similar and whether the hydrolytic stability of the $ZrA_{2.5}$ species is possibly related to steric factors involved in its structure must await further investigations of this system at low Tiron ratios.

Finally, since the $ZrA_{2.5}$ species is binuclear and since the ZrA_4 species is probably mononuclear, it follows that the reactions depicted in (6) and (7) above represent a polymerization and a depolymerization, respectively. Such processes are appreciably affected by the concentration of metal ion present in the systems, and in the present study, where, following Martell, *et al.*, no attempt has been made to keep either the metal ion or metal chelate ion concentrations constant throughout the course of a particular run, calculation of stability constants for these processes from the data is vitiated by the variable drift in their values. For this reason it is hoped to study this system further using the methods of Sillén, *et al.*, to determine accurately the stability constant values for the processes depicted by the above equations.

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CONTRIBUTION FROM THE DEPARTMENT OF CHEMISTRY,
BRUNEL UNIVERSITY, ACTON, LONDON W. 3, ENGLAND

Formation and Hydrolysis of Zirconium(IV) Chelates in Aqueous Media. II. Light-Scattering Study of Zirconium(IV)–Tiron Chelates in 3 *M* Sodium Perchlorate Medium[1]

BY B. H. MASSEY AND F. G. R. GIMBLETT[2]

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The structures of the species present in hydrolyzed and nonhydrolyzed solutions of Zr^{IV}–Tiron chelates in 3 *M* $NaClO_4$ at 25° and at high Tiron/Zr(IV) ion ratios have been investigated by a light-scattering method. The results show that the $ZrA_{2.5}$ species (where A = Tiron) formed in this system possesses a dimeric structure and that, as previously predicted, successive addition of further Tiron to this entity causes it to break down to yield the monomeric species ZrA_4. The dimeric entity $ZrA_{2.5}$ and the monomeric ZrA_4 are highly charged in solution, and although formal identification of the sign of the charges possessed by these species was not possible, the results indicate that both chelates are partially stabilized in solution through outer-sphere complexing by the ions of the solvent medium. Studies on the complex of empirical formula $ZrA_{2.5}(OH)_{1.5}$, formed when the species $ZrA_{2.5}$ hydrolyzes, indicate that its formation is achieved through the depolymerization of the latter.

Introduction

In part I of this series[3] we have described and discussed the results of a potentiometric study of the formation and hydrolysis of zirconium(IV)–Tiron chelates in 3 *M* sodium perchlorate medium at 25°. The conclusions of this study were that at low Tiron ratios in this system mixed hydroxo–Tiron chelates are formed, but that at Tiron/Zr(IV) ion ratios of 2.5 and above the initial chelate formed appears to be an unhydrolyzed species of empirical formula $ZrA_{2.5}$ (where A = Tiron). Addition of further Tiron to this species results in its conversion to ZrA_4 which remains unhydrolyzed even at pH values greater than 12 in the system.

The present study has been undertaken in an attempt to verify our previous suggestions regarding the behavior of the species present in the system at and above a Tiron/Zr(IV) ion ratio of 2.5, and to establish, as far as possible, the structures of these particular metal chelate species. Since there is some evidence to suggest that concentration effects, produced by both metal chelate and supporting medium, play a part in determining the structure of the species in solution,[4] the light-scattering studies reported here have been undertaken using conditions closely similar to those used in our potentiometric studies. As is apparent from our results, the experimental difficulties normally associated with light-scattering studies of small molecular weight entities in solution are, in this instance, more than offset by the light-scattering abilities of the metal atoms in the chelate structures.

Experimental Section

Reagents.—Zirconium(IV) perchlorate, sodium perchlorate, and 1,2-dihydroxybenzene-3,5-disulfonic acid, disodium salt (Tiron), were prepared and/or assayed by methods described previously.[3]

Preparation of Solutions.—Stock solutions of $Zr(ClO_4)_4$–$(Na,H)ClO_4$ were prepared as previously described,[3] using a saturated aqueous solution of sodium perchlorate to adjust the total perchlorate ion molarity of these solutions to 3 *M*.

Titrant solutions of NaOH–$NaClO_4$, 3 *M* in ClO_4^- ion concentration, were prepared from BDH "solutions for analytical use" by diluting the latter with saturated $NaClO_4$ solution and doubly distilled water in appropriate volumes.

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[1] Taken from the Ph.D. thesis of B. H. Massey, Brunel University, 1969.

[2] Author to whom all correspondence regarding this paper should be addressed.

[3] F. G. R. Gimblett and B. H. Massey, *Inorg. Chem.*, **9**, 2038 (1970).

[4] F. G. R. Gimblett and E. F. Thairs, unpublished results.

Solutions of Zr^{IV}–Tiron and hydrolyzed Zr^{IV}–Tiron complexes were prepared by adding sufficient acid metal stock solution to solid Tiron to produce the required Tiron/Zr(IV) ion ratio in the final solution. After such addition, the sample was cooled to 0° in an ice bath and the required volume of a 2 *M* NaOH solution, 3 *M* in ClO_4^- ion, was added dropwise while the sample was agitated vigorously by a fast stream of nitrogen. Finally the sample was made up to volume in a graduated flask by addition of appropriate volumes of saturated sodium perchlorate solution and doubly distilled water to bring the perchlorate ion concentration of the solution to 3 *M*.

When freshly prepared, or after storage in a refrigerator, all the Zr^{IV}–Tiron chelate or hydrolyzed chelate solutions studied in this investigation exhibited low optical densities (<0.03) at both wavelengths employed. However, since prolonged exposure to the atmosphere, especially in the presence of sunlight, leads to a significant increase in the optical densities of these solutions (particularly at 436 mμ), preparation was always carried out in diffused light, as was the dilution of these solutions, necessary for both refractive index increment and turbidity studies. No measurable increase in the optical densities of these solutions could be detected as a result of their exposure to the light sources used in these studies.

Light-Scattering Measurements.—Measurements of the turbidity at 25 ± 0.5° were made with unpolarized light using a "Sofica" light-scattering photometer.[5] Zr^{IV}–Tiron complexes show strong absorption bands below 370 mμ but, as mentioned above, relatively low absorption within the range 380–700 mμ. For this reason turbidimetric and differential refractometric measurements were made either at 436 or 546 mμ depending on the relative absorptions of the Tiron complexes at these wavelengths. Thus the absorption of the $ZrA_{2.5}$ species is less at 436 mμ than at 546 mμ and this species was consequently studied at the former wavelength, but all other species studied showed the reverse behavior and were therefore studied at 546 mμ.

The light-scattering photometer was calibrated at both of these particular wavelengths using pure BDH "Molecular Weight" grade benzene, filtered by passage through a 0.22-μ Millipore filter until a constant value (<1.01) of the dissymmetry was obtained. The turbidities of benzene used in this calibration were those quoted by Dezilic and Kratohvil,[6] *i.e.*, 8.00×10^{-4} cm^{-1} at 436 mμ and 2.76×10^{-4} cm^{-1} at 546 mμ, respectively. The accuracy of this calibration was checked by reference to a standard opal-glass diffuser supplied by the instrument manufacturers and this diffuser was also used to check any changes in instrument sensitivity which might occur from day to day or during a series of measurements. In no case was the ratio $I_{90(GR)}/I_{90(Bz)}$, where $I_{90(GR)}$ and $I_{90(Bz)}$ are the 90° scatter from the glass diffuser and from benzene, respectively, found to differ by more than 1% from the value of 1.41 quoted by the manufacturers for this ratio at 436 and 546 mμ, respectively.

Solutions for turbidimetric investigation were prepared, as required, by diluting aliquots of equilibrated chelate stock solution with 3 *M* sodium perchlorate solution which had been repeatedly filtered through a 0.22-μ Millipore filter. The solutions were checked for the absence of large dust particles by examining for a Tyndall effect and then filtered direct into the scattering cell through a 0.22-μ filter. The turbidity was determined by measuring the intensity of the light scattered at angles of 45, 90, and 135°, respectively, from the solution contained in a circular cell relative to that for the incident beam, the electronics of the light-scattering instrument being such that these values could be measured directly. The absence of dust from each solution investigated was inferred from the low values of their respective dissymmetries. Typical values were 1.01 at 436 mμ and 1.04 at 546 mμ for the solvent (usually achieved after five to ten filtrations) and 1.03–1.05 for solutions at both of these wavelengths. The normalized scattering envelope, calculated by multiplying the experimental values of the turbidity by $\sin\theta/(1 + \cos^2\theta)$, corresponded to that of an isotropic scatterer. No measurable fluorescence was observed from any of the solutions investigated at either of the wavelengths employed.

Density and Refractive Index Increment Measurements.—Densities were measured pycnometrically at 25°. Refractive index increment measurements were made at 25° and at 436 and 546 mμ using a Polymer Consultants Ltd. (PCL) differential refractometer[7] which had been calibrated with sucrose solutions.

Results

According to Tobias and Tyree,[8,9] for a monodisperse polymer PX_z which ionizes in solution to give P^{z+} and zX^- ions, two supporting electrolytes HX and BX, and a solvent (water), the turbidity due to PX_z is given by

$$\tau^* = \frac{\phi H''\psi_2^2}{1/m_2 + Z_2^2/2(m_3 + m_5)} \qquad (1)$$

where ϕ is the volume fraction of the solvent, $H'' = 8000\pi^3(n + n_0)^2/3\mathfrak{N}\lambda^4$, where $\mathfrak{N}$ is Avogadro's number, λ is the wavelength of the incident light, and n and n_0 are the refractive indices of the solution and of the pure solvent (water), respectively, m_2 is the molarity of the polymeric electrolytic component 2 of charge Z_2, and m_3 and m_5 are the molarities of components 3 and 5 in the system and are approximately equal to [HX] and [BX].

The refractive index increment of component 2, ψ_2, is given by the relationship

$$\psi_2 = \mathrm{d}n/\mathrm{d}m_{PX_z} - Z_2m_3/(2(m_3 + m_5)\mathrm{d}n/\mathrm{d}m_3 - Z_2m_5/2(m_3 + m_5)\mathrm{d}n/\mathrm{d}m_5 \qquad (2)$$

where $\mathrm{d}n/\mathrm{d}m_{PX_z}$ is the gross refractive index increment of a solution of the polymeric component in the supporting electrolyte and $Z_2m_3/2(m_3 + m_5)\mathrm{d}n/\mathrm{d}m_3$ and $Z_2m_5/2(m_3 + m_5)\mathrm{d}n/\mathrm{d}m_5$ are the contributions made to this gross refractive index increment by HX and BX, respectively. This expression for ψ_2 follows from the definition of component 2 as $[PX_z] - Z_2m_3/2(m_3 + m_5)\cdot[HX] - Z_2m_5/2(m_3 + m_5)[BX]$.

Tobias and Tyree found that in practice the application of eq 1 to a particular system is considerably simplified if the polymeric solute is expressed in terms of its monomeric unit, *i.e.*, as

$$[M(H)_{\bar{n}}X_{\bar{\nu}}{}^{(z+\bar{n}-\bar{\nu})+}X^-{}_{(z+\bar{n}-\bar{\nu})}]_N$$

where N is the degree of polymerization, z is again the charge on the ion M, $\bar{\nu}$ is the average number of X^- ions bound per M^{2+} ion, and $\bar{n}$, the average number of hydrogen ions consumed per mole of M, may be obtained from potentiometric data.

With this redefinition of the polymeric solute, it is necessary to introduce further relationships, *viz.*, $Z' = Z_2/N = z - \bar{n} - \bar{\nu}$, $M' = M_2/N$, $m' = m_2N$, and $\psi' = \psi/N$, and substituting these quantities into eq 1 and rearranging gives

$$\frac{1}{N_{Z'}} = \frac{\phi H''\psi'^2m'}{\tau^*} - \frac{Z'^2m'}{2(m_3 + m_5)} \qquad (3)$$

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[5] "Sofica" Photogonic Diffusometer, Model 42000, Applied Research Laboratories, Luton, England.

[6] G. J. Dezilic and J. P. Krathovil, *Kolloid-Z.*, **173**, 38 (1960).

[7] Based on the design of D. W. Ovenall and F. W. Peaker, *Makromol. Chem.*, **33**, 222 (1959).

[8] R. S. Tobias and S. Y. Tyree, Jr., *J. Amer. Chem. Soc.*, **81**, 6385 (1959).

[9] R. S. Tobias and S. Y. Tyree Jr.,, *ibid.*, **82**, 3244 (1960).

where $1/N_{Z'}$ is the reciprocal of the degree of polymerization of the polymeric species in the solution whose value depends on the choice of Z' values used in eq 3. When the correct value of Z' is taken, the value of $(1/N_{Z'})$ will be independent of m' and a plot of $(1/N_{Z'})$ *vs.* m' will be a straight line of zero slope.

In this present work it has been assumed that eq 1–3 also apply to a system consisting of a monodisperse polymeric metal chelate dissolved in a solvent (water) together with two supporting electrolytes, $HClO_4$ and $NaClO_4$, respectively. Since the results of our previous potentiometric studies[3] indicate that all the species investigated in the present work are formed within the pH range 4–7.5, this means that the concentration of free acid, in comparison with that of $NaClO_4$, in the system will be negligible insofar as the light-scattering studies are concerned. For this reason the $(m_3 + m_5)$ term which appears in eq 1–3 may be put equal to m_5, thus simplifying eq 1 and 3 and reducing eq 2 to

$$\psi_2 = \mathrm{d}n/\mathrm{d}m_{\mathrm{PX}_z} - {}^1/_2 Z_2 \mathrm{d}n/\mathrm{d}m_5 \qquad (2')$$

Volume and Refractive Index Measurements.—The volume fraction of solvent ϕ used in this study was calculated from density measurements on 3 M sodium perchlorate solutions alone since (a) the contribution of free acid in the system is negligible and (b) we have assumed that the contribution of the polymeric species in the solution is also negligible.[10]

These measurements showed that at 25° a solution of strength 2.9596 M in sodium perchlorate has a density of 1.22672 ± 0.00005 g ml^{-1}. This leads to a value of 0.864 for ϕ, in good agreement with a value of 0.861 calculated from the data of Wirth and Collier[11] on similar solutions. This value may be compared with that of 0.95 obtained by Tobias and Tyree[9] for the volume fraction of water in 1 M $NaClO_4$ and values of 0.88–0.90 obtained by Craig and Tyree[12] for measurements in 2 M $NaClO_4$ solution. By direct comparison between the chelate solution and a blank solution containing 3 M $NaClO_4$ alone, the refractive index increments of a variety of species, at one or both wavelengths studied, were obtained. These are listed in Table I, together with that of $NaClO_4$ solution at 546 mμ obtained by comparison of that solution against water.

From these refractive index increments it is possible to compute directly the refractive index (n) of a given solution. In particular, it is possible to calculate n for a 3 M $NaClO_4$ solution at 436 and 546 mμ, respectively.

TABLE I

REFRACTIVE INDEX INCREMENT VALUES FOR SOME Zr^{IV}–TIRON SPECIES AT 25°

Empirical formula of species[a]	Wave-length, mμ	$\mathrm{d}n/\mathrm{d}m' \times 10^2$, M^{-1}	Concn range, M
$ZrA_{2.5}$	436	15.28	$0–4.302 \times 10^{-2}$
$ZrA_{2.5}(OH)_{1.5}$	436	16.20	$0–4.302 \times 10^{-2}$
$ZrA_{3.0}$	436	18.33	$0–4.302 \times 10^{-2}$
$ZrA_{3.0}(OH)$	436	19.37	$0–3.442 \times 10^{-2}$
$NaClO_4$	546	0.7071	0–3.0
$ZrA_{2.5}(OH)_{1.5}$	546	17.93	$0–5.22 \times 10^{-2}$
$ZrA_{3.0}$[b]	546	18.38	$0–1.04 \times 10^{-2}$
$ZrA_{3.0}$[c]	546	18.34	$0–5.02 \times 10^{-2}$
$ZrA_{3.5}$	546	21.72	$0–8.922 \times 10^{-2}$

[a] The empirical formulas of some of the species listed are more accurately related to the Zr(IV) ion/Tiron ratio in the system rather than to the formation of a definite species. Thus, as has been suggested previously,[3] the $ZrA_{3.0}$ "species" is really a mixture of the two species $ZrA_{2.5}$ and ZrA_4, respectively, and the same is true for the $ZrA_{3.5}$ "species." [b] Equilibrated in a darkened thermostat at 25° for 24 hr. [c] Equilibrated in a refrigerator at 25° for 25 hr.

At 436 mμ the refractive index increment of $NaClO_4$ solution has been given by Tobias and Tyree[9] as $\Delta n = 8.178 \times 10^{-3}m - 5.95 \times 10^{-4}m^{3/2}$. This value has been used in the present study. At 546 mμ the results recorded in Table I indicate that $\Delta n = 7.071 \times 10^{-3}m$. The refractive index of pure water at 25° at these two wavelengths is 1.34030 and 1.33447, respectively.[13]

If these values for $\Delta n = \mathrm{d}n/\mathrm{d}m_5$ are substituted into eq 2′ above, the refractive index increment of the polymeric component 2 in the system may be expressed as

$$\psi_2 = \mathrm{d}n/\mathrm{d}m_{\mathrm{PX}_z} - 3.574 \times 10^{-3} Z_2 \qquad (2a')$$

$$\psi_2 = \mathrm{d}n/\mathrm{d}m_{\mathrm{PX}_z} - 3.536 \times 10^{-3} Z_2 \qquad (2b')$$

at the wavelengths 436 and 546 mμ, respectively.

Turbidimetric Measurements and the Calculation of Z' and $N_{Z'}$ for the Various Species Studied.—Turbidimetric measurements were made on solutions containing the species $ZrA_{2.5}$, $ZrA_{3.0}$, $ZrA_{3.5}$, and $ZrA_{2.5}(OH)_{1.5}$, respectively. In each case the 45, 90, and 135° scatter from each solution was measured as a ratio of the intensity of light scattered at these angles to that for the incident light beam. In each case the measured scatter was corrected for instrument sensitivity and the corrected scatter for the solute computed by subtracting the corrected scatter for the solvent (3 M $NaClO_4$) from that for the solution.

Conversion of the corrected 90° scatter for the solute (I'_{90}) into values of the solute turbidity (τ^*) was achieved through the use of the relationships

$$\tau^* = 8.251 \times 10^{-4} I'_{90} \quad \text{(at 436 m}\mu\text{)} \qquad (4a)$$

$$\tau^* = 3.038 \times 10^{-4} I'_{90} \quad \text{(at 546 m}\mu\text{)} \qquad (4b)$$

The values of τ^* thus obtained were used in conjunction with values of ϕ and ψ_2 in eq 3 to construct plots of $1/N_{Z'}$ *vs.* m' for various values of Z'. Examples of these plots for the four systems studied are given in

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(10) Although this assumption has been employed by a number of other workers in this field, its application in this instance does introduce a small error into the reported results. If the Zr–Tiron volumes in this system are of the same order as those determined by R. L. Gustafson and A. E. Martell, *J. Amer. Chem. Soc.*, **86**, 344 (1964), for the Zr–EDTA–Tiron system, then at the highest chelate concentrations investigated (~0.1 M) the polymer contribution could be as much as 5% toward the total volume. Since this contribution varies with the total concentration of chelate present in the system, however, any error due to its neglect will be reflected as a slight change in the slope of the $1/N_{Z'}$ *vs.* m' plots reported in this study and hence in the value of Z' necessary to obtain a zero slope in these plots. These slight changes in the numerical values of Z' have no influence on the intercepts of these plots and are well within the experimental accuracy claimed for the Z' values reported here.

(11) H. E. Wirth and F. N. Collier, *J. Amer. Chem. Soc.*, **72**, 5292 (1950).

(12) H. P. Craig and S. Y. Tyree, Jr., *Inorg. Chem.*, **4**, 997 (1965).

(13) "International Critical Tables," Vol. 7, McGraw-Hill, New York, N. Y., 1926, p 1.

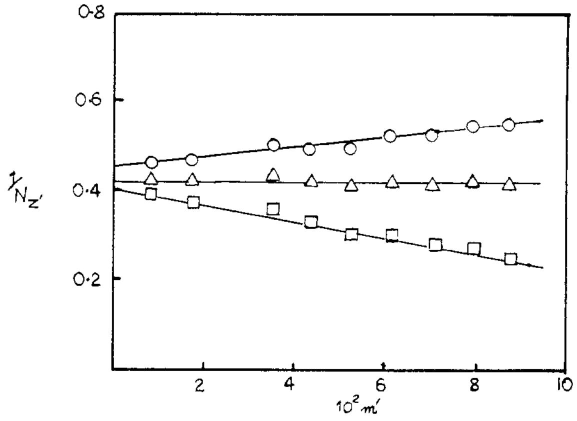

Figure 1.—$1/N_{Z'}$ *vs.* m' plots for a solution containing species of empirical composition $ZrA_{2.5}$ (A = Tiron). Points designated ○, △, and □ have been calculated using values of Z' of 3.0, 4.0, and 5.0, respectively, in eq 3.

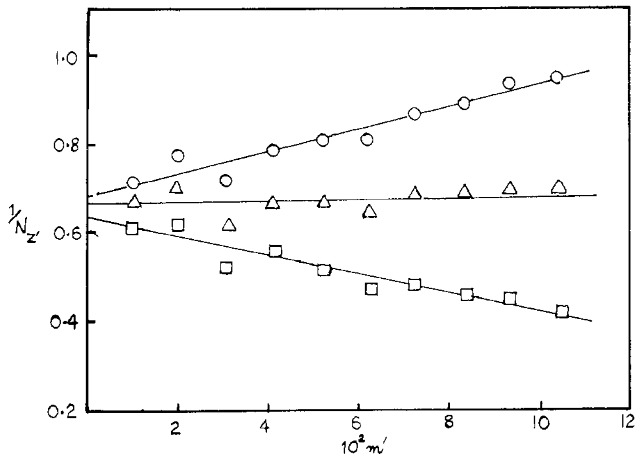

Figure 2.—$1/N_{Z'}$ *vs.* m' plots for a solution containing species of empirical composition $ZrA_{3.0}$ (A = Tiron). Points designated ○, △, and □ have been calculated using values of Z' of 5.0, 6.0, and 7.0, respectively, in eq 3.

Figures 1–4, respectively; the $1/N_{Z'}$ and Z' values (accurate to ±0.005 and ±0.2, respectively) corresponding to the line of zero slope in each of these plots are listed separately in Table II.

Table II

Experimental Values of $1/N_{Z'}$ and Z' Obtained for the Species Present in the Hydrolyzed and Nonhydrolyzed Zr^{IV}–Tiron Chelate System in 3 M $NaClO_4$ at 25°

Empirical formula of species[a]	Wavelength, mμ	Exptl values $1/N_{Z'}$	Z'
$ZrA_{2.5}$	436	0.43	3.85
$ZrA_{3.0}$	546	0.635	6.2
$ZrA_{3.5}$	546	0.76	7.5
$ZrA_{2.5}(OH)_{1.5}$	546	0.64	4.15

[a] See footnote *a* of Table I.

Discussion

The following reaction scheme has been suggested for the formation and behavior of Zr^{IV}–Tiron chelates in 3 M $NaClO_4$ solution at 25° and at high (⩾2.5) Tiron/Zr(IV) ion ratios[3]

$$Zr(IV) + 2.5A^{4-} \rightleftharpoons ZrA_{2.5}^{6-} \qquad (5)$$

$$ZrA_{2.5}^{6-} + 1.5A^{4-} \rightleftharpoons ZrA_4^{12-} \qquad (6)$$

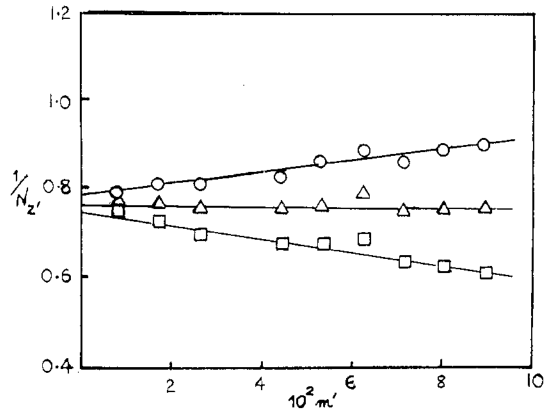

Figure 3.—$1/N_{Z'}$ *vs.* m' plots for a solution containing species of empirical composition $ZrA_{3.5}$ (A = Tiron). Points designated ○, △, and □ have been calculated using values of Z' of 7.0, 7.5, and 8.0, respectively, in eq 3.

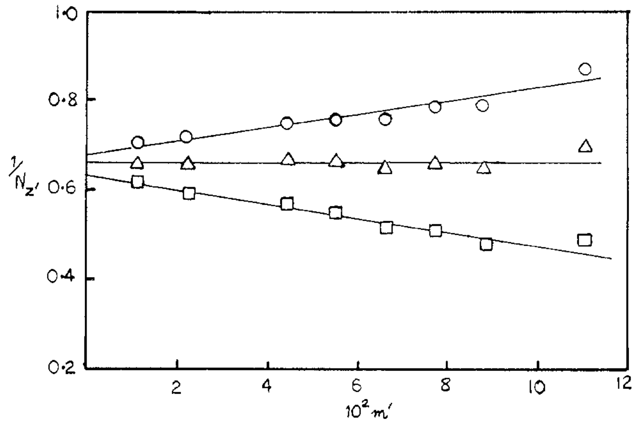

Figure 4.—$1/N_{Z'}$ *vs.* m' plots for a solution containing species of empirical composition $ZrA_{2.5}(OH)_{1.5}$ (A = Tiron). Points designated ○, △, and □ have been calculated using values of Z' of 3.0, 4.0, and 5.0, respectively, in eq 3.

The results recorded in Table II fully support this suggested scheme and further suggest that the species $ZrA_{2.5}^{6-}$ is dimeric and should be correctly represented as $Zr_2A_5^{12-}$. Thus at a Tiron/Zr(IV) ion ratio of 2.5, if the whole of the chelate present in the system is dimeric, the value of $1/N_{Z'}$ should be 0.5, and the value of 0.43 obtained experimentally in this study is in good agreement with this prediction. Whether the small divergence between the calculated and observed values of $1/N_{Z'}$ obtained in this case has any physical significance is debatable in view of the low molecular weight of the species involved. However, when compared with the much closer agreement between these values at Tiron/Zr(IV) ion ratios of 3.0 and 3.5, it is possible that this divergence may indicate the presence of small amounts of higher polymer in the system.

If it is accepted that the $ZrA_{2.5}^{6-}$ species is dimeric, then at a Tiron/Zr(IV) ion ratio of 3.0 eq 6 predicts that depolymerization will occur in the system, and this will occur according to the equation

$$3Zr_2A_5^{12-} + 3A^{4-} \rightleftharpoons 2Zr_2A^{12-} + 2ZrA_4^{12-} \qquad (7)$$

yielding the monomeric species ZrA_4^{12-}.

Now light-scattering measurements yield weight-average molecular weights, and consequently when a mixture of species is examined by this method, the weight-average degree of polymerization, $\overline{\mathrm{DP}_\mathrm{w}}$, will be measured. $\overline{\mathrm{DP}_\mathrm{w}}$ may be defined as

$$\overline{\mathrm{DP}_\mathrm{w}} = \Sigma_i N_i(\mathrm{DP}_i)^2/\Sigma_i N_i(\mathrm{DP}_i) \qquad (8)$$

where N_i represents the number of moles of i-mers having a degree of polymerization DP_i.

It follows from eq 8 that for a system consisting of 2 mol of dimer and 2 mol of monomer, as predicted in eq 7, $\overline{\mathrm{DP}_\mathrm{w}} = 1.67$ or $1/N_{Z'} = 0.60$.

Similarly for a Tiron/Zr(IV) ion ratio of 3.5, the state of the system will be represented by the equation

$$3\mathrm{Zr_2A_5}^{12-} + 6\mathrm{A}^{4-} \rightleftharpoons \mathrm{Zr_2A}^{12-} + 4\mathrm{ZrA_4}^{12-} \qquad (9)$$

which, from eq 8, predicts that $\overline{\mathrm{DP}_\mathrm{w}} = 1.33$ or $1/N_{Z'} = 0.75$ under these conditions.

The predicted values of $1/N_{Z'}$ for the system at the various Tiron/Zr(IV) ion ratios agree closely with those observed experimentally and listed in Table II, thus verifying the proposals regarding the conversion of $\mathrm{ZrA_{2.5}}^{6-}$ species to $\mathrm{ZrA_4}^{12-}$ on further addition of Tiron to the system.

Equations 5 and 6 also predict that the species formed in 3 M $\mathrm{NaClO_4}$ solution with increasing Tiron ratio should possess large negative charges and this is also supported, in part, by the values of Z', listed in Table II, which yield $1/N_{Z'}$ *vs.* m' plots with zero slope. The values of the charge parameter, listed in this table, are higher than any previously reported, although those were for unchelated metal species. They are, however, less than the values predicted by these equations for the dimeric and monomeric species involved, and these decreased values may be attributed to outer-sphere complexing of these species by the ions of the medium itself.

Some measure of this outer-sphere complexing may be obtained if it is assumed that the charge per metal ion Z' is an additive property in this particular system. If this is so, then the total charge Z'_T for a mixture of a dimer and a monomer may be written as

$$Z'_\mathrm{T} = \frac{(2N_\mathrm{D}Z'_\mathrm{D}) + (N_\mathrm{M}Z'_\mathrm{M})}{2N_\mathrm{D} + N_\mathrm{M}} \qquad (10)$$

where N_D is the number of moles of dimer having a charge per metal ion Z'_D, and N_M is the number of moles of monomer having a charge per metal ion Z'_M.

Substitution of values of $Z'_\mathrm{D} = 4$ and $Z'_\mathrm{M} = 10$ into eq 10 yields predicted values of Z'_T in close agreement with the values of Z' obtained experimentally. Both sets of values are listed together in Table III. As the charge parameter is included as its square in the term for $1/N_{z'}$ (*cf.* eq 3) it is not possible to determine the sign of the charge from light-scattering studies alone. Equations 5 and 6 above, however, predict a *negative* value for these charges, and if this prediction is correct, the results recorded in Table III would indicate complexing of each dimer ion, $\mathrm{Zr_2A_5}^{12-}$, by four Na^+ ions and of each monomer ion, $\mathrm{ZrA_4}^{12-}$, by two Na^+ ions, the positive ions being derived from the solvent medium.

TABLE III

OBSERVED AND PREDICTED VALUES OF THE CHARGE PARAMETER FOR THE SPECIES PRESENT IN UNHYDROLYZED $\mathrm{Zr^{IV}}$–TIRON CHELATE SYSTEMS IN 3 M $\mathrm{NaClO_4}$ AT 25°

Empirical formula of species[a]	Rel quantities of monomer and dimer in system[b]	Z'_T	
		Z'_exptl	Eq 10
$\mathrm{ZrA_{2.5}}$	$\mathrm{Zr_2A_5}$	3.85	4.0
$\mathrm{ZrA_{3.0}}$	$\mathrm{Zr_2A_5 + ZrA_4}$	6.2	6.0
$\mathrm{ZrA_{3.5}}$	$\mathrm{Zr_2A_5 + 4ZrA_4}$	7.5	8.0

[a] See footnote *a* of Table I. [b] To avoid confusion the charges associated with these species have been omitted.

The light-scattering data on the species $\mathrm{ZrA_{2.5}(OH)_{1.5}}$ indicate that on hydrolysis the dimer $\mathrm{Zr_2A_5}^{12-}$ again depolymerizes. In this case, however, it is no longer a relatively simple matter to predict the nature of the species formed on depolymerization, and information on this point must await further studies on this system.

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