

[CONTRIBUTION OF THE DEPARTMENT OF CHEMISTRY, CLARK UNIVERSITY, WORCESTER, MASSACHUSETTS]

Solvent Extraction Studies on the 1:1.5 Thorium(IV)-pyrocatechol-3,5-disulfonate System<sup>1</sup>BY RAYMOND F. BOGUCKI,<sup>2a</sup> YUKITO MURAKAMI<sup>2b</sup> AND ARTHUR E. MARTELL

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The application of solvent extraction measurements to the determination of the degree of polymerization of metal chelate compounds has been investigated using the 1:1.5 Th(IV)-pyrocatechol-3,5-disulfonate (Tiron) system. The distribution of Th<sup>234</sup> tracer between a cyclohexane phase containing thenoyltrifluoroacetone and an aqueous phase containing Tiron has been determined at various thorium concentrations. Mathematical treatment of the data obtained has shown that the 1:1.5 Th(IV)-Tiron chelate is binuclear at pH 4.3.

In a previous paper Murakami and Martell<sup>3</sup> have shown the formation of a unique chelate of Th(IV) ion with pyrocatechol-3,5-disodium disulfonate (Tiron). This chelate has the empirical formula (ThA<sub>1.5</sub>)<sub>n</sub><sup>2n-</sup>, in which A<sup>4-</sup> represents the tetra-negative anion of Tiron with both phenolic protons dissociated, and *n* represents an even integer. It is of considerable interest to determine the value of *n* and thus the degree of polynuclearity in this chelate compound which is an example of the process of polymerization through chelation.

## Experimental

The method chosen for this investigation is a solvent extraction technique which utilizes the Th<sup>234</sup> tracer to determine the distribution of Th(IV) species between a cyclohexane phase containing thenoyltrifluoroacetone (TTA) and an aqueous phase containing Tiron. The only thorium species present in the aqueous phase under the experimental conditions employed is the polynuclear species (ThA<sub>1.5</sub>)<sub>n</sub><sup>2n-</sup>.

Zebroski, *et al.*,<sup>4</sup> have shown that in a system consisting of an aqueous phase and a benzene phase containing TTA, the only thorium complex of TTA formed to any extent in the benzene phase is the tetrakis-thenoyltrifluoroacetono-Th(IV) chelate. For the present investigation it was assumed that this 4 to 1 chelate is also the only one formed in cyclohexane under the conditions of excess TTA. The measurement of the distribution of thorium between the two chelating agents in the two phases affords a convenient means for determining the value of *n* in the aqueous chelate.

The Th<sup>234</sup> tracer (half-life 24.1 days) was prepared by Mr. Taku Matsuo of these Laboratories. The radioactive samples were counted with a well type scintillation crystal combined with a single channel analyzer.

**Reagents.**—A sample of TTA obtained from Graham Crawley and Associates, Inc., was distilled under 4 mm. pressure and the fraction boiling in the range 85.0–86.0 and melting at 43° was collected. Tiron, purchased from LaMotte Chemical Products Co., Baltimore, Md., was used to prepare an aqueous stock solution which was standardized by potentiometric titration with base. Reagent grade Th(NO<sub>3</sub>)<sub>4</sub>·4H<sub>2</sub>O, obtained from Allied Chemical and Dye Corp., N.Y., was standardized gravimetrically and used to make up a stock solution for use in the extraction measurements. Spectro grade cyclohexane, obtained from Distillation Products Industries, Rochester, N. Y., was redistilled, and the fraction boiling between 80.5–81.0° was used to make up a stock solution of TTA for the extraction studies.

**Tetrakis-thenoyltrifluoroacetono-Th(IV).**—A mixture which consisted of 100 ml. of 1.058 × 10<sup>-3</sup> M aqueous thorium nitrate, 100 ml. of 4.23 × 10<sup>-3</sup> M TTA in cyclohexane and 4.42 ml. of 9.58 × 10<sup>-2</sup> M NaOH solution was thoroughly shaken in a separatory funnel. Fine white crystals began to separate from the cyclohexane phase in a short period of time after mixing. The reaction mixture

was allowed to stand for several hours and the crystals were filtered off. This product, which melted at 225°, was analyzed for thorium content by ignition to ThO<sub>2</sub>.

*Anal.* Calcd. for C<sub>32</sub>H<sub>16</sub>O<sub>8</sub>F<sub>12</sub>S<sub>4</sub>Th: C, 34.41; H, 1.44; Th, 20.8. Found: C, 34.20, H, 1.43, Th 21.5.

**Procedure.**—Five ml. samples of aqueous solutions containing the (ThA<sub>1.5</sub>)<sub>n</sub><sup>2n-</sup> chelate in varying concentrations were placed in a series of amber bottles. Then 10 ml. portions of an aqueous solution containing a constant amount of excess ligand (H<sub>2</sub>A<sup>2-</sup>) and of the Th<sup>234</sup> tracer were added. The aqueous layer was completed by the addition of 5 ml. portions of a pyridine-pyridinium ion buffer solution. Finally, to each bottle was added 20 ml. of a cyclohexane solution of TTA. A teflon-sealed magnet was placed in each bottle and the bottles were then sealed with a double thickness of Mylar film, covered in turn by a double thickness of aluminum foil. The bottles were then sealed with a screw cap turned down tightly against the foil.

The bottles were placed in a thermostatted bath at 25.0° and agitated vigorously with a magnetic stirrer for 24 hr. Each bottle was then opened and a 3 ml. sample was withdrawn for counting purposes from each of the two layers. The bottles were then resealed and agitation was continued for another 24 hr. interval. The bottles were then opened a second time and a second 3 ml. sample was withdrawn from each layer. The second set of samples was used as a check against the first set to determine if equilibrium had been established.

The distribution of Th<sup>234</sup> between the aqueous and organic phases was then determined by counting the activity in each of the samples withdrawn from the reaction bottles. After the series of samples was counted several times the value of -log[H<sup>+</sup>] for each sample was determined with a Beckman model G pH meter fitted with extension glass and saturated calomel electrodes previously calibrated with acetic acid to read -log[H<sup>+</sup>] values directly.

## Results

The concentrations of each component present in the reaction bottles before the start of equilibration are shown in Table I. Average results obtained

TABLE I  
COMPOSITIONS OF Th-TIRON-TTA SOLUTIONS BEFORE EQUILIBRATION

Bottle	Th <sup>total(aq)</sup> × 10 <sup>5</sup>	KCl(aq.) M	Excess tiron(aq) × 10 <sup>3</sup> M	Pyridine- pyri- dinium buffer, M	TTA in cyclo- hexane × 10 <sup>3</sup> M
I	109.0	0.125	2.902	0.01	2.00
II	54.5	.125	2.902	.01	2.00
III	21.8	.125	2.902	.01	2.00
IV	16.4	.125	2.902	.01	2.00
V	10.9	.125	2.902	.01	2.00
VI	5.45	.125	2.902	.01	2.00

from counting experiments carried out on several successive days are shown in Table II, where *R* signifies the ratio of the number of counts per minute in the organic phase to the number of counts per minute in the aqueous phase. Small random differences in the ratios of *R* between the first and sec-

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(2) (a) Boston College, Chestnut Hill 67, Mass. (b) Kyushu University, Fukuoka, Japan.

(3) Y. Murakami and A. E. Martell, *THIS JOURNAL*, **82**, 5605 (1960).

(4) E. L. Zebroski, H. W. Alter and F. K. Heumann, *ibid.*, **73**, 5646 (1951)

TABLE II<sup>a</sup>

AVERAGE OF COUNTING RESULTS AND DISTRIBUTION OF Th(IV) SPECIES BETWEEN AQUEOUS AND CYCLOHEXANE LAYERS

Bottle	Fraction in aqueous phase	R	$n[(\text{ThA}_{1.5})_n]^{2n-}]_a$
I	0.796	0.256	$8.68 \times 10^{-4}$
II	.637	0.568	$3.47 \times 10^{-4}$
III	.281	2.55	$6.13 \times 10^{-5}$
IV	.191	4.23	$3.13 \times 10^{-5}$
V	.0797	11.55	$8.69 \times 10^{-6}$
VI	.0146	68.0	$7.96 \times 10^{-7}$

Bottle	$[\text{ThB}_4]_0$	$[\text{HB}]_0 \times 10^3$	$[\text{H}_2\text{A}^{2-}]_a \times 10^3$	$-\log [\text{H}^+]_a$
I	$2.22 \times 10^{-4}$	0.95	3.24	4.31
II	$1.98 \times 10^{-4}$	1.03	3.20	4.31
III	$1.57 \times 10^{-4}$	1.17	3.14	4.34
IV	$1.33 \times 10^{-4}$	1.26	3.10	4.35
V	$1.00 \times 10^{-4}$	1.37	3.05	4.37
VI	$5.37 \times 10^{-5}$	1.53	2.98	4.35

<sup>a</sup> All concentrations are expressed in moles per liter;  $n[(\text{ThA}_{1.5})_n]^{2n-}$  represents total concentration of thorium in the aqueous phase;  $[\text{HB}]_0$  represents the concentration of unbound TTA in the organic phase.

ond set of samples indicated that an equilibrium condition had been reached before withdrawal of the first set of samples.

The concentrations in Table II were calculated according to the relationships

$$\begin{aligned} T_{\text{Th}} &= [\text{ThB}_4]_0 + n[(\text{ThA}_{1.5})_n]^{2n-}]_a \\ T_{\text{A}} &= [\text{H}_2\text{A}^{2-}]_0 + 1.5n[(\text{ThA}_{1.5})_n]^{2n-}]_a \\ T_{\text{B}} &= 4[\text{ThB}_4]_0 + [\text{HB}]_{0a}[\text{HB}]_a \\ &[\text{HB}]_0/[\text{HB}]_a = 5.67 \end{aligned}$$

where  $T_{\text{Th}}$  is the total concentration of thorium in the aqueous phase before equilibration with the cyclohexane phase,  $T_{\text{A}}$  is the total concentration of Tiron, bound and unbound, in the aqueous phase and  $T_{\text{B}}$  is the total concentration of TTA in the organic phase before equilibration. The summation of the concentrations of species in both phases is valid since the volumes of the two phases were identical in all cases.

A separate spectrophotometric determination was made of the distribution of TTA between the aqueous and the organic phases in a control solution in which the aqueous phase had the same composition as in the reaction vessels, except that no thorium was present. The ratio of the amount of TTA in the organic phase to that in the aqueous phase was found to be 5.67. Thus a small amount of uncomplexed TTA was present in the aqueous phase in the reaction vessels. However, it was assumed that since there was a considerable excess of Tiron present in the aqueous phase, the formation of any complexes of thorium with TTA in the aqueous phase would be negligible.

**Treatment of Distribution Data.**—The data were treated as though the activity of each species remained constant at constant ionic strength. Under the experimental conditions for which the pH in the aqueous phase was buffered at approximately 4.3, all of the thorium present in the aqueous layer is present as the species  $(\text{ThA}_{1.5})_n]^{2n-}$ . Further, since the first  $pK$  of Tiron is 7.66,<sup>5</sup> essentially all

(5) A. Willi and G. Schwarzenbach, *Helv. Chim. Acta*, **34**, 528 (1951).

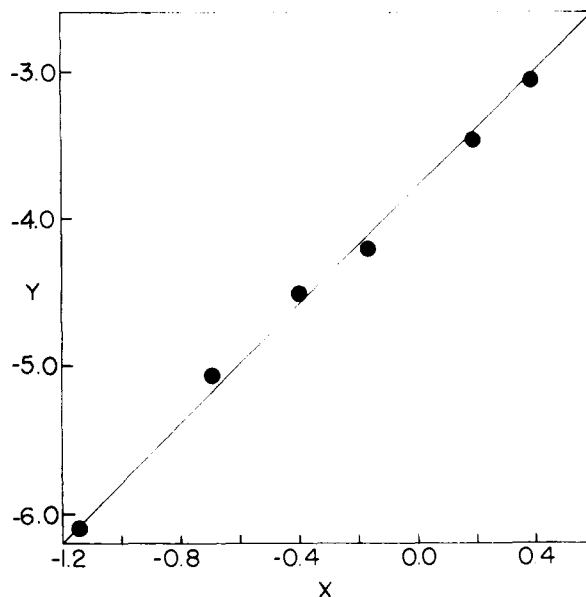
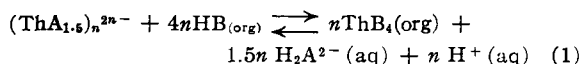


Fig. 1.—Plot of experimental data according to equation 3 demonstrating the presence of a binuclear 1:1.5 Th(IV)-Tiron chelate at pH 4.3. Y represents  $\log n[(\text{ThA}_{1.5})_n]^{2n-}$  and X represents  $(\log [\text{ThB}_4] + 1.5 \log [\text{H}_2\text{A}^{2-}] + \log [\text{H}^+] - 4 \log [\text{HB}])$ . The solid line is drawn with a slope of  $n = 2.00$ .

of the uncomplexed Tiron is present as the species with both phenolic hydrogens undissociated and represented as  $\text{H}_2\text{A}^{2-}$ .

The extraction equilibrium is assumed to be



in which HB represents the undissociated and uncomplexed form of TTA.

The equilibrium expression for equation 1 is

$$K_{\text{eq}} = \frac{[\text{ThB}_4]_a [\text{H}_2\text{A}^{2-}]^{1.5n} [\text{H}^+]^n}{[(\text{ThA}_{1.5})_n]^{2n-}] [\text{HB}]_a^{4n}} \quad (2)$$

The counting procedure yields the total concentration of thorium in the aqueous phase which is represented by  $n[(\text{ThA}_{1.5})_n]^{2n-}$ . In order to obtain this quantity in expression 2, both sides of the equation are divided by the quantity  $n$ . Then the logarithm of each side of the equation is taken and the equation is rearranged to yield

$$\log n[(\text{ThA}_{1.5})_n]^{2n-}] = n(\log [\text{ThB}_4] + 1.5 \log [\text{H}_2\text{A}^{2-}] + \log [\text{H}^+] - 4 \log [\text{HB}]) - \log \frac{K}{n} \quad (3)$$

This expression has the form of a straight line equation. Thus if the previous assumptions are correct, a plot of values of  $\log n[(\text{ThA}_{1.5})_n]^{2n-}]$  as ordinates versus the sums of the quantities inside the parentheses in equation 3 as abscissas should yield a straight line with a slope equal to  $n$  and an intercept equal to  $-\log K/n$ .

Figure 1 demonstrates the linearity of such a plot. The experimental points fall along a straight line with theoretical slope = 2, while the value for  $\log K/n$  from the intercept is 3.76. Thus the equilibrium constant for reaction 1 is  $K_{\text{eq}} = 1.16 \times 10^4$ . Since the value of  $n$  is restricted to an even integer, there can be little doubt that there are two thorium

ions in each polynuclear ion. This is in agreement with the results obtained by Gustafson and Martell<sup>6</sup> who employed a non-equilibrium ultracentrifugation technique to determine the degree of polymerization of the 1:1.5 Th(IV)-Tiron chelate. A poly-

(6) R. L. Gustafson and A. E. Martell, *THIS JOURNAL*, **82**, 5610 (1960).

nuclearity of two has previously been reported by Bogucki and Martell<sup>7</sup> for the hydroxo-bridged thorium chelates of ethylenediaminetetraacetic acid (EDTA) and cyclohexanediaminetetraacetic acid (CDTA).

(7) R. F. Bogucki and A. E. Martell, *ibid.*, **80**, 4170 (1958).

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## Ultracentrifugation of 1 : 1 Th(IV)-Diethylenetriaminepentaacetic Acid and 1 : 1.5 Th(IV)-Pyrocatechol-3,5-disulfonate Chelates<sup>1,2</sup>

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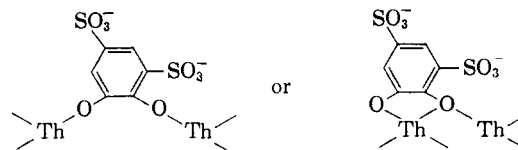
The application of ultracentrifuge measurements to the determination of molecular weights of charged metal chelates has been investigated using the 1:1Th(IV)-diethylenetriaminepentaacetate (DTPA) and 1:1.5 Th(IV)-pyrocatechol-3,5-disulfonate (Tiron) systems. The Archibald non-equilibrium method of determining molecular weights as described by Klainer and Kegeles has been applied to the methods of dealing with charged polymers as outlined by Johnson, *et al.* The calculated values of the molecular weight of the monomeric Th(IV)-DTPA chelate (which was employed as a model system) were approximately 10% lower than the actual value, presumably because of the fact that a non-ideal supporting electrolyte, 1 *M* NaNO<sub>3</sub>, was employed. The substitution of KNO<sub>3</sub> for NaNO<sub>3</sub> resulted in molecular weight values which were only 3% below the theoretical value. Investigation of the 1:1.5 Th(IV)-Tiron system in 1 *M* NaCl showed that a binuclear chelate is the predominant species. The effects of varying type and concentration of the supporting electrolyte have been studied and discussed in terms of the primary and secondary salt effects.

The work recently carried out in these Laboratories on the hydrolytic properties of metal chelates has shown remarkable tendencies of these chelates to polymerize through hydroxo bridges to form polynuclear chelates having varying degrees of complexity. Although potentiometric and spectrophotometric investigations have been sufficient in some cases to determine the degree of aggregation of these polymeric chelates, numerous systems which have been studied have not yielded to these techniques, and much doubt still exists regarding the extent of polymerization which occurs. In view of the successful application of ultracentrifuge measurements to the polymerization of metal ions by Johnson, *et al.*,<sup>3,4</sup> it seemed desirable to apply ultracentrifugation techniques to the determination of molecular weights of polynuclear metal chelate compounds. The systems chosen for the initial experiments were the 1:1 Th(IV)-diethylenetriaminepentaacetic acid (DTPA) and 1:1.5 Th(IV)-pyrocatechol-3,5-disulfonic acid (Tiron) chelates.

Bogucki and Martell<sup>5</sup> have shown that the Th(IV)-DTPA chelate is completely formed at *pH* values as low as 1.5. In view of the fact that the chelate appears to be octadentate, completely satisfying the coordination requirements of the Th(IV) ion, the absence of polymeric species of Th(IV)-DTPA appears certain. This system, therefore, may be considered to be a model on

which to test the limitation of sedimentation theory as applied to charged metal chelates.

Murakami and Martell<sup>6</sup> have shown that at *pH* 5 a stable chelate is formed containing an average of 1.5 Tiron molecules per Th(IV) atom. Since this chelate appears to be nearly completely formed in *pH* regions where the Th(IV) ion has been shown<sup>7,8</sup> to undergo a negligible degree of hydrolysis, it may be assumed that polymerization takes place *via* chelate bridges of the type



rather than by hydroxo bridges. It follows that if only a single polymeric component is present it must contain an even integral number, *n*, of thorium atoms, and the formula of the chelate is (ThA<sub>1.5</sub>)<sub>*n*</sub>(H<sub>2</sub>O)<sub>*x*</sub>, where A represents the fully dissociated Tiron anion. The conditions under which this compound probably exists in solution have been described by Murakami and Martell.<sup>6</sup>

In this research the Archibald non-equilibrium method of determining molecular weights as described by Klainer and Kegeles<sup>9</sup> has been applied to the methods of dealing with charged polymers as outlined by Johnson, *et al.*<sup>3</sup> The latter treatment requires that these conditions be approximately satisfied: (a) the polymeric species must be monodisperse; (b) the partial specific volumes of the polymeric component and the supporting

(1) This work was supported by the U. S. Atomic Energy Commission under contract no. AT(30-1)-1823.

(2) Abstracted from a dissertation submitted by Richard L. Gustafson to the faculty of Clark University in partial fulfillment of the requirements for the degree of Doctor of Philosophy.

(3) J. S. Johnson, K. A. Kraus and G. Scatchard, *J. Phys. Chem.*, **58**, 1034 (1954).

(4) J. S. Johnson, K. A. Kraus and R. W. Holmberg, *THIS JOURNAL*, **78**, 26 (1956).

(5) R. Bogucki and A. E. Martell, *ibid.*, **80**, 4170 (1958).

(6) Y. Murakami and A. E. Martell, *ibid.*, **82**, 5605 (1960).

(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. M. Klainer and G. Kegeles, *J. Phys. Chem.*, **59**, 952 (1955).