ions in each polynuclear ion. This is in agreement with the results obtained by Gustafson and Martell[6] who employed a non-equilibrium ultracentrifugation technique to determine the degree of polymerization of the 1:1.5 Th(IV)-Tiron chelate. A polynuclearity of two has previously been reported by Bogucki and Martell[7] for the hydroxo-bridged thorium chelates of ethylenediaminetetraacetic acid (EDTA) and cyclohexanediaminetetraacetic acid (CDTA).

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

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

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

Ultracentrifugation of 1:1 Th(IV)-Diethylenetriaminepentaacetic Acid and 1:1.5 Th(IV)-Pyrocatechol-3,5-disulfonate Chelates[1,2]

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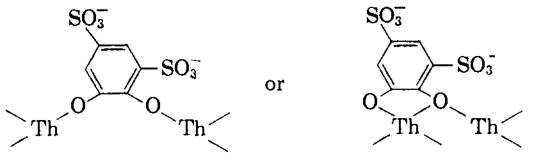
The application of ultracentrifuge measurements to the determination of molecular weights of charged metal chelates has been investigated using the 1:1Th(IV)-diethylenetriaminepentaacetate (DTPA) and 1:1.5 Th(IV)-pyrocatechol-3,5-disulfonate (Tiron) systems. The Archibald non-equilibrium method of determining 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* $NaNO_3$, was employed. The substitution of KNO_3 for $NaNO_3$ 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.*,[3,4] 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[5] have shown that the Th(IV)-DTPA chelate is completely formed at *p*H values as low as 1.5. In view of the fact that the chelate appears to be octadentate, completely satisfying the coördination 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[6] have shown that at *p*H 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 *p*H regions where the Th(IV) ion has been shown[7,8] 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 $(ThA_{1.5})_n$-$(H_2O)_x$, 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.[6]

In this research the Archibald non-equilibrium method of determining molecular weights as described by Klainer and Kegeles[9] has been applied to the methods of dealing with charged polymers as outlined by Johnson, *et al.*[3] 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

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[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).

electrolyte must be constant; (c) the density of the solution must be constant; (d) the activity coefficients of all species must be constant. In addition, it is assumed that the supporting electrolyte sediments in the same manner both in the presence of and in the absence of the polymeric component.

Experimental

Centrifugations.—Ultracentrifugation experiments were carried out with a Spinco Model E Ultracentrifuge. All photographs were made at a bar angle of 80° with Kodak Metallographic plates. The details of centrifugation and of measurements of the plates are precisely as described by Klainer and Kegeles.[9] Each experiment required three centrifugations. The first was carried out on a solution containing the metal chelate at an appropriate supporting electrolyte concentration. The second ultracentrifugation was carried out on the supporting electrolyte alone. In the latter case it was necessary to maintain the same temperature and speed of rotation and adjust the volume of solution so that the phase boundaries at the top and bottom of the cell were at precisely the same distance from the center of rotation as was the case in the centrifugation of the chelate solution. In both cases a false bottom of carbon tetrachloride was used to form the lower boundary. Photographs were taken at 8, 16 and 24 or 32 minutes after the rotor reached constant speed. The temperature was maintained at 25.0° and was measured before, during and after each centrifugation. In the first two centrifugations, a four degree, 12 mm. cell centerpiece was used, while in the third centrifugation, which was necessary to determine the initial concentration of the polymeric component in terms of refractive index units, a two degree, boundary-forming centerpiece, described by Kegeles,[10] was employed.

Reagents.—Thorium chloride was obtained from the Fairmount Chemical Co. and was dried for 12 hr. at 120°. The material was analyzed for thorium by precipitation of hydrolysis products with ammonia and subsequent ignition to ThO_2. Neutralization of the hydrogen ions liberated after addition of an excess of Tiron required only 1.97 moles of base per mole of metal ion whereas previous results by Murakami and Martell[6] showed that 3.00 moles of base were required to reach the first inflection at *p*H 5. Chloride analysis by the Mohr method showed that 2.97 moles of chloride were present per mole of Th(IV). In this analysis the thorium was removed by the use of a Dowex 50 ion-exchange column prior to the chloride determination. Thus, this partially hydrolyzed thorium salt was shown to correspond to the formula $Th(OH)_{1.03}Cl_{2.97}(H_2O)_{2.40}$. Baker's analyzed thorium nitrate was dried for several days at 85–90°. Direct ignition to ThO_2 showed that the salt corresponded to the formula $Th(NO_3)_4 \cdot 2.82\ H_2O$. Diethylenetriaminepentaacetic acid was obtained through the courtesy of the Dow Chemical Co. After a single recrystallization from water the material was dried at 120°. Potentiometric titration with standard KOH indicated the composition $DTPA \cdot 0.39\ H_2O$. The Tiron was obtained from the LaMotte Chemical Products Co., Baltimore, Md., and was dried at 120° for 12 hr. Potentiometric titration of this compound with standard KOH indicated the composition $Tiron \cdot 0.96\ H_2O$. Determination of the first equivalence point was accomplished by the method of Gran.[11] All 1:1 electrolytes employed were Fisher Certified Reagent grade.

The polymeric 1:1.5 Th(IV)-Tiron solutions were prepared in the following way. Weighed amounts of thorium salt and Tiron were rinsed into a calibrated 50 ml. volumetric flask with a 1.000 *M* NaCl solution of known density. The flask was weighed, after which standard NaOH–NaCl solution corresponding to 1.97 moles of hydroxide per gram-atom of thorium was added. This 1 *M* sodium hydroxide which was prepared from an aliquot of 16 *M* carbonate-free solution also contained sufficient NaCl such that the solution was 1.000 *M* in neutral salt. The flask was reweighed in order to determine the exact weight of NaOH–NaCl solution used. Finally the volume of solution was brought to 50 ml. with NaCl solution. From the data thus obtained plus the densities of the various solutions, it was possible to calculate the exact compositions of the polymeric solutions as well as the partial specific volumes of the polymeric electrolyte.

The preparation of the Th(IV)-DTPA solutions which were used in the determination of partial specific volumes was similar to that described above except that the solvent employed was 1.000 *M* $NaNO_3$ and no NaOH was added to neutralize the hydrogen ions produced upon chelate formation. Since two counter ions, H^+ and Na^+, were present in these solutions, they could not be used for the centrifugation experiments. For the latter purpose solutions were prepared containing weighed amounts of metal salt, ligand and supporting electrolyte as well as sufficient 2 *M* LiOH, NaOH or KOH to neutralize the hydrogen ions formed.

Determination of Partial Specific Volumes: Th-DTPA.—The reaction which takes place upon preparation of the thorium DTPA sample is

$$Th(NO_3)_4 \cdot 2.82H_2O + H_5A \cdot 0.39H_2O \rightleftarrows ThA^- + 5H^+ + 4NO_3^- + 3.21H_2O$$

The apparent molar volume of the products of the above reaction was calculated using the formula

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

where c is the molar concentration of Th(IV) (and hence of the product $HThA(HNO_3)_4(H_2O)_{3.21}$), M is the molecular weight of the combined products (931.25), ρ_0 is the density of the solvent and ρ is the density of the solution. Density measurements were carried out at 25.0° using a Rieschauer pycnometer. 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)-DTPA REACTION IN 1.000 *M* $NaNO_3$

Concn. Th(IV), $M \times 10^{-2}$	ρ (g./ml.)	ϕ_v (ml./mole)
1.856	1.06130	415.0
2.981	1.06680	417.1
4.142	1.07251	417.2
5.056	1.07722	413.3
6.762	1.08573	412.7
8.362	1.09377	411.7
	ρ_0 = 1.05212	

The experimental data fit the empirical equation

$$\phi_v\ (\text{products}) = 421.0 - 30.5\ c^{1/2}$$

within an 0.3% average deviation. The partial molar volumes of the products were calculated by the use of the expression

$$\bar{V}_{(\text{products})} = \phi_{v(\text{products})} + \left[\frac{1000 - c\phi_v}{2000 + c^{3/2}\ \partial\phi_v/\partial c^{1/2}}\right] c^{1/2}\ \partial\phi_v/\partial c^{1/2} \qquad (2)$$

where $\partial\phi_v/\partial c^{1/2} = -30.5$. The partial specific volumes, $\bar{v}$, of the lithium, sodium or potassium salts were calculated using the equation

$$\bar{v}_{\text{RThA}} = \frac{\bar{V}_{(\text{products})} - 5\bar{V}_{\text{HNO}_3} - 3.21\bar{V}\text{H}_2\text{O} + \bar{V}_{\text{RNO}_3}}{M} \qquad (3)$$

where R represents either Li, Na or K and *M* is the molecular weight of the chelate. The partial molar volumes of HNO_3, $LiNO_3$ and $NaNO_3$ at 25° are not available but were calculated from available data[12] using the equation

$$\bar{V}_{\text{RNO}_3} = \bar{V}_{\text{KNO}_3} + \bar{V}_{\text{RCl}} - \bar{V}_{\text{KCl}}$$

The values of $\bar{V}_{(\text{products})}$ obtained in 1 *M* $NaNO_3$ solutions were assumed to be valid under varying conditions of concentration and type of supporting electrolyte.

Th(IV)-Tiron (1:1.5).—The molecular weight of the Th(IV)-Tiron monomer unit $ThA_{1.5}$ is 677.43. The reaction which apparently takes place upon preparation of the

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(10) G. Kegeles, THIS JOURNAL, 74, 5532 (1952).

(11) G. Gran, *Analyst*, 77, 661 (1952).

(12) H. S. Harned and . B. Owen, "The Physical Chemistry of Electrolytic Solutions," 2 Ed., Reinhold Publ. Corp., New York, N. Y., 1950.

chelate sample is

$$Th(OH)_{1.03}Cl_{2.97}(H_2O)_{2.40} + 1.5C_6H_2(OH)_2(SO_3)_2 \cdot 2Na + 1.97\ NaOH \rightleftarrows (Th(C_6H_2O_2)(SO_3)_2)_{1.5} \cdot 2Na + 2.97NaCl + 5.40H_2O$$

The experimental values of ϕ_v as a function of the Th(IV) concentration are listed in Table II.

The above data fit the empirical equation

$$\phi_v(\text{products}) = 359.8 - 93.2c^{1/2}$$

within a 1% deviation.

TABLE II

DETERMINATION OF APPARENT MOLAR VOLUME OF THE PRODUCTS OF THE Th(IV)-TIRON–NaOH REACTION IN 1.000 M NaCl

Conc. Th(IV), $M \times 10^{-2}$	ρ (g./ml.)	ϕ_v (ml./mole)
1.278	1.04455	351.3
1.719	1.04729	342.3
2.464	1.05155	348.5
3.558	1.05834	338.5
4.202	1.06185	346.2
6.226	1.07454	334.4
	ρ_0 = 1.03709	

Mathematical Treatment of Data

Treatment of Three Component Systems.—The equilibrium distribution of a component in a centrifugal field may be defined by the equation[13]

$$\frac{\mathrm{d}\ln a}{\mathrm{d}(x^2)} = \frac{M(1 - \bar{v}\rho)\omega^2}{2RT} = \frac{L\omega^2}{2RT} = A \qquad (4)$$

where a is the activity of the polymer, x the distance from the center of rotation, M the molecular weight, $\bar{v}$ the partial specific volume, ρ the solution density, ω the angular velocity, R the molar gas constant and T the absolute temperature.

Johnson, *et al.*,[3] have derived a series of equations permitting the estimation of the degree of polymerization, N, as a function of the assumed charge, z', per monomer unit. They have simplified the calculations by defining the polymeric component (component 2) as having the formula $PX_{z/2}B_{-z/2}$ where P is the polymeric ion, X is the counter ion, BX is the supporting electrolyte and z is the charge of the polymeric ion. Thus the polymeric component has a molecular weight $M_2 = M_{PX_z} - (z/2)M_{BX}$ where M_{PX_z} is the molecular weight of the polymer and M_{BX} that of the supporting electrolyte. The supporting electrolyte, BX, will be referred to as component 3. Its concentration c_3 may be expressed by the equations

$$c_3 = c_B + (z/2)c_2 \qquad (5a)$$

$$c_3 = c_X - (z/2)c_2 \qquad (5b)$$

If it is assumed that the activity coefficients remain constant throughout the cell, it follows that by the use of equations 4, 5a and 5b that

$$\frac{\mathrm{d}\ln a_2}{\mathrm{d}(x)^2} = \frac{\mathrm{d}\ln c_P c_X{}^{z/2} c_B{}^{-z/2}}{\mathrm{d}(x^2)}$$

$$= \frac{\mathrm{d}\ln c_2 + (z\eta/(1 - \eta^2))(\mathrm{d}\ln c_2 \text{-} \mathrm{d}\ln c_3)}{\mathrm{d}(x^2)} = A_2 \qquad (6)$$

where $\eta = zc_2/2c_3$.

If it is assumed that $1 - \eta^2 = 1$, equation 6 may be written in the form

$$N = \frac{\mathrm{d}\ln c_2'/\mathrm{d}(x^2)}{A_2' - z'\eta(\mathrm{d}\ln c_2'/\mathrm{d}(x^2) - \mathrm{d}\ln c_3/\mathrm{d}(x^2))} \qquad (7)$$

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

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

$$\eta = z'c_2'/2c_3 = 1/(1 + 2c_B/z'c_2')$$

Here the primed symbols refer to the monomer unit according to the relationships $NM_{PX_z}' = M_{PX_z}$ and $z' = z/N$. M_{PX_z}' and $\bar{v}_{PX_z}$ represent the molecular weight and partial specific volume of the monomer unit, PX_z, whereas M_{BX} and $\bar{v}_{BX}$ represent the same quantities for the supporting electrolyte, BX.

Although equation 7 is useful for treating data from equilibrium ultracentrifugations, it is difficult to apply to nonequilibrium data because of the difficulty in determining the slope $\mathrm{d}\ln(1/x)(\mathrm{d}c_2'/\mathrm{d}x)/d\,(x^2)$ (which may be shown to be equal to $\mathrm{d}\ln c_2'/\mathrm{d}(x^2)$)at the upper and lower phase boundaries. However, since $\mathrm{d}\ln c_2'\mathrm{d}(x^2) = (\mathrm{d}c_2'/\mathrm{d}x)/2c_2'x$, equation 7 may be written as

$$\frac{(\mathrm{d}c_2'/\mathrm{d}x)/2c_2'x}{A_2' - z'\eta((\mathrm{d}c_2'/\mathrm{d}x)/2c_2'x - (\mathrm{d}c_3/\mathrm{d}x)/2c_3x)} \qquad (8)$$

If it is assumed that neglect of the quantity $(\mathrm{d}c_3/\mathrm{d}x)/2c_3x$ results in an insignificant change in N, equation 8 reduces to

$$N = \frac{1}{2A_2'c_2'x/(\mathrm{d}c_2'/\mathrm{d}x) - z'\eta} \qquad (9)$$

Treatment of Four Component Systems.—Johnson, *et al.*,[3] have defined the polymeric component in the presence of two supporting electrolytes as having the formula $PX_{z/2}B_{-zc3/2(c_3+c_4)}C_{-zc_4/2(c_3+c_4)}$ where P is the polymeric ion, X is the counter ion and BX and CX are the supporting electrolyte components 3 and 4, respectively. Component 2 has a molecular weight, M_2 expressed by

$$M_2 = M_{PX_z} - (cz_3/2(c_3 + c_4))M_{BX} - (zc_4/2(c_3 + c_4))M_{CX}$$

The concentrations of the various species are given by the equations

$$c_P = c_2 \qquad (10a)$$

$$c_B = c_3 - zc_2c_3/2(c_3 + c_4) \qquad (10b)$$

$$c_C = c_4 - zc_2c_4/2(c_3 + c_4) \qquad (10c)$$

$$c_X = c_3 + c_4 + zc_2/2 \qquad (10d)$$

Treatment of equation 4 in an analogous manner to that applied in the case of the three component system gives

$$N = \frac{1}{2A_2'c_2'x/(\mathrm{d}c_2'/\mathrm{d}x) - z'\eta^*} \qquad (11)$$

where

$$\eta^* = z'c_2'/2(c_3 + c_4)$$

Here

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

$$L_2' = M_{PX_z}'(1 - \bar{v}_{PX_z}\,\rho) - (z'c_3/2(c_3 + c_4))M_{BX}(1 - \bar{v}_{BX}\rho) - (z'c_4/2(c_3 + c_4))M_{CX}(1 - \bar{v}_{CX}\rho)$$

$$c_3 = c_B/(1 - z'c_2'/2(c_3 + c_4)$$

and

$$c_4 = c_C/(1 - z'c_2'/2(c_3 \times c_4)$$

In order to solve equations 9 and 11, it is necessary to evaluate the quantity c_2'. Klainer and Kegeles[9] have that

$$c_2'(\text{top}) = c_0 - \frac{1}{x_0{}^2}\int_{x_0}^{X} x^2(\mathrm{d}c_2'/\mathrm{d}x)\mathrm{d}x \qquad (12)$$

$$c_2'(\text{bottom}) = c_0 + \frac{1}{x_b{}^2}\int_{X}^{x_b} x^2(\mathrm{d}c_2'/\mathrm{d}x)\mathrm{d}x \qquad (13)$$

where the notations c_2'(top) and c_2'(bottom) refer to concentrations of polymeric solute at the top and bottom phase boundaries, respectively, x_0 and x_b are the distances of the top and bottom phase boundaries from the center of rotation and X is the coördinate in the x direction on the photographic plate at which $\mathrm{d}c_2'/\mathrm{d}x$ is equal to zero. The quantity c_0 of equations 12 and 13 is determined by integration of a refractive index gradient picture obtained using the two degree boundary forming cell according to the equation

$$c_0 = \int_{x_0}^{x_b}(\mathrm{d}c_2'/\mathrm{d}x)\mathrm{d}x \qquad (14)$$

In practice the Philpot–Svensson optical system records a plot of $\mathrm{d}n/\mathrm{d}x$ *versus* x, where n is the refractive index, on the photographic plate. The values of $\mathrm{d}n/\mathrm{d}x$ for the supporting electrolyte centrifugation are subtracted from the corresponding values for the polymer centrifugation to yield the contribution of the polymeric component alone, $\mathrm{d}n^*/\mathrm{d}x$. The values of $\mathrm{d}n^*/\mathrm{d}x$ obtained by extrapolation of refractive index gradient data to the upper and lower

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(13) T. Svedberg and K. O. Pedersen, "The Ultracentrifuge," The Clarendon Press, Oxford, 1940.

phase boundaries, x_0 and x_b, are used in place of dc_2'/dx in equations 9 and 11. This makes it necessary to express the term c_2' in terms of refractive index units rather than molar concentration. For this purpose equations 12, 13 and 14 may be integrated with the aid of the approximate expressions

$$c_2'(\text{top}) = c_0 - \frac{0.03}{Fx_0^2}\sum_{x=0}^{X} x^2(dn^*/dx) \qquad (12a)$$

$$c_2'(\text{bottom}) = c_0 + \frac{0.03}{Fx_b^2}\sum_{x=X}^{b} x^2(dn^*/dx) \qquad (13a)$$

$$c_0 = \frac{0.03}{F}\sum_{x_0=0}^{x} (dn/dx) \qquad (14a)$$

Here $F = 2.18$ is the magnification factor and 0.03 cm. is the length of the increments along the x coördinate.

In order to calculate η and η^*, one must be careful to keep the units of concentration of c_2' and c_3 the same. Here the molarity scale is more convenient and c_2' may be calculated using the proportionality

$$\frac{c_2'(\text{moles/liter})}{\text{Initial Th(IV) conc.}} = \frac{c_2'(\text{refractive index units})}{c_0} \qquad (15)$$

In connection with equation 15, it has been assumed that the concentrations of supporting electrolytes c_3 and c_4 are the same throughout the cell and equal to the initial concentration.

Results and Discussion

Th(IV)-DTPA.—In Fig. 1 values of the degree of polymerization N are plotted against the assumed charge z' per monomer unit for a series of five experiments in which the concentration of Th(IV)-DTPA was varied over more than an eight fold range while the sodium nitrate concentration was maintained constant at 1.000 M. Since the chelate is undoubtedly monomeric with charge −1 a unique intersection of the plots is to be expected at the point corresponding to these values. In practice this is not observed and the values of N are approximately 10% lower than expected at $z' = 1$. The results of Table III show that (disregarding experiment 1, the results of which agree with 2–5, when calculated from data obtained at the lower meniscus but differ from the average by 15% at the upper meniscus) $N = 0.82 \pm 0.02$ at $z' = 0$ and $N = 0.90 \pm 0.02$ at $z' = 1$. Whereas for many polyelectrolytes such as proteins the addition of neutral salts often completely eliminates charge effects in molecular weight determinations, in the present case roughly a 20% error is introduced if charge effects are ignored. The surprising result is the low value obtained for N when the actual charge of the chelate is accounted for in the calculations. Certainly in the 1 molar supporting electrolyte medium any variations in the activity coefficients of the chelate would be expected to be small, and even in the case of experiment 5 where the chelate to neutral salt ratio is the least favorable, the quantity $(1 - \eta^2)$ which was assumed to be equal to unity is actually equal to 0.998 when $z' = 1$.

TABLE III

CALCULATED VALUES OF N AS A FUNCTION OF z' FOR Th(IV)-DTPA CHELATES IN 1.000 M NaNO$_3$

Exp.	Conc. Th-DTPA, $M \times 10^2$	$N(z' = 0)$	$N(z = 1)$
1	1.008	0.88 ± 0.06	0.94 ± 0.06
2	1.957	.82 ± .02	.89 ± .02
3	3.538	.82 ± .02	.89 ± .02
4	5.801	.80 ± .01	.87 ± .01
5	8.693	.84 ± .01	.93 ± .01

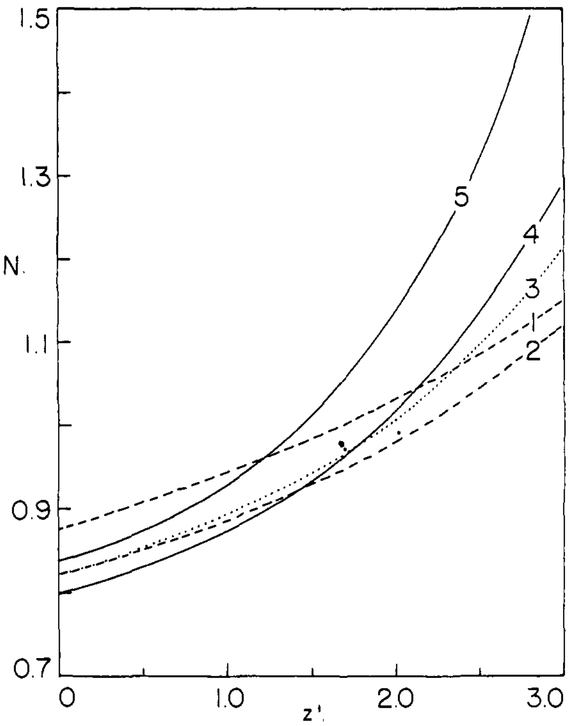

Fig. 1.—Centrifugation of 1:1 Th(IV)-DTPA chelates in 1.000 M NaNO$_3$. Initial chelate concentrations: 1, 1.01 × 10^{-2}; 2, 1.96 × 10^{-2}; 3, 3.54 × 10^{-2}; 4, 5.80 × 10^{-2}; 5, 8.69 × 10^{-2} M.

It was considered desirable to check the effect of varying the supporting electrolyte concentration on the calculated values of N. Accordingly a series of experiments were carried out in which the chelate concentration was maintained at approximately 3.5 × 10^{-2} M and the NaNO$_3$ concentration was varied from 1.35 × 10^{-1} to 2.000 M. The lower salt concentration was the smallest which could be used since some NaNO$_3$ is produced when the chelate is prepared. The results of these experiments are plotted in Fig. 2 and the average values of N at z' values of 0 and 1 are presented in Table IV. Here it will be noticed that an increase in supporting electrolyte concentration to 2 M does not improve the results but actually produces a slightly lower calculated value of N. On the other hand reduction of the NaNO$_3$ concentration below 1 M results in an increase in the calculated values of N although a smooth cor-

TABLE IV

CALCULATED VALUES OF N AS A FUNCTION OF z' FOR Th(IV)-DTPA CHELATES AT VARIOUS NaNO$_3$ CONCENTRATIONS

Exp.	Conc. Th-DTPA, $M \times 10^2$	Conc. NaNO$_3$, M	$N(z' = 0)$	$N(z' = 1)$
6	3.368	0.135	0.83 ± 0.03	0.99 ± 0.03
7	3.585	.250	.82 ± .01	.94 ± .01
8	3.276	.500	.84 ± .02	.94 ± .02
3	3.538	1.000	.82 ± .02	.89 ± .02
9	3.415	2.000	.81 ± .01	.87 ± .01

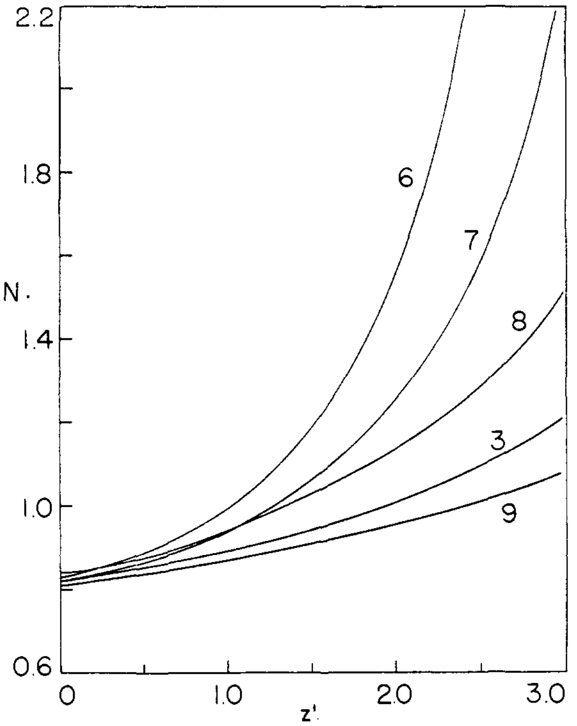

Fig. 2.—Centrifugation of 3×10^{-2} M Th(IV)-DTPA solutions at various $NaNO_3$ concentrations. Salt concentrations: 6, 0.135; 7, 0.250; 8, 0.500; 3, 1.000; 9, 2.000 M.

relation of N with $NaNO_3$ concentration is not obtained.

Pedersen[14] has discussed the effects of charge upon sedimentation in the ultracentrifuge and has shown that two types of salt effects must be considered. The "primary charge effect" is produced as a result of the different sedimentation tendencies of the heavier macro ion and the lighter counter ion, the net result being an increased degree of sedimentation for the counter ion and a lesser degree for the macro ion. The addition of neutral salt to the polymeric electrolyte reduces the intensity of the electric field about the sedimenting species such that as the ratio PX_z/BX approaches zero, the value of the calculated molecular weight approaches M_{PX_z}. This effect is commonly termed the "primary salt effect." The addition of neutral salt produces the "secondary salt effect" which is observed when the supporting electrolyte is composed of ions which have different sedimentation coefficients s. The limiting value of the calculated molecular weight of the chelate salt, PX_z, is dependent upon the nature of the supporting electrolyte and will be equal to M_{PX_z} only if B^+ and X^- (or B^- and X^+) have equal values of s. The degree of disparity will be proportional to $|s_{\text{cation}} - s_{\text{anion}}|$. In the case of a macro ion of negative charge, the calculated molecular weight will be less than M_{PX_z} if the sedimentation constant of the counter cation is less than that of the anion and will be greater than M_{PX_z} if the sedimentation constant of the anion is less than that of the cation of the supporting electrolyte.

In Table V are presented values of sedimentation constants at 25° as given by Pedersen[14] for several monovalent ions. From these data it may be seen that in $NaNO_3$ s_{25} for NO_3^- is 0.121 Svedberg units greater than that for Na^+. Thus it is seen that the limiting calculated value for the molecular weight of Th(IV)-DPTA should be less than the actual value.

TABLE V

SEDIMENTATION CONSTANTS (IN SVEDBERG UNITS) FOR MONOVALENT IONS AT 25°

Ion	s_{25°
Li^+	0.033
Na^+	.131
K^+	.239
Cl^-	.144
NO_3^-	.252
Br^-	.462
I^-	.747

In Table VI are given values of N calculated from solutions which were 1.000 M in Li, Na or K salts and approximately 3.5×10^{-2} M in Th(IV)-DTPA. Also listed are values of Δs_{25} for the supporting electrolytes employed. Here it would be expected that because of the secondary salt effect the calculated values of N should decrease with respect to salt type in order $KNO_3 > LiCl \sim NaNO_3 > NaBr > KI$. Although the experimental deviations are rather large, the results shown in Table VI conform roughly to the predicted order. However, the average value of N obtained at $z' = 0$ in KNO_3 is 11% lower than expected from such an electrolyte, suggesting that the primary charge effect has not been completely masked even in 1 molar supporting electrolyte.

TABLE VI

EFFECT OF SALT TYPE ON THE CALCULATED VALUE OF N FOR Th(IV)-DTPA CHELATES. TOTAL NEUTRAL SALT = 1.000 M; t = 25.0°

Exp.	Conc. chelate, $M \times 10^2$	Salt	Conc., M	Δs_{25}	$N(z' = 0)$
10	3.271	KNO_3	(1.000)	0.013	0.89 ± 0.05
11	3.371	LiCl	(0.865)	.111	.91 ± .05
		$LiNO_3$	(0.135)	.219	
3	3.538	$NaNO_3$	(1.000)	.121	.82 ± .02
12	3.316	NaBr	(0.867)	.331	.82 ± .06
		$NaNO_3$	(.133)	.121	
13	3.353	KI	(.866)	.508	.85 ± .06
		KNO_3	(.134)	.013	

Th(IV)-Tiron (1:1.5).—The values of N as a function of z' are illustrated graphically in Fig. 3 for the sedimentation of 1:1.5 Th(IV)-Tiron chelates in 1 M sodium chloride. Since Δs_{25} for NaCl is only 0.013, a negligible secondary salt effect is to be expected. Each curve in Fig. 3 represents the average of the six experimental points obtained at each Th(IV) concentration employed. The unique intersection of curves 1,2,4 and 6 at $z' \sim 3$ and $N \sim 2.4$ suggests that the degree of polymerization and the electronic charge are both greater than 2. Although the charge on the $Th(Tiron)_{1.5}$ monomer unit is −2, it is possible that in the medium employed the actual charge is greater because of chloro complexing.

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[14] K. O. Pedersen, *J. Phys. Chem.*, **62**, 1282 (1958).

Waggener and Stoughton[15] have shown that in a solution 1.00 *M* in chloride ion, the distribution of chloro-thorium (IV) complexes is such that an average of 0.8 chloride ions are bound per metal ion. If the affinity of the thorium-Tiron chelate for chloride ions is as great as that of the aquo ion, an average charge of −2.8 per monomer would exist. Actually it is to be expected that the affinity for additional donor groups would be far less for the chelated thorium ion than for the aquo ion. Therefore, the anticipated charge per monomer unit would be expected to be only slightly in excess of 2. Even if z' were approximately 3, the plots in Fig. 3 indicate that the species is most probably a dimer. The wide divergence of the curves at $N = 4$ suggests the improbability of the presence of tetramers of $\mathrm{Th(Tiron)_{1.5}}$.

The effect of varying supporting electrolyte concentration upon the calculated values of *N* may be seen in the data of Table VIII. A decrease in the value of *N* when $z' = 2$ was observed as the concentration of supporting electrolyte was increased. A similar trend was observed in the centrifugation of the 1:1 Th(IV)-DTPA chelates, although in the latter case it could be explained qualitatively in terms of the secondary salt effect since $NaNO_3$ was the supporting electrolyte employed. In the Th(IV)-Tiron experiments using NaCl, no immediate explanation for the observed salt effects is apparent.

TABLE VII

CALCULATED VALUES OF *N* AS A FUNCTION OF z' FOR 1:1.5 Th(IV)-TIRON CHELATES IN 1 *M* NaCl

Exp.	Conc. Th(IV), $M \times 10^2$	$N(z' = 0)$	$N(z' = 2)$
1	0.528	1.96	2.19
2	1.278	1.84	2.11
3	1.719	1.65	1.91
4	2.464	1.60	1.91
5	3.558	1.64	2.01
6	4.202	1.46	1.81
7	6.226	1.62	2.14

TABLE VIII

CALCULATED VALUES OF *N* AS A FUNCTION OF z' FOR 1:1.5 Th(IV)-TIRON CHELATES AT VARIOUS NaCl CONCENTRATIONS

Exp.	Conc. Th(IV), $M \times 10^2$	Conc. NaCl, *M*	$N(z' = 0)$	$N(z' = 2)$
8	2.899	0.156	1.40 ± 0.03	3.03 ± 0.40
9	2.342	0.594	1.76 ± .05	2.25 ± .13
4	2.464	1.014	1.60 ± .14	1.91 ± .24
10	2.861	4.175	1.42 ± .09	1.56 ± .10

It was considered desirable to check the validity of some of the approximations made in the derivation of the equations. A check of the constancy of $(1 - \bar{v}\rho)$ in experiment 1 showed that there was a difference of less than 0.3% between values obtained at the two boundaries. In the other experiments the deviations were even less. Although $(dc_3/dx)/c_3$ is actually approximately 10% of $(dc_2'/dx)c_2'$, neglect of the former term introduces only an 0.2% error in the calculated value of *N*. The quantity $1 - \eta^2$, which was assumed to be equal to unity, may be shown to be equal to more than 0.99 in all experiments performed in 1 *M* NaCl. In addition inclusion of this term merely results in converting $z'\eta$ to $z'\eta/(1 - \eta^2)$ in equation 11, the net result being an error of less than 0.1% in *N*. Hence it may be seen that the assumptions involved in the derivation of the equations introduce only small errors in the calculation of *N*.

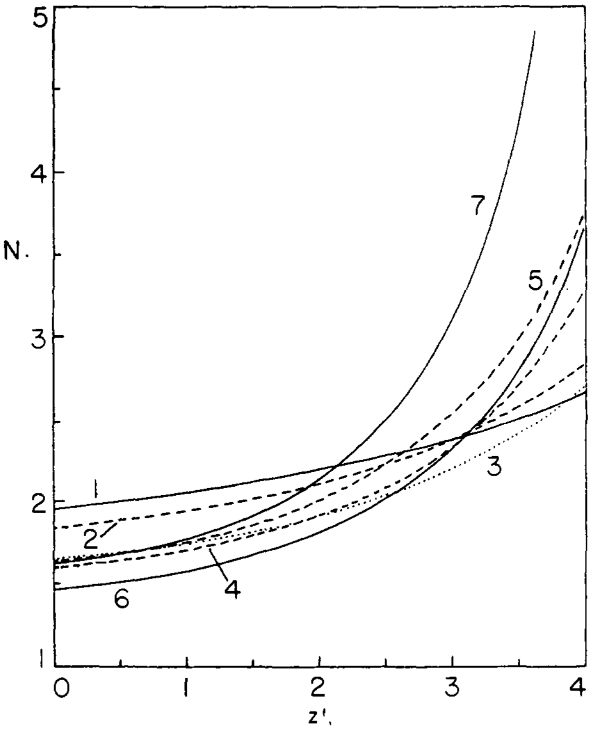

Fig. 3.—Centrifugation of 1:1.5 Th(IV)-Tiron system in 1 *M* NaCl. Initial Th(IV) concentrations: 1, 5.28×10^{-3}; 2, 1.28×10^{-2}; 3, 1.72×10^{-2}; 4, 2.46×10^{-2}; 5, 3.56×10^{-2}; 6, 4.20×10^{-2}; 7, 6.23×10^{-2} *M*.

The chief causes of discrepancies between calculated and anticipated values of molecular weights of charged polyelectrolytes are due chiefly to primary salt effects, secondary salt effects and lack of constancy of activity coefficient derivatives, $d\gamma/dx$. In 1 *M* NaCl at 25° $d\gamma/dc$ is approximately zero. Thus, changes in supporting electrolyte concentrations will result in relatively small changes in values of the activity coefficients in this medium. Coupled with the fact that secondary salt effects are small in NaCl, it is perhaps not surprising that the average calculated degree of aggregation of 1:1.5 Th(IV)-Tiron chelates is very close to the even, integral value of 2.0. In the $NaNO_3$ medium, not only are secondary salt effects considerable, but a plot of activity coefficient *vs.* $NaNO_3$ concentration shows a significant slope at 1 *M* salt concentration at 25°. The adverse effects probably contribute appreciably to the low values of molecular weight calculated for Th(IV)-DPTA in $NaNO_3$.

In conclusion it may be stated that the determination of the degree of aggregation of charged polymeric chelates may be calculated within

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(15) W. C. Waggener and R. W. Stoughton, *J. Phys. Chem.*, **56**, 1 (1952).

relatively close limits provided the charge per monomer unit is known. In most cases involving monodisperse chelate systems, the value of the charge may be determined from potentiometric titration data, although some ambiguity exists if there is the possibility of complexing by chloride or other negative ions. Since the calculation of N is often rather insensitive to changes in the value of the assumed charge per monomer unit, z', it is difficult to determine the charge with any degree of certainty from ultracentrifugation data. Conversely it is possible to obtain a good approximation to the molecular weight of a species even though its charge is unknown provided that the charge is of small magnitude, *i.e.*, approximately 2.

[CONTRIBUTION FROM THE NOYES CHEMICAL LABORATORY, UNIVERSITY OF ILLINOIS, URBANA, ILLINOIS]

Some Disubstituted Aminolysis Products of Tetrameric Phosphonitrilic Chloride

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The interaction of tetrameric phosphonitrilic chloride with aliphatic, aromatic or heterocyclic amines in mole ratio 1:2 or 1:4 yields the corresponding disubstituted aminolysis products. Nuclear magnetic resonance spectra suggest that the two substituents are in *trans* ring positions. The properties of these compounds are described.

Although a variety of partially substituted amine derivatives of trimeric phosphonitrilic chloride have been described,[1-7] considerably less is known about those of tetrameric phosphonitrilic chloride. Most of the derivatives of the tetramer have been obtained by using the corresponding partially substituted reactants in the initial synthesis reaction rather than by direct substitution.[8-12] Tetrameric phosphonitrilic chloride itself has been used directly only in the synthesis of completely substituted derivatives with aniline,[13] dimethylamine,[6] ethyleneimine,[14] methoxyl[15] and isothiocyanate[16] and of partially substituted derivatives with ammonia.[17] It is probable that both the reduced availability of the tetrameric chloride and its somewhat enhanced reactivity have limited studies of this type.

It has been found possible, however, to obtain disubstituted aminolysis products by using

1. Mixed solvents, *e.g.*, ether-water or benzene-water, and (a) treating the phosphonitrilic chloride dissolved in the organic liquid with standardized aqueous solutions of the amine hydrochloride and potassium hydroxide

$$(PNCl_2)_4 + 2R_2NH_2Cl + 4KOH \longrightarrow P_4N_4Cl_6(NR_2)_2 + 4KCl + 4H_2O$$

or (b) treating the phosphonitrilic chloride with the free amine in the mole ratio 1:4 and employing the water to remove the amine hydrochloride formed

$$(PNCl_2)_4 + 4R_2NH \longrightarrow P_4N_4Cl_6(NR_2)_2 + 2R_2NH_2Cl$$

2. Anhydrous media, *e.g.*, ether, benzene or acetonitrile, and adding to a well-stirred, refluxing solution of the amine a diluted solution of tetrameric phosphonitrilic chloride in the mole ratio 4:1

$$(PNCl_2)_4 + 4R_2NH \longrightarrow P_4N_4Cl_6(NR_2)_2 + 2R_2NH_2Cl$$

In the first procedure, removal of by-products and hydrolysis products is facilitated by their water

TABLE I

INFRARED DATA FOR TETRAMERIC PHOSPHONITRILES

Compound	Solvent	Frequency, cm.$^{-1}$	Interpretation	Ref.
$P_4N_4Cl_8$	CS_2	1315	P = N stretch	18
$P_4N_4Cl_6(NHCH_3)_2$	Nujol mull	1310	P = N stretch	
$P_4N_4Cl_6[N(CH_3)_2]_2$	$CHCl_3$	1310	P = N stretch	
$P_4N_4Cl_6(NHC_2H_5)_2$	CS_2	1310	P = N stretch	
$P_4N_4Cl_6[NHC(CH_3)_3]_2$	CS_2	1312	P = N stretch	
$P_4N_4Cl_6(NHC_6H_5)_2$	Nujol mull	1225 1287		
$P_4N_4Cl_6[N(CH_3)(C_6H_5)]_2$	CS_2	1308	P = N stretch	
$P_4N_4Cl_6(o\text{-}NHC_6H_4CH_3)_2$	Nujol mull	1232 1258		
$P_4N_4Cl_6(m\text{-}NHC_6H_4CH_3)_2$	Nujol mull	1275		
$P_4N_4Cl_6(p\text{-}NHC_6H_4CH_3)_2$	CH_3CN	1220 1275		
$P_4N_4Cl_6[N(CH_2CH_2)_2O]_2$	$CHCl_3$	1315	P = N stretch	
$P_4N_4Cl_6(NC_5H_{10})_2$	Nujol mull	1310	P = N stretch	
$P_4N_4(NHC_6H_5)_8$	Nujol mull	1214 1260		[a]
$P_4N_4[N(CH_3)_2]_8$	?	1209 1265		15

[a] Prepared according to ref. 13.

TABLE II

NUCLEAR MAGNETIC RESONANCE SPECTRA

Compound	Chemical shift, p.p.m. (reference H_3PO_4)	Solvent	RF frequency, Mc.
$P_4N_4Cl_6(NHC_6H_5)_2$	+2.4, +4.6, +7.1; +11.0, +13.5, +16.4	$(C_2H_5)_2O$	16.2
$P_4N_4Cl(n\text{-}NHC_6H_4CH_3)_2$	+3.3, +5.6, +7.9; +11.2, +13.5, +14.9	$(C_2H_5)_2O$	16.2
$P_4H_4Cl_6(o\text{-}NHC_6H_4CH_3)_2$	+4.4, +5.9, +7.5; +9.7, +11.6, +12.3	$(C_2H_5)_2O$	16.2

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