

presence of other components of active nitrogen capable of attacking propylene is not thereby excluded. The present work unfortunately does not contribute to knowledge of the composition of active nitrogen.

Mechanistic Speculations.—It is pointed out above that C_2H_4 and CH_3CN appear to have a common precursor or precursors. It seems most probable that

such a precursor would contain nitrogen, *e.g.*, $\overset{\text{N}}{\text{C}}\text{H}_2-\text{CH}_2$ (I) in ground or excited states might be expected to undergo unimolecular or bimolecular rearrangement to CH_3CN and loss of N_2 at the wall or in a bimolecular reaction. At reduced concentration unimolecular rearrangement might predominate, a consideration which may be partially responsible for the roughly threefold increase in the ratio of CH_3CN to C_2H_4 at lowest substrate concentration. The fact that C-1 preponderates over C-3 in these products suggests that at least some proportion of intermediate I results from attack on the original double bond of propylene. If the simplifying assumption is made that ^{14}S atomic nitrogen is the only significant reagent, then such initial attack can be visualized as proceeding *via* a relatively slow spin-forbidden addition to the double bond followed by rearrangement and loss of CH_2 . An interesting alternative involves the concerted formation of monoradical I and diradical CH_2 in a process which conserves spin.

The deficiency of C-2 in HCN and the nearly equal contributions from C-1 and C-3 suggest a precursor in which the latter atoms become equivalent to each other but different from C-2. The necessary symmetry could be achieved, for instance, *via* initial spin-forbidden abstraction of hydrogen from C-3 followed by the fast reaction of the resulting allyl radical, presumably with atomic nitrogen, at its terminal atoms, associated with cleavage, or *via* formation of an unstable four-membered ring, followed by decomposition to HCN and other fragments. Alternatively, the indicated symmetry might be achieved by direct attack of nitrogen atom on propene to form an unstable four-membered ring, with loss or rearrangement of hydrogen. Similar processes are consistent with the indicated symmetry of the precursors of acetylene.

The present data are, of course, not capable of doing more than indicating the structural symmetries of the precursors of some of the products and the suggested precursors are only meant to be illustrative. It is not meant to imply that any of the observed products, with the possible exception of propane, is formed with a single reaction path.

Acknowledgment.—N. N. L. is indebted to the National Science Foundation for a Senior Postdoctoral Fellowship and to the Isotope Department of the Weizmann Institute of Science for its hospitality, both of which facilitated the preparation of this paper.

[CONTRIBUTION FROM THE DEPARTMENTS OF CHEMISTRY OF CLARK UNIVERSITY, WORCESTER, MASS., AND OF ILLINOIS INSTITUTE OF TECHNOLOGY, CHICAGO, ILL.]

Determination of Molecular Weights of Polynuclear Zirconium and Thorium Chelates by Nonequilibrium Ultracentrifugation¹

BY RICHARD L. GUSTAFSON AND ARTHUR E. MARTELL²

RECEIVED MAY 29, 1963

The degrees of aggregation of 1:1 Th(IV)-N-hydroxyethylethylenediamine triacetate (HEDTA), 1:1:1 Th(IV)-HEDTA-pyrocatechol 3,5-disulfonate (Tiron), 1:1 Zr(IV)-HEDTA, and 1:1:1 Zr(IV)-ethylenediamine tetraacetate (EDTA)-Tiron chelates have been calculated from data obtained by nonequilibrium centrifugation in sodium chloride solutions at 25°. The 1:1 Th(IV)-HEDTA chelate has been shown to be most probably hexameric, whereas solutions containing equimolar amounts of Th(IV), HEDTA, and Tiron to which have been added $4\frac{2}{3}$ and 6.0 moles of sodium hydroxide per mole of metal ion were shown to be polydisperse. Solutions of Zr(IV) and HEDTA at pH 6 were shown to be composed of mixtures of monomers and dimers. A value of $K_D = [\text{dimer}]/[\text{monomer}]^2 = 10^{2.14}$ was obtained from the sedimentation data. The data obtained for the 1:1:1 Zr(IV)-EDTA-Tiron systems at pH 7 suggest that a mixture of monomers and dimers is present.

Introduction

Studies carried out by many workers have elucidated the nature of the hydrolysis and olation reactions of a large number of metal ions and metal chelates on the basis of potentiometric, spectrographic, polarographic, and ion-exchange data. However, in many cases, particularly those of highly charged metal ions, it has been impossible to determine the degrees of aggregation of the polymers which are formed. An important step in this direction was the adaptation by Kraus, Johnson, and co-workers of equilibrium ultracentrifugation measurements to the calculation of the degrees of polymerization of Zr(IV),^{3,4} Hf(IV),^{4,5} Bi(III),⁶ In(III),⁷ Au(III),⁷ Hg(I),⁷ Hg(II),⁷ Pb(II),⁸ and Sn(IV).^{8,9}

ions at various pH and concentration levels. Subsequently, Gustafson and Martell¹⁰ successfully adapted the methods of dealing with the ultracentrifugation of charged polymers as outlined by Johnson, Kraus, and Scatchard¹¹ to the Archibald¹² nonequilibrium technique as developed by Klainer and Kegeles¹³ in order to determine the degrees of aggregation of 1:1 Th(IV)-diethylenetriamine pentaacetate and 1:1.5 Th(IV)-pyrocatechol 3,5-disulfonate (Tiron) systems. In the present study, the application of the nonequilibrium ultracentrifugation technique has been extended to 1:1 Th(IV)-N-hydroxyethylethylenediamine triacetate (HEDTA), 1:1:1 Th(IV)-HEDTA-Tiron, 1:1 Zr(IV)-HEDTA, and 1:1:1 Zr(IV)-ethylenediamine tetraacetate (EDTA)-Tiron systems. Bogucki and Martell¹⁴ have attempted to elucidate the structure of

(1) This work was supported by the U. S. Atomic Energy Commission under Contracts AT-(30-1)-1823 (Clark University) and AT-(11-1)-1020 (Illinois Institute of Technology).

(2) Illinois Institute of Technology, Chicago, Ill.

(3) K. A. Kraus and J. S. Johnson, *J. Am. Chem. Soc.*, **75**, 5769 (1953).

(4) J. S. Johnson and K. A. Kraus, *ibid.*, **78**, 3937 (1956).

(5) J. S. Johnson, K. A. Kraus, and R. W. Holmberg, *ibid.*, **78**, 26 (1956).

(6) R. W. Holmberg, K. A. Kraus, and J. S. Johnson, *ibid.*, **78**, 5506 (1956).

(7) J. S. Johnson and K. A. Kraus, *ibid.*, **79**, 2034 (1957).

(8) J. S. Johnson and K. A. Kraus, *ibid.*, **81**, 1569 (1959).

(9) J. S. Johnson and K. A. Kraus, *J. Phys. Chem.*, **63**, 440 (1959).

(10) R. L. Gustafson and A. E. Martell, *J. Am. Chem. Soc.*, **82**, 5610 (1960).

(11) J. S. Johnson, K. A. Kraus, and G. Scatchard, *J. Phys. Chem.*, **68**, 1034 (1954).

(12) W. J. Archibald, *ibid.*, **51**, 1204 (1947).

(13) S. M. Klainer and G. Kegeles, *ibid.*, **69**, 952 (1955).

the polynuclear chelate formed when a solution containing equimolar amounts of Th(IV) and N-hydroxyethylthylenediaminetriacetic acid (HEDTA) is adjusted to pH 7 by addition of $4\frac{2}{3}$ moles of base per mole of metal chelate. Mathematical analysis of their potentiometric data indicated that a polymer was formed having the general formula $\text{ThA}(\text{Th}[\text{OH}]_2\text{A})_n$, where A represents the ligand molecule and $[\text{OH}]$ represents either a coordinated hydroxo or dissociated hydroxyethyl group. However, the value of n in the above formula could not be determined unambiguously. Bogucki and Martell¹⁴ have obtained potentiometric titration data for 1:1:1 Th(IV)-HEDTA-Tiron mixtures at various concentrations and have shown that inflections are obtained at $m = 4\frac{2}{3}$ and 6.0, respectively. Here m represents the number of moles of sodium hydroxide added per mole of metal ion. Attempts at mathematical solution of the various equilibria involved were unsuccessful because of the apparent complexity of the system.

Potentiometric titrations of solutions containing equimolar concentrations of Zr(IV) ion and HEDTA differ markedly from those of the Th(IV)-HEDTA chelate in that they produce a single steep inflection upon the addition of four moles of hydroxide ion per mole of metal chelate.¹⁵ Calculations based on the titration data of this system suggest that the chelate formed is polynuclear. Intorre and Martell¹⁶ have recently shown that the 1:1:1 Zr(IV)-EDTA-Tiron system is composed of a mixture of monomeric and dimeric species and have calculated equilibrium constants for the reactions involved.

Experimental

Centrifugations.—Ultracentrifugation experiments were carried out with a Spinco Model E ultracentrifuge. The details of the centrifugation procedure are precisely as described previously.¹⁰

Reagents.—In the preparation of the Th(IV)-HEDTA solutions, Baker analyzed reagent grade thorium nitrate was finely ground and used without drying. Direct ignition to ThO_2 showed that the salt corresponded to the empirical formula $\text{Th}(\text{NO}_3)_4 \cdot 5.06\text{H}_2\text{O}$. Thorium chloride was obtained from the Fairmount Chemical Co. and was used in the 1:1:1 Th(IV)-HEDTA-Tiron studies. It was analyzed for thorium content by precipitation with ammonia and ignition to ThO_2 . After removal of thorium by the use of a Dowex 50 ion-exchange column, chloride analyses were carried out by means of the Mohr method. The number of hydroxyl groups bound per thorium atom was determined by neutralization of the hydrogen ions liberated after addition of an excess of Tiron. Previous work by Murakami and Martell¹⁷ showed that 3.00 moles of hydroxide per mole of thorium was required to reach the first inflection at pH 5. The difference between 3.00 and the number of moles of base required to reach the neutralization point was equal to the number of OH groups bound per Th(IV) atom.

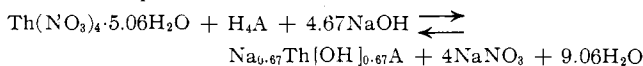
Zirconium chloride was obtained from the National Lead Co., Niagara Falls, N. Y. Zirconium content was determined by precipitation with ammonia and subsequent ignition to ZrO_2 . The amount of standard sodium hydroxide required for titration of a solution containing equimolar amounts of the Zr(IV) salt, the disodium salt of EDTA, and Tiron permitted the calculation of the number of hydroxo groups bound per zirconium atom, while the chloride content was determined by difference. The effective molecular weight of the Zr(IV) salt was calculated to be 235.6, corresponding to the formula $\text{Zr}(\text{OH})_{0.057}\text{Cl}_{3.943} \cdot 0.200\text{H}_2\text{O}$.

The disodium salt of EDTA was obtained from Distillation Products Industries, Rochester 3, N. Y., and Tiron was obtained from the LaMotte Chemical Co., Baltimore, Md. HEDTA was donated by the Dow Chemical Co., Midland, Mich. All ligands were standardized by potentiometric titration with standard base both with and without the addition of a slight (1-2%) excess of nickel nitrate. Standard 2 M NaOH was prepared from saturated, carbonate-free solutions such that the standard hydroxide solutions were also 1.000 or 1.200 M in NaCl. The solvent employed in making up all chelate solutions used in the ultracentrifugation experiments was 1.200 M NaCl, except

for the case of the Th(IV)-HEDTA solutions which were 1.00 M in NaCl.

The various chelate solutions were prepared by rinsing (with 1.000 or 1.200 M NaCl) weighed amounts of metal salts and ligands into 100-ml. volumetric flasks. Each flask was weighed, after which the appropriate volume of standard NaOH solution (containing NaCl) was added. Each flask was reweighed in order to determine the exact weight of NaOH-NaCl solution used. Finally the volume was brought to 100 ml. with 1.000 or 1.200 M NaCl solution. Correlation of the data thus obtained with density measurements permitted the calculation of the compositions of the chelate solutions and the partial specific volumes of the polymeric components.

Determination of Partial Specific Volume—1:1 Th(IV)-HEDTA.—The reaction which takes place in preparation of the Th(IV)-HEDTA sample is



The apparent molar volume, ϕ_v , of the products of this reaction was calculated with the aid of the formula

$$\phi_v(\text{products}) = \frac{1000}{c\rho_0}(\rho_0 - \rho) + \frac{M}{\rho_0} \quad (1)$$

Here c is the molar concentration of Th(IV), ρ is the solution density, and M represents the total molecular weight of the products of reaction. The experimental values of ρ and ϕ_v obtained at various Th(IV) concentrations are listed in Table I.

TABLE I

DETERMINATION OF APPARENT MOLAR VOLUME OF THE PRODUCTS OF THE Th(IV)-HEDTA REACTION IN 1.000 M NaCl AT 25.0°

Concn. Th(IV), $\times 10^2 M$	ρ , g./ml.	ϕ_v , ml./mole
9.513	1.08767	485.5
7.289	1.07585	485.1
3.969	1.05811	485.9
1.980	1.04761	481.6
1.075	1.04231	521.6

$$\rho_0 = 1.03698 \text{ g./ml.}$$

Since the accuracy of apparent molar volume measurements increases with an increase in concentration, only the results from the three most concentrated samples were used. The average value thus obtained for ϕ_v is 485.5 \pm 0.3 ml./mole. The approximation that $\partial\phi_v/\partial c^{1/2} = 0$ gave the relationship $\bar{V}_{\text{products}} = \phi_v(\text{products}) = 485.5$, where $\bar{V}_{\text{products}}$ is the partial molar volume of the products of reaction. The partial specific volume of the polymeric component PX_2 was determined from the equation

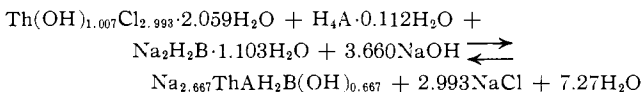
$$\bar{v}_{\text{PX}_2} = (\bar{V}_{\text{products}} - 4\bar{V}_{\text{NaNO}_3} - 9.06\bar{V}_{\text{H}_2\text{O}})/M'_{\text{PX}_2}$$

where M'_{PX_2} represents the molecular weight of the monomer unit of the polymeric component, 533.02. The values of \bar{V}_{NaNO_3} were calculated from data tabulated by Harned and Owen¹⁸ with the relationship

$$\bar{V}_{\text{NaNO}_3} = \bar{V}_{\text{KNO}_3} + \bar{V}_{\text{NaCl}} - \bar{V}_{\text{KCl}}$$

The concentration term used for NaNO_3 in the calculation was equal to the sum of the NaCl and NaNO_3 concentrations of each sample employed.

1:1:1 Th(IV)-HEDTA-Tiron at $m = 4\frac{2}{3}$.—The reaction which takes place when $4\frac{2}{3}$ moles of alkali hydroxide per mole of metal ion are added to a 1:1:1 mixture of Th(IV), HEDTA, and Tiron, may be written as

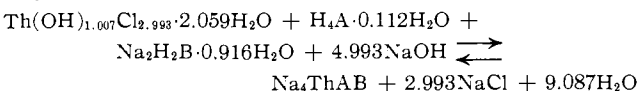


where A represents the tetranegative anion of HEDTA and B represents the tetranegative anion of Tiron. The experimental values of ρ and ϕ_v obtained over a tenfold range of Th(IV) concentration are shown in Table II. Again, with the assumption that $\partial\phi_v/\partial c^{1/2} = 0$, or that $\bar{V}_{\text{products}} = 511$ ml./mole, \bar{v}_{PX_2} may be calculated from the relationship

$$\bar{v}_{\text{PX}_2} = (\bar{V}_{\text{products}} - 2.993\bar{V}_{\text{NaCl}} - 7.274\bar{V}_{\text{H}_2\text{O}})/M'_{\text{PX}_2}$$

where $M'_{\text{PX}_2} = 847.3$.

1:1:1 Th(IV)-HEDTA-Tiron at $m = 6$.—The reaction of Th(IV) ion, HEDTA, Tiron, and 6 moles of sodium hydroxide may be written as



(14) R. F. Bogucki and A. E. Martell, unpublished results.

(15) B. J. Intorre and A. E. Martell, *J. Am. Chem. Soc.*, **82**, 358 (1960).

(16) B. J. Intorre and A. E. Martell, *Inorg. Chem.*, **3**, 81 (1964).

(17) Y. Murakami and A. E. Martell, *J. Am. Chem. Soc.*, **82**, 5605 (1960).

(18) H. S. Harned and B. B. Owen, "The Physical Chemistry of Electrolytic Solutions," 3rd Ed., Reinhold Publ. Corp., New York, N. Y., 1959.

TABLE II

DETERMINATION OF ϕ_v FOR PRODUCTS OF Th(IV)-HEDTA-TIRON REACTION AT $m = 4\frac{2}{3}$ IN 1.200 M NaCl

Th(IV) concn., M	ρ , g./ml.	ϕ_v , ml./mole
1.146×10^{-1}	1.11558	512.6
8.024×10^{-2}	1.09413	515.1
4.585×10^{-2}	1.07329	508.6
2.293×10^{-2}	1.05906	507.6
1.146×10^{-2}	1.05180	517.6

$$\rho_0 = 1.04478$$

$$\text{Av. value of } \phi_v \text{ (expt. 1-4)} = 511 \pm 3$$

TABLE III

DETERMINATION OF ϕ_v FOR PRODUCTS OF Th(IV)-HEDTA-TIRON REACTION AT $m = 6$ IN 1.200 M NaCl

Th(IV) concn., M	ρ , g./ml.	ϕ_v , ml./mole
1.058×10^{-1}	1.11189	541.8
7.408×10^{-2}	1.09171	541.0
4.233×10^{-2}	1.07153	539.1
2.117×10^{-2}	1.05799	538.6
1.058×10^{-2}	1.05116	543.2

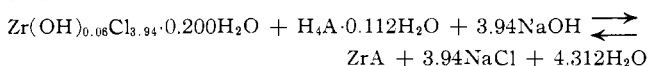
$$\rho_0 = 1.0443$$

Experimental values of ρ and ϕ_v (products) are listed in Table III. The partial specific volume for the polymeric component alone may be calculated by use of the equation

$$\bar{v}_{PX_2} = (\bar{V}_{\text{products}} - 2.993\bar{V}_{\text{NaCl}} - 9.087\bar{V}_{\text{H}_2\text{O}})/864.6$$

where 864.6 is the molecular weight of the monomer unit $\text{Na}_4\text{-ThAB}$.

1:1 Zr(IV)-HEDTA.—The reaction which takes place upon preparation of the Zr(IV)-HEDTA solution is



In this case the molecular weight of the combined products is 673.6. The experimental values of density and apparent volume are listed in Table IV. The data fit the empirical equation

$$\phi_v(\text{products}) = 341.0 - 4.5c^{1/2}$$

TABLE IV

DETERMINATION OF APPARENT MOLAR VOLUME OF PRODUCTS OF THE Zr(IV)-HEDTA REACTION IN 1.200 M NaCl SOLUTION AT 25°

Zr(IV) concn. $\times 10^2 M$	ρ , g./ml.	ϕ_v , ml./mole
9.603	1.07632	330.7
6.722	1.06672	332.8
3.841	1.05715	337.3
1.921	1.05096	338.3
0.960	1.04788	338.8

$$\rho_0 = 1.04481 \text{ g./ml.}$$

The partial molar volumes of the products were calculated by the use of the expression

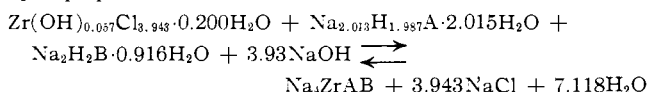
$$\bar{V}_{\text{products}} = \phi_v(\text{products}) + \left[\frac{1000 - c\phi_v}{2000 + c^{1/2}\partial\phi_v/\partial c^{1/2}} \right] c^{1/2}\partial\phi_v/\partial c^{1/2} \quad (2)$$

where $\partial\phi_v/\partial c^{1/2} = -4.5$. The partial specific volume of the Zr(IV)-HEDTA chelate was calculated with the equation

$$\bar{V}_{\text{ZrA}} = (\bar{V}_{\text{products}} - 3.94\bar{V}_{\text{NaCl}} - 4.312\bar{V}_{\text{H}_2\text{O}})/M$$

where M is the molecular weight of the chelate species, 365.5.

1:1:1 Zr-EDTA-Tiron.—The reaction which takes place upon preparation of the Zr-EDTA-Tiron solution is



where A and B represent the tetranegative anions of EDTA and Tiron, respectively. The experimental values of ρ and ϕ_v obtained at various Zr(IV) concentrations are listed in Table V, where it may be seen that an average value of ϕ_v (products) of 516 is obtained for the four most concentrated solutions. If the approximation is made that $\bar{V}_{\text{products}} = \phi_v(\text{products})$, the partial specific volume of the polymeric component PX_2 may be

TABLE V

DETERMINATION OF APPARENT MOLAR VOLUME OF PRODUCTS OF THE Zr(IV)-EDTA-TIRON REACTION IN 1.200 M NaCl

Zr(IV) concn. $\times 10^2 M$	ρ , g./ml.	ϕ_v , ml./mole
8.530	1.09219	515.5
5.872	1.07717	518.7
4.285	1.06854	514.8
2.388	1.05796	514.2
1.188	1.05139	503.0

$$\rho_0 = 1.04461$$

$$\text{Av. value of } \phi_v \text{ (expt. 1-4)} = 516 \pm 2$$

determined by the equation

$$\bar{v}_{PX_2} = (\bar{V}_{\text{products}} - 3.943\bar{V}_{\text{NaCl}} - 7.118\bar{V}_{\text{H}_2\text{O}})/M'_{PX_2}$$

where M'_{PX_2} represents the molecular weight of the monomer unit of the polymeric component, 737.6.

Mathematical Treatment of Data

Calculations of the degree of polymerization N were carried out with the aid of the equation

$$N = \frac{1}{2A_2'c_2'x/(dc_2'/dx) - z'\eta} \quad (3)$$

where

$$A_2' = L_2'\omega^2/2RT$$

$$L_2' = M'_{PX_2}(1 - \bar{v}_{PX_2}\rho) - \frac{z'}{2}M_{\text{BX}}(1 - \bar{v}_{\text{BX}}\rho)$$

and

$$\eta = 1/(1 + 2c_{\text{B}}/z'c_2')$$

The primed symbols refer to the monomer unit according to the relationships $NM'_{PX_2} = M_{PX_2}$ and $z'N = z$; M'_{PX_2} and \bar{v}_{PX_2} represent the molecular weight and partial specific volume of the monomer unit, whereas M_{BX} and \bar{v}_{BX} represent the same quantities for the supporting electrolyte BX (which is in some cases actually a mixture of NaCl and NaNO_3); c_2' is the concentration of the monomer unit expressed in refractive index units; (dc_2'/dx) is the refractive index gradient (dn^*/dx) as measured at the upper and lower phase boundaries; x is the distance from the center of rotation; z' is the assumed charge per monomer unit; ω is the angular velocity; c_{B} is equal to the sum of the chloride and nitrate concentrations; R is the molar gas constant; and T is the absolute temperature. The details of the calculations are discussed in a previous publication.¹⁰

The approximations that

$$\bar{v}_{\text{BX}} = \frac{(\bar{v}_{\text{NaCl}})(c_{\text{NaCl}}) + (\bar{v}_{\text{NaNO}_3})(c_{\text{NaNO}_3})}{c_{\text{NaCl}} + c_{\text{NaNO}_3}}$$

and that

$$M_{\text{BX}} = \frac{(M_{\text{NaCl}})(c_{\text{NaCl}}) + (M_{\text{NaNO}_3})(c_{\text{NaNO}_3})}{c_{\text{NaCl}} + c_{\text{NaNO}_3}}$$

introduce a negligible difference in the calculation of N , relative to the values obtained when the more rigorous equations pertaining to a four-component system (polymeric component, NaCl, NaNO_3 , and water) are employed.

Results

1:1 Th(IV)-HEDTA.—In Fig. 1 values of the degree of polymerization N of the 1:1 Th(IV)-HEDTA chelate are plotted as a function of the assumed charge per monomer unit. Each curve represents the average of the six sets of data obtained in each experiment. The results show that for a z' value of 0.67 an average of 5.2 monomer units are bound per polymer. The small random distribution of results over a wide concentration range (average deviation of N at $z' = 0.67$ based on 30 pieces of experimental data is $\pm 4\%$) is evidence that the system is not polydisperse. The presence of a single polymeric species containing an average of two thirds of a hydroxo group per monomer unit requires that the degree of aggregation be some multiple of three. The results suggest that the Th-EDTA chelate polymer is most probably a hexamer.

It is impossible to decide on the basis of potentiometric or spectrophotometric evidence whether or not the hydroxyethyl group is bound to the metal ion. The value of the molecular weight per monomer unit

was based on the assumption that the alkoxy group is involved in coordination. If the alkoxy group were not bound in this way, M'_{PX} would be increased from 533 to 551 or by a difference of the molecular weight of one water molecule. This would also result in a lower value of $(1 - \bar{v}_{PX,\rho})$, the net result being a slight change in the calculation of the degree of polymerization. Calculations have shown that the assumption that $M'_{PX} = 551$ rather than 533 results in a change of less than 0.2% in the calculated value of N .

The samples which were used for the molecular weight determination were allowed to stand for approximately 2 weeks before the centrifugations were carried out. These experiments did not parallel the potentiometric measurements since the latter were usually completed in a single day. Despite the fact that the previous ultracentrifugation experiments indicated a monodisperse system, it was decided to check the possibility that a slow polymerization reaction might be taking place over a period of time. Accordingly, a Th-HEDTA sample was centrifuged within 2 hr. after its preparation. The results shown in Table VI indicate good agreement with the previous determinations.

TABLE VI
CENTRIFUGATION OF FRESHLY PREPARED Th(IV)-HEDTA SOLUTION

Exposure, min.	$N (z' = 0)$	$N (z' = 0.5)$	$N (z' = 1.0)$
8 (top)	4.80	5.06	5.59
16 (top)	5.12	5.40	5.98
32 (top)	4.87	5.12	5.62
8 (bot.)	4.74	5.02	5.65
16 (bot.)	5.55 ^a	5.92 ^a	6.79 ^a
32 (bot.)	6.49 ^a	6.97 ^a	8.25 ^a

^a High values of N obtained using 16 min. (bot.) and 32 min. (bot.) data may be caused by inaccuracy in extrapolation of (dn/dx) vs. x plot.

Th-HEDTA-Tiron at $m = 4\frac{2}{3}$.—In Table VII are shown the calculated values of N , obtained at various values of the assumed charge, z' , upon ultracentrifugation of pH 5.5 solutions containing $4\frac{2}{3}$ moles of sodium hydroxide per mole of Th(IV), HEDTA, and Tiron. The upward trend of values of N with increasing metal chelate concentration strongly suggests that the system is polydisperse. The average value of N at $z' = 2.67$ (which would be the actual charge per monomer unit if the system were monodisperse) indicates that the average degree of polymerization corresponds to a preponderance of binuclear species. From the inflection in the potentiometric titration curve at $m = 4\frac{2}{3}$, it was expected that the value obtained for the degree of polymerization, N , would be some multiple of three. While the over-all picture is not clear, it appears that the largest polymers present in solution under the conditions described are trimers.

TABLE VII

CALCULATED VALUES OF N AS A FUNCTION OF z' FOR Th(IV)-HEDTA-TIRON CHELATES AT $m = 4\frac{2}{3}$

Th(IV) concn., M	$z' = 1.0$	$z' = 2.0$	$z' = 2.67$	$z' = 3.0$	$z' = 3.5$
1.146×10^{-1}	1.55	1.96	2.59	3.19	5.20
8.024×10^{-2}	1.52	1.82	2.22	2.54	3.37
4.585×10^{-2}	1.44	1.62	1.83	1.97	2.28
2.293×10^{-2}	1.30	1.41	1.51	1.57	1.69
1.146×10^{-2}	1.22	1.29	1.35	1.39	1.45

Th-HEDTA-Tiron at $m = 6.0$.—In Table VIII the values of N are listed as a function of the assumed charge, z' , per monomer unit of the chelate produced by the addition of 6.00 moles of sodium hydroxide per

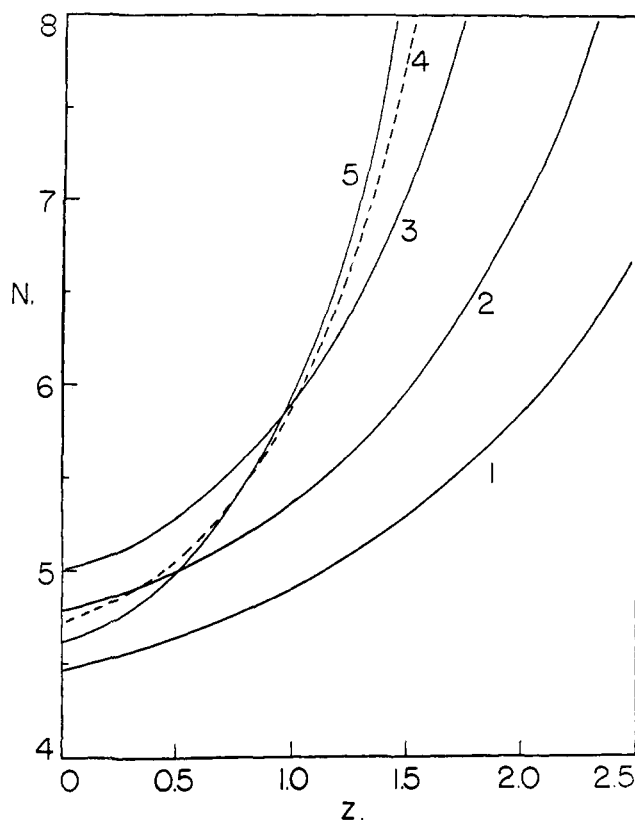


Fig. 1.—Ultracentrifugation of 1:1 Th(IV)-HEDTA chelate at pH 7 in approximately 1 M NaCl; initial chelate concentrations: 1, $1.08 \times 10^{-2} M$; 2, $1.98 \times 10^{-2} M$; 3, $3.97 \times 10^{-2} M$; 4, $7.29 \times 10^{-2} M$; 5, $9.51 \times 10^{-2} M$.

mole of a 1:1:1 Th(IV)-HEDTA-Tiron mixture. The results obtained at $z' = 4$, which would be the charge of a Th-HEDTA-Tiron monomer unit, indicate that the system may be polydisperse. However, the relative constancy of the N values at lower assumed values of z' suggests that the system is actually monodisperse and that the chelate may be dimeric. The marked upward drift in N with increase in z' may be due in part to the extreme sensitivity of the calculation of the degree of polymerization to small experimental deviations at high z' values.

TABLE VIII

CALCULATED VALUES OF N AS A FUNCTION OF z' FOR Th(IV)-HEDTA-TIRON CHELATES AT $m = 6.0$

Th(IV) concn., M	$z' = 2.0$	$z' = 3.0$	$z' = 3.5$	$z' = 4.0$
1.058×10^{-1}	1.8	2.8	4.1	9
7.408×10^{-2}	1.8	2.5	3.3	5.0
4.233×10^{-2}	1.84	2.26	2.6	3.2
2.117×10^{-2}	1.95	2.23	2.4	2.7
1.058×10^{-2}	1.73	1.88	1.98	2.1

1:1 Zr(IV)-HEDTA.—The calculated values of the degrees of polymerization of the neutral Zr(IV)-HEDTA chelate are shown in Table IX. Since the plots of dn^*/dx vs. x at the lower phase boundaries were extremely steep, resulting in considerable error in extrapolation to the phase boundaries, only data obtained at the upper phase boundaries are presented. Because of the low values of the refractive indices of the Zr(IV)-HEDTA solutions, it was necessary to carry out the experiments at high centrifugation speeds. This resulted in a considerable degree of sedimentation, which produced a low concentration of chelate at the upper meniscus and a high concentration at the lower meniscus. The results of ultracentrifugation of the $9.6 \times 10^{-3} M$ chelate solution were not calculated

TABLE IX
ULTRACENTRIFUGATION OF 1:1 Zr(IV)-HEDTA CHELATES IN
1.200 M NaCl AT 25°

Time, ^a min.	$N (z' = 0)$	T_M $\times 10^2 M$	$[M]$ $\times 10^2 M$	$[D]$ $\times 10^2 M$	$K_D \times 10^2$
8	1.72	9.23	1.50	3.86	1.71
16	1.70	9.13	1.61	3.76	1.45
24	1.70	9.06	1.60	3.73	1.46
8	1.61	6.33	1.53	2.40	1.02
16	1.63	6.22	1.41	2.41	1.21
24	1.67	6.11	1.21	2.45	1.68
8	1.59	3.40	0.88	1.26	1.64
16	1.60	3.32	.83	1.25	1.81
24	1.59	3.26	.84	1.21	1.71
8	1.37	1.71	.79	0.46	0.75
16	1.39	1.65	.72	.46	0.88
24	1.42	1.59	.65	.47	1.11

Av. $K_D = 137 \pm 30$; av. $\log K_D = 2.14 \pm 0.08$.

^a Time = time of centrifugation.

because too small a gradient was observed even at the maximum operating speed of the centrifuge.

The data in Table IX show that there is a systematic increase in the values of N as the Zr(IV)-chelate concentration is increased. This suggests that the system is polydisperse, since an opposite trend would normally be expected for a monodisperse system, due to increased nonideality with corresponding increases in polymer concentrations.

If the assumption is made that the Zr(IV)-HEDTA system is composed of a mixture of monomers and dimers, the following equations represent the solution equilibria

$$K_D = [D]/[M]^2$$

$$T_M = [M] + 2[D]$$

$$N = T_M/([M] + [D])$$

Here K_D represents the equilibrium constant for the reaction of monomers $[M]$ to form binuclear chelates $[D]$; T_M represents the total molar concentration of metal species in both forms as calculated from ultracentrifugation data obtained at the upper phase boundaries. The relative constancy of the values of K_D (Table IX) over a sixfold range of chelate concentration is consistent with the assumption that a mixture of mononuclear and binuclear chelates exists in the concentration range studied.

Zr(IV)-EDTA-Tiron.—The data obtained upon ultracentrifugation of this mixed chelate are presented in Table X. Each value of N represents the average of

TABLE X
CALCULATED VALUES OF N AS A FUNCTION OF z' FOR Zr(IV)-
EDTA-TIRON CHELATES IN 1.200 M NaCl AT 25°

Zr(IV) concn. $\times 10^2 M$	$N (z' = 3)$	$N (z' = 4)$	$N (z' = 5)$
8.53	1.07	1.41	2.29
5.87	1.06	1.32	1.84
4.29	1.00	1.19	1.51
2.39	0.98	1.10	1.28
1.19	0.94	1.02	1.13

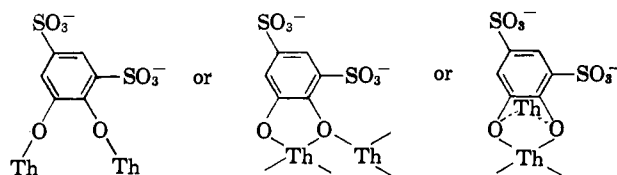
the three sets of data obtained at the upper phase boundaries in each experiment. Because of the difficulty encountered in attempting to extrapolate the dn^*/dx vs. x plots to the lower phase boundaries, the results of calculations are not shown for these data. The upward trend of N values at $z' = 4$, which is the charge per monomer unit of this mixed chelate, suggests that the system contains a mixture of mononuclear and binuclear species. This is in agreement with the results of Intorre and Martell,¹⁶ who have calculated dimerization constants from potentiometric data. Cal-

culatation of dimerization constants from our ultracentrifugation data produced values of K_D which drifted upward over a wide range as the chelate concentration increased.

Discussion

The most interesting observation with respect to the results of this investigation is that polydentate ligands containing alcoholic or phenolic groups show a remarkable tendency to combine with metal ions to form polynuclear chelates. Similar tendencies have been noted previously in the cases of dimerization of Fe(III), UO₂(VI), and Th(IV) chelates of 8-hydroxyquinoline-5-sulfonate¹⁹ and in the trimerization of UO₂(VI)-Tiron chelates.²⁰ It has been suggested previously on the basis of entropy of dimerization calculations^{21,22} that the formation of binuclear chelates of Cu(II)-dihydroxyethylethylenediamine takes place through alkoxy bridges. The tendency for Fe(III)-N-hydroxyethylethylenediamine triacetate chelates to hydrolyze and polymerize in the range pH 3-4 indicates that the hydroxyethyl groups act as bridging groups in this case also.²²

Previous ultracentrifugation experiments on the 1:1.5 Th(IV)-Tiron system¹⁰ proved the presence of a binuclear 2:3 chelate at low pH. Presumably polymerization can only take place in this case by means of phenolate bridges of the types



rather than by hydroxo bridges.

Since the ultracentrifugation data show no evidence of polydispersity in the Th(IV)-HEDTA system, it appears quite certain that the degree of aggregation is six. Since, if the polymer were linear, there would seem to be no valid reason for the presence of hexamers as opposed to smaller or larger molecules, it is suggested that the polymer may be cyclic in nature. Each thorium ion is probably bound to its neighbor by means of an alkoxy bridge and, in addition, further bridging is effected by the four hydroxide ions which are bound per polymeric ion.

Although precise interpretation of the 1:1 Th(IV)-HEDTA-Tiron data is not possible, it seems probable that polymers of N greater than 3 are not formed despite the presence of a large number of potential bridging oxygen atoms. Previous results have shown that the 2:3 Th(IV)-Tiron binuclear chelate is completely formed at pH 5.5¹⁰ and that the hexameric Th(IV)-HEDTA chelate is completely formed at pH 7 and nearly completely formed at pH 5.5.¹⁴ Potentiometric evidence indicates that in equimolar solutions of Th(IV) ion, HEDTA, and Tiron, both ligands are bound to the metal ion at pH 5.5.¹⁴ It is possible that a mixture of species containing such forms as binuclear 2:3 Th(IV)-Tiron, polymeric Th(IV)-HEDTA, and monomeric or polymeric Th(IV)-HEDTA-Tiron chelates is present.

There is no immediately obvious reason for the striking differences between the nature of the polymeric chelates of Zr(IV)- and Th(IV)-HEDTA. In view of the generally greater hydrolytic tendencies of the

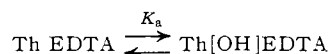
(19) C. F. Richard, R. L. Gustafson, and A. E. Martell, *J. Am. Chem. Soc.*, **81**, 1033 (1959).

(20) R. L. Gustafson, C. F. Richard, and A. E. Martell, *ibid.*, **82**, 1526 (1960).

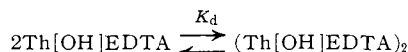
(21) R. L. Gustafson and A. E. Martell, *ibid.*, **81**, 525 (1959).

(22) R. L. Gustafson and A. E. Martell, *J. Phys. Chem.*, **67**, 576 (1963).

zirconium ion, it is surprising that the Zr(IV)-HEDTA chelate undergoes less hydrolysis and polymerization than its Th(IV) analog. This behavior is not completely without precedent, however. Whereas Bogucki and Martell²³ have calculated values of $pK_a = 7.04$ and $\log K_d = 4.3$ for the reactions



and



similar values obtained by Intorre and Martell¹⁶ for the hydrolysis and dimerization reactions of Zr(IV)-EDTA were $pK_a = 6.2$ and $\log K_d = 3.5$, respectively. Although the tendency toward hydrolysis of the Zr(IV)

(23) R. F. Bogucki and A. E. Martell, *J. Am. Chem. Soc.*, **80**, 4170 (1958).

chelate is greater than that of the Th(IV) compound, the latter chelate dimerizes to a greater extent. The observed behavior in the cases of both Zr(IV)-EDTA and Zr(IV)-HEDTA chelates may be due to steric effects (associated with the smaller size of the Zr(IV) ion) which make it more difficult for additional donor atoms to approach the central metal ion.

The behavior of the Zr(IV)-EDTA-Tiron system is similar to that of Zr(IV)-EDTA in that both apparently form binuclear complexes. In the latter case hydroxide ions serve as bridging groups, while in the case of the mixed chelate bridges are presumably formed through the use of the phenolate groups of the Tiron molecules. Comparison with the data of Intorre and Martell¹⁶ on these systems shows that the less basic phenolic groups of Tiron interact with the Zr(IV) ion at a lower pH than do the more basic hydroxide ions.

[CONTRIBUTION FROM THE DEPARTMENT OF CHEMISTRY, UNIVERSITY OF WISCONSIN, MADISON, WIS.]

The Kinetics of the Oxidation of Bis-(2,3-dimercapto-1-propanolato)-iron(II) by Cystine in Alkaline Solutions¹

BY D. L. LEUSSING² AND J. P. MISLAN

RECEIVED JUNE 20, 1963

In alkaline solutions containing an excess of DMP (2,3-dimercapto-1-propanol) one mole of cystine (CSSC) is reduced by two moles of $\text{Fe(II)(DMP)}_2^{-2}$ to give two moles of cysteine and two moles of the intense red Fe(III) complex of DMP. The principal reaction path consists of two steps: the first is the reaction of CSSC with DMP to give the mixed disulfide CSDMP, and the second involves the displacement of DMP coordinated to an Fe(II) nucleus by CSDMP. The mixed complex is involved in the electron transfer. This second step shows both a first- and a second-order dependence on Fe(II). A slow, parallel reaction in which CSSC reacts directly to give Fe(III)³ is also present. As an aid in verifying the mechanism and the values of the rate constants, the reactions were simulated with an analog computer.

Thiols are usually quantitatively oxidized to the disulfide by iron(III). This is the case for mercaptoacetate,³ which in coordinating metal ions serves as an oxygen-sulfur donor, but with cysteinate, which is a sulfur-nitrogen donor, the oxidized form cystine has been found to react with the iron(II) complex to form a low, but detectable, concentration of the iron(III) cysteinate.⁴ This reaction has been used to evaluate the potential of the cysteine-cystine couple.⁴

Finally, with the sulfur-sulfur donor, 2,3-dimercapto-1-propanol, the iron(III) mercaptide in alkaline solutions is found to be highly stable with regard to the oxidation of mercaptide to disulfide and reduction of iron(III) to iron(II).⁵

The kinetics of the iron(III) oxidations of mercaptoacetate and cysteinate have been studied and it was found in these reactions that the electron transfer proceeds via a bimolecular reaction between two iron(III) complexes.⁶⁻⁸ The activated complex apparently consists of a binuclear species in which two electrons are transferred from coordinated mercaptide groups to the two iron(III) nuclei. Similar reactions of this type involving a two-electron oxidation of coordinated ligands with the concomitant reduction of two metal ions have been reported.⁹⁻¹⁴ The iron(II)-DMP sys-

tem offers an opportunity of studying the reverse reaction where an oxidized form of a ligand may be reduced in a two-electron step by metal ions which undergo a one-electron oxidation. In the present work this process was studied by adding cystine to ammoniacal solutions of Fe(II) containing an excess of DMP and following the formation of the intense red Fe(III)-DMP complex spectrophotometrically at a wave length of 507 μ . Under these conditions Fe(II) is bound as the light red Fe(DMP)_2^{-2} ¹⁵ and Fe(III) forms the intensely colored species Fe(DMP)(OH) and $\text{Fe(DMP)(OH)(NH}_3\text{)}$.⁵

Experimental

The techniques used in conducting the kinetic studies under air-free conditions were similar to those previously described.^{5,8,15} In a typical experiment an ammonia buffer was placed in a reaction flask, the flask was capped, and the contents de-aerated. Aliquots of air-free partially neutralized DMP and ferrous ammonium sulfate solutions were added. The concentrations were adjusted so the final solution had a volume of 100 ml. and was 0.10 M in NH_4Cl .

A light red color was noted immediately on mixing, but it was found necessary to equilibrate the solutions for 12 hr. at 25.0° in order for the initial values of absorbance to become constant. The color changes apparently result from the fact that the iron(II)-DMP system is relatively slow to equilibrate: dark red polynuclear species¹⁵ appear to be formed rapidly on mixing. Traces of disulfides which are present initially also contribute to the absorbance. A typical initial absorbance at 507 μ is of the order of 0.1-0.2 unit.

(1) This work was supported by a grant from the National Science Foundation.

(2) To whom correspondence regarding this paper should be addressed: Department of Chemistry, The Ohio State University, Columbus, Ohio.

(3) R. Andreasch, *Ber.*, **12**, 1391 (1879).

(4) N. Tanaka, I. M. Kolthoff, and W. Stricks, *J. Am. Chem. Soc.*, **77**, 1996, 2004 (1955).

(5) D. L. Leussing and J. P. Mislán, *J. Phys. Chem.*, **64**, 1908 (1960).

(6) D. L. Leussing and L. Newman, *J. Am. Chem. Soc.*, **78**, 552 (1956).

(7) H. Lamfrom and S. O. Nielsen, *ibid.*, **79**, 1956 (1957).

(8) D. L. Leussing, J. P. Mislán, and R. J. Goll, *J. Phys. Chem.*, **64**, 1070 (1960).

(9) E. M. Kosower, "Molecular Biochemistry," McGraw-Hill Book Co., Inc., New York, N. Y., 1962, p. 157.

(10) J. H. Baxendale and D. T. Westcott, *J. Chem. Soc.*, 2347 (1959).

(11) P. Saffir and H. Taube, *J. Am. Chem. Soc.*, **82**, 13 (1960).

(12) K. Shug, VIIth International Coordination Chemistry Conference, Stockholm, 1962.

(13) D. L. Leussing and T. N. Tischer, "Reactions of Coordinated Ligands," D. Busch, Ed., *Advances in Chemistry Series*, No. 37, American Chemical Society, Washington, D. C., 1963.

(14) A. Haim and H. Taube, *J. Am. Chem. Soc.*, **85**, 495 (1963). These authors discuss some factors which may be important in deciding between one- and two-electron reactions of coordinated ligands.

(15) D. L. Leussing and J. Jayne, *J. Phys. Chem.*, **66**, 426 (1962).