

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

Ultracentrifugation of Uranyl Citrate Chelates¹

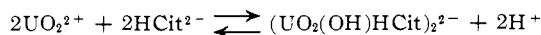
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The degrees of polymerization of uranyl citrate chelates corresponding to the empirical formulas $(\text{UO}_2\text{Cit})_{n-n^-}$ and $(\text{UO}_2[\text{OH}]_{1.67}\text{Cit})_{n^{2.67n^-}}$ ($\text{H}_3\text{Cit} = \text{H}_3\text{L} = \text{citric acid}$) have been calculated from data obtained by non-equilibrium ultracentrifugation of the chelates in 1.2 *M* sodium chloride solutions at 25°. A value of $n = 1.99 \pm 0.08$ was obtained for the $(\text{UO}_2\text{Cit})_{n-n^-}$ system in solutions which varied from 3.8×10^{-2} to 9.6×10^{-2} in molar concentration of chelate, thus giving strong support to the postulate of dimer formation. The data indicate that the $(\text{UO}_2[\text{OH}]_{1.67}\text{Cit})_{n^{2.67n^-}}$ system is polydisperse, probably consisting chiefly of a mixture of trimers and hexamers in the 10^{-2} to 10^{-1} *M* concentration range studied.

Introduction

There is some disagreement on the nature of the initial complex formed upon interaction of uranyl ion with citric acid ($\text{H}_3\text{Cit} = \text{H}_3\text{L}$). Li and co-workers³ have reported a constant of $\log K_{\text{ML}} = 8.55 \pm 0.04$ for the reaction $\text{UO}_2^{2+} + \text{Cit}^{3-} \rightleftharpoons \text{UO}_2\text{Cit}^{1-}$ at 25° in an NaCl medium. Here it was assumed that the three carboxylate groups of the ligand were utilized in chelate formation. More recently, Feldman, *et al.*,⁴ reported a constant of $\log K^{1/2} = 3.84$ for the reaction



where the product is presumably a binuclear diolated species containing a protonated (uncoordinated) carboxylic acid group. In the latter studies, constant values of the equilibrium constant were obtained over a tenfold concentration range at 25° in 0.1 *M* KNO_3 , whereas the results of Li, *et al.*, were calculated at a single concentration. Previous potentiometric⁵ and polarographic⁶ results by Feldman and coworkers are consistent with the postulation of dimer formation.

In view of the successful application on nonequilibrium ultracentrifugation measurements to the determination of molecular weights of charged Th(IV) and Zr(IV) chelates,^{7,8} it seemed desirable to examine the uranyl citrate system by this technique. Centrifugations were carried out on solutions containing equimolar quantities of uranyl nitrate and citric acid and either 3.0 or 4.67 moles of carbonate-free sodium hydroxide per mole of uranyl ion. According to Feldman,^{4,5} these conditions correspond to the complete formation of binuclear and ternuclear chelates, respectively.

Experimental

Ultracentrifugations.—Ultracentrifugation experiments were carried out with a Spinco Model E ultracentrifuge. The procedure was precisely as described previously by Klainer and Kegeles⁹ and by Gustafson and Martell.⁷ In the nonequilibrium ultracentrifugation method, each experiment requires three centrifugations, two of which are carried out in a cell containing a four degree sector-shaped centerpiece. The first centrifugation was carried out on a solution containing the uranyl citrate chelate at a suitable supporting electrolyte (NaCl) concentration, while the second involved the identical NaCl concentration

in the absence of the chelate. The degree of sedimentation was recorded photographically wherein the refractive index gradient, dn/dx , was plotted as a function of the distance, x , from the center of rotation. Since equilibrium conditions are maintained at all times at the upper and lower phase boundaries, according to the theory of Archibald,¹⁰ the values of dn/dx obtained at these boundaries may be considered to be equilibrium values and may be used in calculation of the molecular weight of the polymeric species. The quantities dn/dx for the polymeric component alone are obtained by subtracting the dn/dx values obtained in the second centrifugation from those of the first.

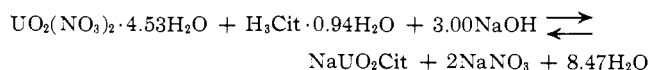
A third centrifugation, in which the supporting electrolyte solution is layered over a solution of the polymer in a two degree boundary forming cell described by Kegeles,¹¹ permits the determination of the initial concentration of the polymeric component in terms of refractive index units.

All experiments were carried out in a sodium chloride medium at 25°. Previous investigations by Pedersen¹² showed that since the sedimentation coefficients of sodium and chloride ions are nearly identical, secondary salt effects in this medium could be considered negligible. All photographs were made at a bar angle of 80° with Kodak metallographic plates.

Reagents.—Reagent grade uranyl nitrate was ground to a fine powder and analyzed for uranium content by ignition to the oxide, U_3O_8 . The results indicated that the salt had an effective molecular weight of 475.6 ± 0.3 corresponding to the formula $\text{UO}_2(\text{NO}_3)_2 \cdot 4.53\text{H}_2\text{O}$. Fisher Certified reagent grade citric acid was analyzed by potentiometric titration employing carbonate-free NaOH as a titrant. An effective molecular weight of 209.1 ± 0.1 was calculated indicating that 0.94 water molecule was bound per mole of citric acid. Standard carbonate-free sodium hydroxide was prepared such that the solution was 1.936 ± 0.001 *M* in NaOH and 1.200 *M* in NaCl. The solvent employed in the preparation of the uranyl citrate solutions was also 1.200 *M* NaCl.

The chelate solutions were prepared by rinsing weighed amounts of solid uranyl nitrate and citric acid into 100-ml. volumetric flasks. After each flask was weighed, appropriate volumes of standard CO_2 -free NaOH solution of known density were added. Each flask was reweighed in order to determine the exact weight of NaOH-NaCl solution added. Finally the volume was brought to 100 ml. with 1.200 *M* NaCl. After equilibration in the dark for 1–2 weeks, density measurements were made on the various chelate solutions. The data thus obtained permitted the calculations of the compositions of the chelate solutions and the partial specific volumes of the polymeric components.

Determination of Partial Specific Volumes.—The reaction which takes place upon the reaction of the 1:1 uranyl nitrate-citric acid mixture with 3.00 moles of NaOH is



The apparent molar volume of the products of this reaction may be calculated by the relationship

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

Here c represents the molar concentration of uranyl ion, M is the molecular weight of the combined products (804.7), and ρ_0 and ρ are the densities of solvent and solution, respectively. The experimental values of density and apparent molar volume obtained at various chelate concentrations are shown in Table I. Since no correlation of apparent molar volume with concentration was obtained, the approximation was made that $\bar{V}(\text{prod-}$

(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.

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(5) I. Feldman, J. R. Havill, and W. F. Neuman, *J. Am. Chem. Soc.*, **76**, 4726 (1954).

(6) W. F. Neuman, J. R. Havill, and I. Feldman, *ibid.*, **73**, 3593 (1951).

(7) R. L. Gustafson and A. E. Martell, *ibid.*, **82**, 5610 (1960).

(8) R. L. Gustafson and A. E. Martell, *J. Phys. Chem.*, in press.

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

(11) G. Kegeles, *J. Am. Chem. Soc.*, **74**, 5532 (1952).

(12) K. O. Pedersen, *J. Phys. Chem.*, **62**, 1282 (1958).

TABLE I

DETERMINATION OF APPARENT MOLAR VOLUME OF URANYL CITRATE CHELATE AT $m = 3^a$ IN 1.200 M NaCl AT 25°

Expt.	UO ₂ (VI) concn., × 10 ² M	(g./ml.)	ϕ_v , ml./mole
1	9.567	1.08586	356.1
2	6.697	1.07328	358.4
3	3.827	1.06097	357.4
4	1.913	1.05273	356.5
5	0.957	1.04858	358.1

Av. value of $\phi_v = 357.3 \pm 0.8$ ml./mole; $\rho_0 = 1.04446$

^a m = number of moles of NaOH added per mole of metal ion.

ucts) = $\phi_v(\text{products}) = 357.3 \pm 0.8$ ml./mole and the partial specific volume \bar{v}_{PX_z} of the polymeric component PX_z may be calculated by the relationship

$$\bar{v}_{PX_z} = \frac{\bar{V}(\text{products}) - 2\bar{V}_{NaNO_3} - 8.47\bar{V}_{H_2O}}{M'_{PX_z}}$$

where M'_{PX_z} represents the molecular weight of the monomer unit of the uranyl citrate chelate, 482.2. The partial molar volume of $NaNO_3$ was calculated from data tabulated by Harned and Owen¹³ with the aid of eq. 2-4.

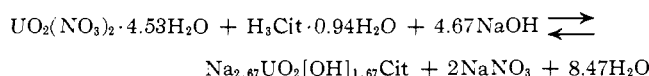
$$\bar{V}_{NaNO_3} = \bar{V}_{KNO_3} + \bar{V}_{NaCl} - \bar{V}_{KCl} \quad (2)$$

$$\phi_v = \phi_v^0 + (\partial\phi_v/\partial c^{1/2})c^{1/2} \quad (3)$$

$$\bar{V} = \phi_v + \frac{1000 - c\phi_v}{2000 + c^{3/2}\phi_v/\partial c^{1/2}} (\partial\phi_v/\partial c^{1/2})c^{1/2} \quad (4)$$

The value of \bar{V}_{H_2O} was assumed to be 18.0 ml./mole under all conditions.

The interaction of uranyl nitrate, citric acid, and $4^{2/3}$ moles of NaOH may be represented by the equation



The experimental values of ρ and ϕ_v obtained at various chelate concentrations under these conditions are shown in Table II. Once again the assumption was made that $\bar{V}(\text{products}) = \phi_v(\text{products}) = 374 \pm 1$ ml./mole. For the uranyl citrate chelate at m , $4^{2/3}$ the molecular weight of the monomer unit, M'_{PX_z} , is 548.9.

TABLE II

DETERMINATION OF APPARENT MOLAR VOLUME OF URANYL CITRATE CHELATE AT $m = 4^{2/3}$ IN 1.200 M NaCl AT 25°

Expt.	UO ₂ (VI) concn., × 10 ² M	(g./ml.)	ϕ_v , ml./mole
6	9.402	1.08971	373.5
7	6.582	1.07604	374.9
8	3.761	1.06234	379.1
9	1.881	1.05356	371.0
10	0.940	1.04897	375.1

Av. value of ϕ_v (expt. 6, 7, 9, 10) = 374 ± 1 ml./mole; $\rho_0 = 1.04446$.

Mathematical Treatment of Data.—Calculation of the molecular weights of the polymeric chelates was based on a combination of the Archibald nonequilibrium method of determining molecular weights as described by Klainer and Kegeles,⁹ with the methods of dealing with charged polyelectrolytes described by Johnson, Kraus, and Scatchard.¹⁴

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

$$N = \frac{1}{2A_2'c_2'x/(dc_2'/dx) - z'\eta} \quad (5)$$

(13) H. S. Harned and B. B. Owen, "The Physical Chemistry of Electrolytic Solutions," 3rd Ed., Reinhold Publ. Corp., New York, N. Y., 1958.

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

$$A_2' = L_2'\omega^2/2RT \quad (6)$$

$$L_2' = M'_{PX_z}(1 - \bar{v}_{PX_z}\rho) - \frac{z'}{2}M_{BX}(1 - \bar{v}_{BX}\rho) \quad (7)$$

$$\eta = 1/(1 + 2c_B/z'c_2') \quad (8)$$

The primed symbols refer to the monomer unit according to the relationships

$$NM'_{PX_z} = M_{PX_z}$$

$$z'N = z$$

M'_{PX_z} and \bar{v}_{PX_z} represent the molecular weight and partial specific volume of the monomer unit while M_{BX} and \bar{v}_{BX} represent the same quantities for the supporting electrolyte BX , 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 the rotation, z' is the assumed charge per monomer unit, ω is the angular velocity, c_B is the anion concentration of the supporting electrolyte, R is the molar gas constant, and T is the absolute temperature. The details of the procedure employed in the evaluation of N may be found in a previous publication.⁷

TABLE III

DATA OBTAINED UPON ULTRACENTRIFUGATION OF 1:1 URANYL CITRATE CHELATE AT $m = 3$

Exposure	x , cm.	c_2'	dn^*/dx	$N(z' = 1)$
Expt. 1: $9.57 \times 10^{-2} M$ UO ₂ ²⁺ ; 1.161 M NaCl; $c_0 = 0.2249$; $\omega = 2.582 \times 10^3$				
8 min. (top)	6.0638	0.2136	0.1882	1.85
16 min. (top)	6.0642	.2090	.1882	1.89
24 min. (top)	6.0637	.2056	.1837	1.87
8 min. (bot.)	7.0447	.2414	.2720	2.06
16 min. (bot.)	7.0454	.2467	.2780	2.07
24 min. (bot.)	7.0434	.2504	.2850	2.09
Expt. 2: $6.70 \times 10^{-2} M$ UO ₂ ²⁺ ; 1.172 M NaCl; $c_0 = 0.1575$; $\omega = 3.093 \times 10^3$				
8 min. (top)	6.0690	0.1448	0.1908	1.89
16 min. (top)	6.0692	.1407	.1927	1.96
24 min. (top)	6.0697	.1374	.1859	1.94
8 min. (bot.)	7.0490	.1757	.2865	2.04
16 min. (bot.)	7.0492	.1809	.2980	2.06
24 min. (bot.)	7.0492	.1853	.3125	2.12
Expt. 3: $3.83 \times 10^{-2} M$ UO ₂ ²⁺ ; 1.184 M NaCl; $c_0 = 0.0900$; $\omega = 3.884 \times 10^3$				
8 min. (top)	6.0717	0.0786	0.1679	1.90
16 min. (top)	6.0711	.0752	.1610	1.90
24 min. (top)	6.0717	.0726	.1583	1.93
8 min. (bot.)	7.0437	.1063	.2784	2.05
16 min. (bot.)	7.0435	.1111	.2970	2.07
24 min. (bot.)	7.0455	.1163	.3138	2.09
Expt. 4: $1.913 \times 10^{-2} M$ UO ₂ ²⁺ ; 1.192 M NaCl; $c_0 = 0.0450$; $\omega = 4.406 \times 10^3$				
8 min. (top)	6.0701	0.0348	0.1197	2.34
16 min. (top)	6.0691	.0334	.1101	2.24
24 min. (top)	6.0704	.0316	.1031	2.22
8 min. (bot.)	7.0485	.0598	.2707	2.69
16 min. (bot.)	7.0463	.0640	.3016	2.80
24 min. (bot.)	7.0483	.0696	.3407	2.92
Expt. 5: $0.957 \times 10^{-2} M$ UO ₂ ²⁺ ; 1.196 M NaCl; $c_0 = 0.0225$; $\omega = 3.884 \times 10^3$				
8 min. (top)	6.0673	0.0156	0.0830	2.00
16 min. (top)	6.0688	.0144	.0725	1.90
24 min. (top)	6.0680	.0132	.0628	1.80
8 min. (bot.)	7.0355	.0354	.3160	2.94
16 min. (bot.)	7.0391	.0412	.4080	3.28
24 min. (bot.)	7.0373	.0463	.4700	3.38

Although four components are present in our system (uranyl citrate chelate, NaCl, NaNO₃, and H₂O), methods of calculation based upon the assumption of the presence of a three-component system have been used in this study. The term c_B is equal to the sum of the molar concentrations of chloride and nitrate ions, and the weighted average values of v_{BX} and M_{BX} have been calculated based on the relative concentrations of sodium chloride and sodium nitrate. Check calculations show that insignificant changes are observed in the calculated values of N with the use of the above approximations relative to the values obtained using equations pertaining to the four-component systems. Considerable time is thus saved in the computational procedure.

It was assumed in the derivation of the equations that only a single polymeric species is present, that the solution density remains constant, and that the activity coefficients and partial specific volumes of the polymeric species and supporting electrolyte are approximately constant throughout the cell during the ultracentrifugation.

Results

UO₂-Citrate Chelate at $m = 3$.—The measured and calculated quantities obtained upon ultracentrifugation of the uranyl citrate chelate at $m = 3$ are shown in Table III. In Fig. 1 values of the degree of aggregation N are plotted as a function of the assumed charge per monomer unit, z' . Each curve represents the average of six sets of data obtained at the upper and lower phase boundaries. The eighteen values obtained in experiments 1–3 give an average value of $N = 1.99 \pm 0.08$ at $z' = -1$, which is the actual charge of the monomer unit of (UO₂Cit)_{*n*}^{*n*-} or (UO₂[OH]HCit)_{*n*}^{*n*-}. The higher values of N which were calculated in experiments 4 and 5 are probably caused by greater experimental errors associated with ultracentrifugation of dilute solutions of polymeric chelates. Since the refractive indices of the uranyl citrate solutions are only one-half to one-third of those observed in previous studies on Zr(IV) and Th(IV) chelates, high centrifugation speeds were required to produce sufficiently large refractive index gradients for measurements. In the cases of the more dilute uranyl citrate solutions, the differences in the values of the refractive index gradients (and hence concentrations) between the upper and lower boundaries is extremely large. This leads to considerable inaccuracy in extrapolation of dn/dx vs. x plots to the lower phase boundaries because of the upward concavity of the curves. Because plots of dn/dx vs. x obtained near the upper phase boundaries are nearly linear, these extrapolated values of dn^*/dx are considered to be more reliable than those obtained at the lower boundaries. It is expected that variations in the activity coefficients of the sedimenting species will be small in the 1.2 *N* NaCl solutions employed.

UO₂-Citrate Chelate at $m = 4^{2/3}$.—The results obtained upon centrifugation of uranyl nitrate-citric acid solutions containing $4^{2/3}$ moles of sodium hydroxide per mole of metal salt (and ligand) are shown in Table IV and Fig. 2. The plots of Fig. 2 indicate considerable polydispersity, since large differences in the calculated values of N were obtained, not only between successive experiments, but also between the upper and lower phase boundaries of the same experiment over the entire tenfold concentration range employed.

Discussion

Uranyl Citrate Chelate at $m = 3$.—The results of centrifugation of uranyl citrate chelates at $m = 3$ indicate that binuclear species predominate in the 0.01–0.1 *M* concentration range. These results are in accord with those of Feldman, *et al.*,^{4–6} who concluded on the basis of potentiometric and polarographic measurements that a binuclear chelate species is the major form present in the 0.01–0.001 *M* range. It may be noted that the calculated degrees of poly-

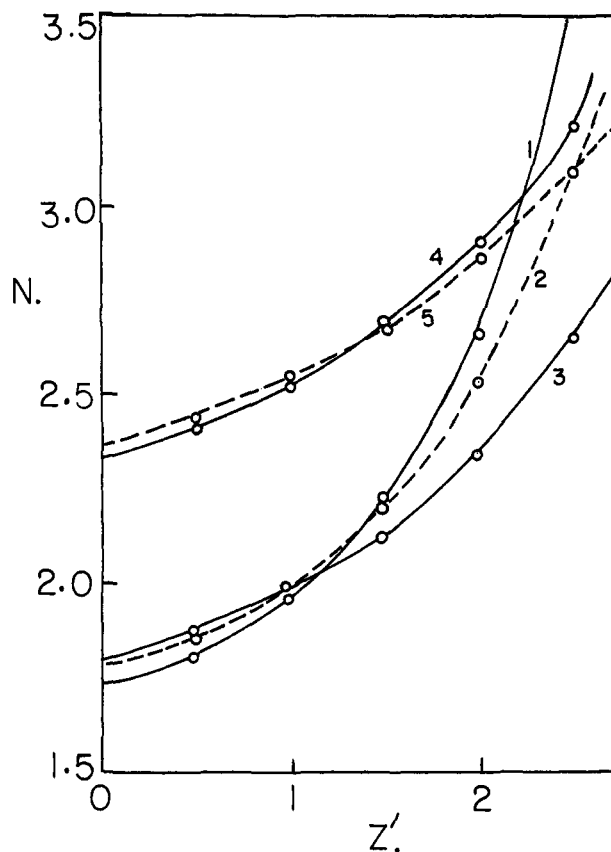


Fig. 1.—Ultracentrifugation of 1:1 uranyl citrate complex formed by the addition of 3 moles of base per mole of citric acid: N = degree of polymerization, z' = charge per monomer unit; numbers refer to experimental runs listed in Table III.

merization in experiments 1–3 were, on the average, 9% higher at the lower phase boundaries than at the upper boundaries. The differences between the concentrations of the chelate at the upper and lower boundaries were approximately 17, 28, and 47% in experiments 1, 2, and 3, respectively. Results of this type are qualitatively consistent with the concept of a monomer-polymer equilibrium in which there is a greater percentage of polymer in the more concentrated solution at the lower phase boundary and a comparatively lower degree of polymer formation in the more dilute solution at the upper boundary. However, the consistency of results obtained at various concentrations in experiments 1–3 is also in accord with the conclusion that the system is primarily monodisperse and that the deviations noted above may be due chiefly to variations in the activity coefficients of the chelate species at various degrees of sedimentation.

Feldman, *et al.*,⁴ have suggested that a binuclear, diolated uranyl citrate chelate is formed in the pH range 2.0–3.5. It is impossible to distinguish, on the basis of ultracentrifugation data, between various degrees of hydration of metal complex species, as well as between various possible conformations of polynuclear complexes involving variation in the degree of solvation. As with other methods of investigation such as potentiometry and polarography, the elucidation of the precise structures of these complexes in solution must await experimental evidence of a microscopic nature.

Uranyl Citrate Chelate at $m = 4^{2/3}$.—It may be shown that sedimentation of a polyelectrolyte in the absence of added salt does not yield the true molecular weight (mol. wt.) but rather mol. wt./($z + 1$) where z is the charge of the polymeric ion. Although the addition of a supporting electrolyte will produce an

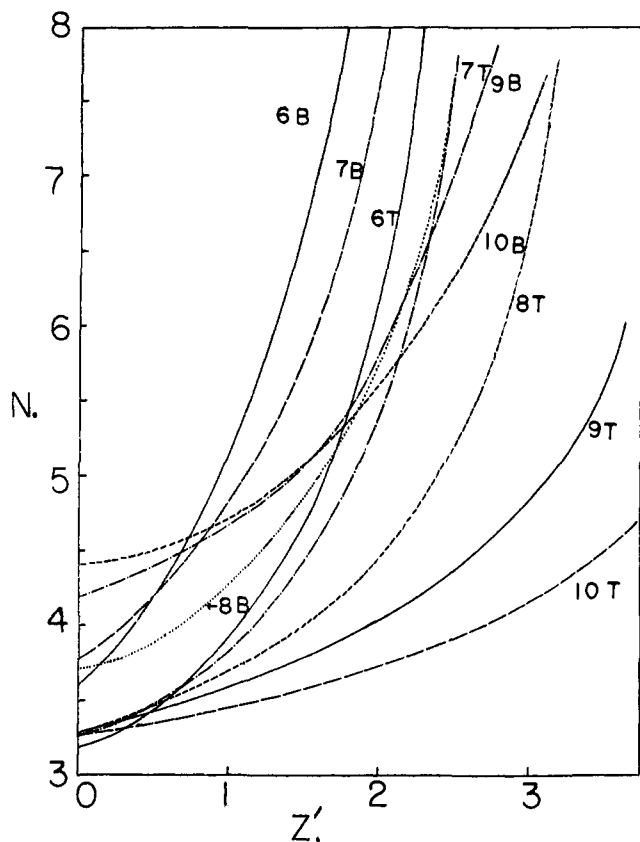


Fig. 2.—Ultracentrifugation of a 1:1 uranyl citrate complex formed by the addition of $4\frac{2}{3}$ moles of base per mole of citric acid: N = degree of polymerization, z' = charge per monomer unit; numbers refer to experimental runs listed in Table IV; T and B indicate data taken from the top and bottom of the ultracentrifugation cell, respectively.

increase in the absence of added salt, the calculated molecular weight will always be less than the actual value if charge effects are ignored, *i.e.*, if z is assumed to be equal to zero, and if unfavorable secondary salt effects¹² are absent. Our calculations at $z = 0$ and $m = 4.67$ all yield values of N which are significantly greater than 3. The inflection at $m = 4\frac{2}{3}$ in the titration curve of a 1:1 mixture of uranyl nitrate and citric acid suggests that the degree of polymerization is some multiple of three. Correlation of potentiometric and ultracentrifugation data leads to the conclusion that a mixture of hexamers with some lower and higher polymers exists in the 10^{-2} and 10^{-1} M concentration range. Although very high values of N were obtained in experiments 6 and 7, these results may be due to the fact that the $z'\eta$ term in eq. 5 is very large in magnitude relative to the value of the $2A_2'c_2'x/(dc_2'/dx)$ term. The net result is that small errors in the measured quantities (produced by nonconformity with the fundamental assumptions made in the derivation of eq. 5 lead to large deviations in the calculated

TABLE IV

DATA OBTAINED UPON ULTRACENTRIFUGATION OF 1:1 URANYL CITRATE CHELATE AT $m = 4.67$

Exposure	x , cm.	c_2'	dn^*/dx	$N(z' = 2.67)$
Expt. 6: 9.40×10^{-2} M UO_2^{2+} ; 1.160 M $NaCl$; $c_0 = 0.2733$; $\omega = 1.805 \times 10^3$				
8 min. (top)	6.0620	0.2601	0.2450	17.0
16 min. (top)	6.0629	.2556	.2420	17.0
24 min. (top)	6.0625	.2523	.2420	17.0
8 min. (bot.)	7.0436	.2911	.3620	^a
16 min. (bot.)	7.0440	.2964	.3700	^a
24 min. (bot.)	7.0420	.3003	.3800	^a
Expt. 7: 6.58×10^{-2} M UO_2^{2+} ; 1.172 M $NaCl$; $c_0 = 0.1913$; $\omega = 2.141 \times 10^3$				
8 min. (top)	6.0636	0.1778	0.2439	9.1
16 min. (top)	6.0642	.1731	.2402	9.0
24 min. (top)	6.0632	.1695	.2372	9.0
8 min. (bot.)	7.0452	.2095	.3761	18.6
16 min. (bot.)	7.0456	.2157	.4005	24.4
24 min. (bot.)	7.0445	.2204	.4163	30.0
Expt. 8: 3.76×10^{-2} M UO_2^{2+} ; 1.184 M $NaCl$; $c_0 = 0.1093$; $\omega = 2.900 \times 10^3$				
8 min. (top)	6.0703	0.0945	0.2420	5.7
16 min. (top)	6.0703	.0903	.2330	5.6
24 min. (top)	6.0711	.0870	.2250	5.6
8 min. (bot.)	7.0436	.1301	.4260	8.4
16 min. (bot.)	7.0413	.1357	.4440	8.7
24 min. (bot.)	7.0437	.1418	.4900	10.4
Expt. 9: 1.881×10^{-2} M UO_2^{2+} ; 1.192 M $NaCl$; $c_0 = 0.0547$; $\omega = 3.293 \times 10^3$				
8 min. (top)	6.0627	0.0446	0.1533	4.7
16 min. (top)	6.0628	.0424	.1421	4.5
24 min. (top)	6.0629	.0406	.1322	4.4
8 min. (bot.)	7.0454	.0712	.3420	7.0
16 min. (bot.)	7.0455	.0761	.3769	7.6
24 min. (bot.)	7.0456	.0804	.4049	8.0
Expt. 10: 0.940×10^{-2} M UO_2^{2+} ; 1.196 M $NaCl$; $c_0 = 0.0273$; $\omega = 3.879 \times 10^3$				
8 min. (top)	6.0640	0.0197	0.0944	4.3
16 min. (top)	6.0641	.0187	.0852	4.0
24 min. (top)	6.0644	.0175	.0750	3.7
8 min. (bot.)	7.0462	.0428	.2950	6.1
16 min. (bot.)	7.0440	.0457	.3340	6.7
24 min. (bot.)	7.0456	.0495	.3660	7.0

^a Calculated value of N is negative since $z'\eta$ is of greater magnitude than $2A_2'c_2'x/(dc_2'/dx)$ in eq. 5.

values of N . Ultracentrifugations of solutions containing high chelate concentrations at higher supporting electrolyte concentrations would tend to reduce the magnitude of the $z'\eta$ term in eq. 5 and would therefore help to confirm the results of this investigation which indicate the presence of highly polymeric species at these concentrations.