed stock within 30 hr of the start of centrifugation. The chloride solution was in a cell with a wedged window, which effected separation between the schlieren patterns for the two cells. The difference in the schlieren displacement for the two solutions was followed at 7.05 cm from the center of rotation, near the outermost limit of the cell. The changes of displacement of the schlieren diagram ΔZ indicate increasing average molecular weight in the chloride solutions with time, since the perchlorate solution was at centrifugation equilibrium within 1 week. The drift is clearly not slowness in attainment of centrifugation equilibrium; a convincing confirmation of this is the fact that, when the solutions were remixed after 3 weeks of centrifugation, the final ΔZ was essentially reestablished in 1 day of centrifugation (Figure 9).

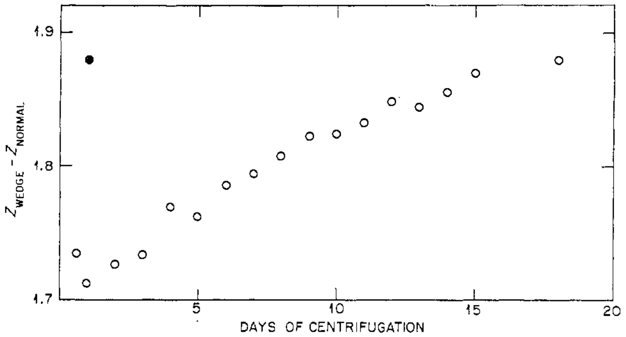

Figure 9.—Progress of aggregation of hydrolyzed Th(IV) in 1 *M* chloride (wedge cell) and perchlorate (normal cell). Solutions 0.05 *M* Th(IV), **n** = 1.5. Displacement, *Z* (cm), of schlieren diagram at 7.05-cm radius. Centrifugation terminated after 18 days, solutions remixed by shaking rotor, centrifugation resumed, and solid point obtained after 1 day. 30-mm single-sector cells, 50° bar angle, 17,980 rpm, ~29°.

We have never attained in chloride media for **n** > 1.0 an unambiguous centrifugation equilibrium. Figure 10 gives differences in aggregation between chloride and perchlorate media, obtained with schlieren optics, for a few cases. Since the degree of polymerization for chloride solutions depends on when the measurement is made, the comparison is only semiquantitative, and the numbers reported, $N_{Z,z=0}$, are the "*Z*"-average degrees of polymerization[16] computed with no correction for charge. It is seen that the Th(IV) is much more aggregated in chloride solutions than in perchlorate.

Neglect of charge tends to make reported values low, while the *Z*-average molecular weight is higher than the weight average for a polydisperse system; the perchlorate results treated in the present manner happen to give values of N_w similar to the interference results reported in Figure 8. For the highly polydisperse chloride solutions, however, the differences between weight averages and *Z*-averages are greater. For example, a 0.015 *M* thorium(IV) chloride solution, **n** = 1.5, gave with interference optics (no charge correction) a degree of polymerization of about 8, and with schlieren optics, measured at the same time and radius, 40. Both are substantially greater than the corresponding interference value of 2 for a similar thorium(IV) perchlorate solution, but the difference between the N_Z and N_w for chloride indicates a considerable contribution of Th(IV) species of rather high aggregation in this medium.

The sharp changes of degree of polymerization in chloride media with time are not strongly reflected in drifts in acidity or hydroxyl number. For example, with a 0.015 *M* Th(IV) solution, **n** = 1.5, in 1 *M* NaCl, the acidity (expressed as $-\log c_H$) drifted from the initial value, about 3.30, during the 6 weeks after preparation by only about 0.02, an amount corresponding to a change in **n** of less than 0.002. One difference in the acidity behavior in the two media was observed, however. Both fresh and aged hydrolyzed thorium(IV) perchlorate solutions reacted and reached a new equilibrium in a short time after addition of acid. Freshly prepared thorium(IV) chloride solutions behaved similarly, but aged solutions responded differently; there was a rapid increase in free acidity, greater than would be observed for the acid addition in question to a fresh solution, followed by a gradual drift downward, as the acid slowly reacted with the hydrolyzed Th(IV) species.

4. High Molecular Weight Aggregates of Th(IV).—In the course of studying the ion-exchange properties of hydrous oxides, Phillips observed that, if thorium hydroxide is precipitated with ammonia from thorium chloride solutions and dried overnight at 300°, the product disperses readily in water, up to 3 g of the hydroxide "dissolving" in 1 g of water in especially favorable preparations. If the drying is carried out at higher or lower temperatures (*e.g.*, 200–400°) or if there are certain other modifications of the procedure, such as excessive washing of the hydrous oxide precipitate before drying, the solid is much less dispersible. Similar precipitates were prepared from thorium nitrate solutions, but the drying temperature for maximum dispersibility was somewhat lower. Some observations of the properties of these materials have been summarized in various Oak Ridge National Laboratory reports.[23] We report here approximate molecular weight determinations of the dispersed material.

These dispersible materials presumably stand somewhere between the hydrolyzed species that are the main topic of this paper and the solid hydrous oxides (or basic salts), probably closer to the latter. Their hydroxyl number is not a completely defined quantity, but can be taken roughly to correspond to four minus their ion-exchange capacity, which, as with hydrous oxides, varies with the composition of the contacting solution.[24] For present purposes in estimating degree of polymerization, **n** is taken to be >3.8, from measurements given in Figure 11. It is of interest that the values of chloride uptake for the dispersible material fall between those of solids dried at higher and lower temperatures.

Equilibrium ultracentrifugations (3100 rpm) were carried out with two solutions, both 0.025 *M* in Th(IV) and both followed by schlieren optics. One solution was in water and the other contained 1 *M* NaCl supporting electrolyte. Both appeared to be somewhat polydisperse, the solution with supporting electrolyte appearing somewhat more so. With NaCl, the slope of log (Z^*/x) *vs.* x^2, which is related to the molecular weight (eq 2), at a radius about $^3/_4$ the maximum in the cell was over twice as great as that at the $^1/_4$ point; in water alone, the slope at the high radius was only about 50% greater. The average degree of polymerization appeared to be about 600 both with and without supporting electrolyte, however (Z-average, computed for $z' = 0$). The similarity of N in the two media can be taken to indicate that there is no great distortion of results by charge effect.

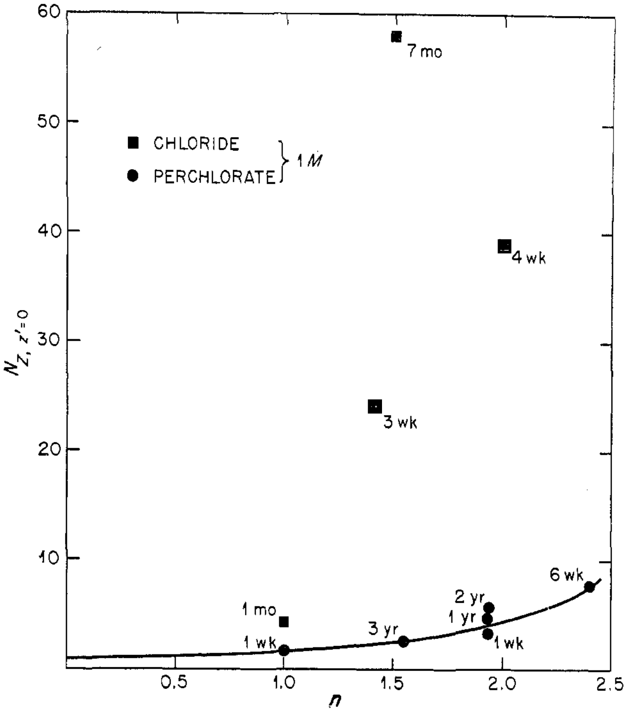

Figure 10.—Comparison of aggregation of Th(IV) in chloride and perchlorate media. Schlieren optics, "Z"-average degree of polymerization, computed for $z' = 0$. Times are approximate periods elapsed between preparation of solutions and termination of centrifugations. Solution *ca.* 0.015 *M* in Th(IV). Temperature ~30°.

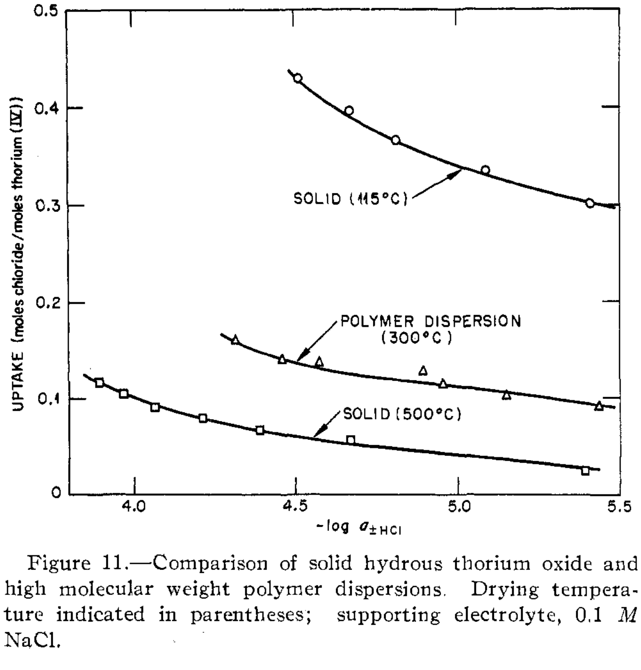

Figure 11.—Comparison of solid hydrous thorium oxide and high molecular weight polymer dispersions. Drying temperature indicated in parentheses; supporting electrolyte, 0.1 *M* NaCl.

[23] (a) K. A. Kraus, T. A. Carlson, J. S. Johnson, and H. O. Phillips, ORNL-1895, 1955, p 199; (b) K. A. Kraus, T. A. Carlson, J. S. Johnson, D. J. Coombe, and H. O. Phillips, ORNL-2057, 1956, p 139; (c) T. A. Carlson, J. S. Johnson, K. A. Kraus, and H. O. Phillips, ORNL-2159, 1956, p 42; (d) T. A. Carlson, J. S. Johnson, and K. A. Kraus, ORNL-2386, 1957, p 104; (e) T. A. Carlson, J. S. Johnson, and K. A. Kraus, ORNL-2584, 1958, p 56.

[24] K. A. Kraus, H. O. Phillips, T. A. Carlson, and J. S. Johnson, *Proc. Intern. Conf. Peaceful Uses At. Energy, 2nd, Geneva, 1958*, **28**, 3 (1958).

Some crude sedimentation velocity measurements, with assumed spherical particles and ideal friction factors, gave estimates for N of about 425, within the uncertainty of the measurements. From light scattering[23b] and X-ray diffraction[23c] the estimates are somewhat higher, but within a factor of 2 of the value from equilibrium ultracentrifugation.

In other velocity measurements, sedimentation coefficients were found to be about the same ($\sim 5 \times 10^{-12}$) for highly dispersible materials, for materials prepared in the presence of excess thorium chloride (a modification in procedure that produces a much less dispersible material), and for materials prepared from nitrate by a similar procedure. On the other hand, a dispersion obtained by room-temperature treatment of hydrous thorium oxides with thorium nitrate solution (another procedure by which high thorium concentrations can be obtained) was highly polydisperse and appeared to have sedimentation coefficients as much as a factor of 20 higher than materials prepared with a drying step. Differences in dispersibility do not seem to correlate with differences in degree of aggregation.

5. Discussion.—Agreement is reasonably good (Figure 8) between the present values of N_w in perchlorate media and those measured by light scattering,[5] a method also sensitive primarily to the weight of solute particles. Both methods also indicate that the average charge on the hydrolyzed species is substantially less than maximum, *i.e.*, that perchlorate ions are complexed by the polymers.

Although the weight-sensitive results demonstrate the limitations of many schemes postulated for Th(IV) hydrolysis, they do not allow a decision among all proposals. The scheme preferred by Baes, *et al.*,[10] for example, agrees reasonably well with the present results (Figure 8) as far as it goes (to $N = 6$, $\mathbf{n} = 2.5$), but the substantially different proposal (based, however, on measurements in 3 M NaCl) of Hietanen and Sillén could not be excluded from weight-sensitive data alone. (The curves of N_w in Figure 8 for the various hydrolysis schemes are computed for 0.01 M Th(IV), but the difference in values for 0.1 M Th(IV) would be barely noticeable.) A scheme of Lefebvre,[25] involving (1,2), (2,2), and (5,12) species (not shown in Figure 8), falls even more closely to the ultracentrifugation results up to $\mathbf{n} = 2$, and there seems to be little reason to believe that, with proper selection of hydroxyl number and formation constant for the higher species he proposes (7,?) agreement could not be extended further. It is our opinion that in cases involving as many species as apparently are formed when thorium hydrolyzes, some of them of such high degrees of polymerization, decision among schemes from fitting of acidity data, even with the help of information from weight-sensitive methods, are not apt to be clear. In such cases, definitive conclusions may depend on finding other techniques which identify major species.[26]

Presence of chloride clearly promotes over a period of time formation of highly aggregated hydrolyzed Th(IV) species, whose reactions are relatively slow. It is possible that the apparently stable species formed in thorium perchlorate hydrolysis are really metastable, and the chloride acts as a catalyst for the formation of the high aggregates. Whether this is the case or whether the highly aggregated species must contain chloride cannot however be firmly established from our results. In an attempt to distinguish, we added 1 mole of NaCl/6 moles of Th(IV) to a sample of a 0.05 M Th(IV), $\mathbf{n} = 1.94$, 1 M $NaClO_4$ solution and centrifuged it and a sample of the original perchlorate solution in a two-cell rotor 3 months later. The degree of polymerization was clearly higher, by about 15%, in the chloride-containing solution, but not to an extent that could not be explained by a contribution of a small concentration of highly aggregated thorium species containing chloride. If the large species do depend on presence of chloride for stability, however, depolymerization when chloride is removed is very slow. Enough NaCl was added to a sample of the same hydrolyzed thorium(IV) perchlorate solution to make it 0.04 M in chloride, and after 6 months the chloride was removed by addition of an equivalent amount of $AgClO_4$. Seven months after the chloride was removed, the solution was centrifuged simultaneously with the original perchlorate solution, and the degree of polymerization of the solution which had once contained chloride was clearly higher than that of the other. In some ways, this aspect of Th(IV) solution chemistry is reminiscent of Pu(IV).[6]

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[25] J. Lefebvre, *J. Chim. Phys.*, **55**, 227 (1958).

[26] J. Aveston, E. W. Anacker, and J. S. Johnson, *Inorg. Chem.*, **3**, 735 (1964).