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

By F. G. R. GIMBLETT[2] and B. H. MASSEY

The formation and subsequent hydrolysis of Zr(IV) chelates with 1,2-dihydroxybenzene-3,5-disulfonic acid (Tiron) has been investigated in a constant 3 *M* NaClO$_4$ medium at 25° using a potentiometric method. The results obtained show that at ligand/metal ion ratios less than 2.5 simultaneous chelation and hydrolysis occurs in the system to yield mixed hydroxo–Tiron chelates. At and above this ratio, however, the initial species formed in the system is the entity ZrA$_{2.5}$ which on further addition of Tiron is converted to ZrA$_4$. ZrA$_{2.5}$ is hydrolyzed only at relatively high ($\geqslant 7$) pH values while ZrA$_4$ is unhydrolyzed even at pH values in excess of 12.

Introduction

During the past 20 years, the hydrolysis of the Zr(IV) ion in aqueous solution has been the subject of numerous investigations using a variety of experimental techniques. Thus, Connick and coworkers,[3-5] using extraction methods, have shown that even in acid media the Zr(IV) ion undergoes aggregation to form polymeric ions, the principal species within the concentration range 5 × 10^{-4}–2 × 10^{-2} *M* Zr(IV) ion being a trimer, Zr$_3$(OH)$_4^{8+}$, and a tetramer, Zr$_4$(OH)$_8$, respectively. Johnson and Kraus,[6,7] from ultracentrifugation studies in acid media over the same Zr(IV) concentration range, have reached similar conclusions, and the presence of small polymeric aggregates in acid Zr(IV) solutions has been reaffirmed, more recently, by Angstadt and Tyree[8] from light-scattering investigations.

Both of these latter studies have shown, however, that increasing the temperature of aging Zr(IV) solutions, or alternatively lowering their acidity, causes a substantial increase in the degree of polymerization of the species present. This effect has been studied in greater detail by Bilinski and Tyree,[9] who have suggested that it is due to the presence of the complex ion, Zr$_4$(OH)$_{15}^+$, which hydrolyzes to a neutral tetrameric hydroxide, the latter polymerizing slowly to form colloidal particles which ultimately separate out as a solid hydroxide precipitate.

Comparable investigations of the behavior of chelated Zr(IV) ions in aqueous solution are very limited. To date, the only extensive study undertaken in this field appears to be that of Intorre and Martell,[10-12] who

have examined the hydrolysis of the chelates formed both with polycarboxylic acids and with polyhydroxy-phenolic compounds. From the basis of potentiometric measurements, these workers have postulated the formation of a variety of species during the hydrolysis of chelated Zr(IV) ions in 0.1 *M* KCl solution. Thus, the 1:1 Zr^{IV}–EDTA chelate, for example, is assumed to form a dimer on hydrolysis, while Zr^{IV}–Tiron[13] complexes yield polymeric hydroxo-bridged networks, chains, or dimers depending on the ratio of Tiron to Zr(IV) ion used in preparing the initial chelate solution.

Since a knowledge of the nature and behavior of the species formed during the chelation and subsequent hydrolysis of Zr(IV) ions in aqueous solution might be of value in understanding the solution chemistry of this, and other, metal ions, it would seem profitable to study further, and in greater detail, those species postulated by Intorre and Martell. In this particular study we have repeated some of their original experiments on the Zr^{IV}–Tiron system, but with one important modification. We have undertaken our investigations in 3 *M* NaClO$_4$ solutions, rather than the 0.1 *M* KCl medium used by these workers for two reasons. First, since the change in the logarithm of the activity coefficient of the metal ion in solution, produced by replacing the cations of the background electrolyte by a given concentration of hydrogen ions, is inversely proportional to the total concentration of the background salt,[14] it would appear advisable in a system such as that investigated in this study, where high concentrations of both hydrogen ions and ligand ions are employed, to use an ionic medium of high concentration. Second, since the chloride ion is known to undergo secondary complexing with the Zr(IV),[12] the use of a weak complexing agent such as perchlorate should greatly limit this additional complication.

Experimental Section

Reagents.—Zirconium(IV) perchlorate was prepared by repeatedly fuming zirconium oxychloride, ZrOCl$_2$·8H$_2$O ("Spec-

(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) R. E. Connick and W. H. McVey, *J. Amer. Chem. Soc.*, **71**, 3182 (1949).

(4) R. E. Connick and W. H. Reas, *ibid.*, **73**, 1171 (1951).

(5) A. J. Zielen and R. E. Connick, *ibid.*, **78**, 5785 (1956).

(6) K. A. Kraus and J. S. Johnson, *ibid.*, **75**, 5769 (1953).

(7) J. S. Johnson and K. A. Kraus, *ibid.*, **78**, 26, 3937 (1956).

(8) R. L. Angstadt and S. Y. Tyree, Jr., *J. Inorg. Nucl. Chem.*, **24**, 913 (1962).

(9) H. Bilinski and S. Y. Tyree, Jr., personal communication.

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

(11) B. J. Intorre and A. E. Martell, *ibid.*, **83**, 3618 (1961).

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

(13) Tiron = 1,2-dihydroxybenzene-3,5-disulfonic acid, disodium salt.

(14) F. J. C. Rossotti and H. Rossotti, "The Determination of Stability Constants," McGraw-Hill, London, 1961, p 26.

pure" from Johnson Matthey Ltd., London), with AnalaR 72% perchloric acid until evolution of HCl from the fuming solution had ceased. The zirconium(IV) perchlorate liquor thus formed was used directly for the preparation of metal ion stock solutions after its Zr(IV) and hydrogen ion contents had been estimated by the methods described by Zielen,[15] using simple titration methods. The total perchlorate ion content of each liquor was estimated by assuming that its composition could be depicted as $xZr(ClO_4)_4 + yHClO_4$.

Stock solutions of $Zr(ClO_4)_4$–$(Na,H)ClO_4$ of 3 M total perchlorate ion molarity were prepared from Zr(IV) perchlorate liquors by dilution with doubly distilled water and appropriate volumes of sodium perchlorate solution. A typical stock solution thus prepared was 144.4 mM in Zr(IV) ion, 659.9 mM in H$^+$ ion, and 2995 mM in ClO_4^- ion. Solutions for potentiometric titration were prepared from such stock solutions by diluting part of the latter with 3 M NaClO$_4$ solution to an approximately 30 mM total Zr(IV) ion concentration and then adding aliquots of this diluted solution to accuractly known weights of solid Tiron to yield, on dilution to 50 ml with 3 M NaClO$_4$, solutions with known Tiron/Zr ratios and known metal chelate concentrations.
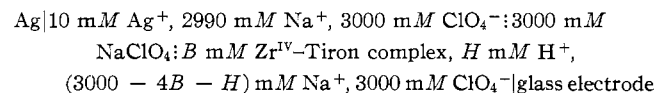
Silver perchlorate was prepared and assayed by the methods described by Biedermann[16] and Hietanen.[17]

Sodium perchlorate (BDH "low in chloride" variety) was used without further recrystallization as its saturated solution suitably diluted.

Tiron (Eastman Laboratory grade) was used, without further purification, after estimation by potentiometric titration against a standard base. The pK values for the ionization of the first and second phenolic protons of Tiron determined by this method were found to be 7.24 and 11.48, respectively, at 25° and 3 M NaClO$_4$, in excellent agreement with the values of 7.25 and 11.49 predicted for this temperature and medium by the equations of Nasanen.[18]

Titrant solutions of NaOH–NaClO$_4$, 3 M in ClO_4^- ion concentration, were prepared directly from BDH "solutions for analytical use."

Apparatus and Procedure.—The hydrogen ion concentrations of the experimental solution were determined with the cell

Ag|10 mM Ag$^+$, 2990 mM Na$^+$, 3000 mM ClO$_4^-$:3000 mM

NaClO$_4$:B mM Zr^{IV}–Tiron complex, H mM H$^+$,

(3000 − 4B − H) mM Na$^+$, 3000 mM ClO$_4^-$|glass electrode

using a Jena Type HT glass electrode (as supplied by Messrs. E. I. L. Ltd, Richmond, Surrey, England), the cell design being similar to that described by Forsling, Hietanen, and Sillén.[19]

The cell potentials were measured by means of a Vibron pH meter, Model 79A, suitably screened and accurate to 0.1 mV after calibration as a millivoltmeter using a National Physical Laboratories calibrated Weston standard cell.

The cell was immersed in a water thermostat maintained at a temperature of 25 ± 0.01°, this thermostat, in turn, being enclosed by an air thermostat maintained at 25 ± 0.5°.

Individual potentiometric titration runs were undertaken by addition of titrant NaOH–NaClO$_4$ solution, *via* buret delivery tubes fitted with "Carbosorb"-filled guard tubes, to the experimental solution contained in a glass multinecked flask of 95-ml capacity, fitted with an N$_2$ inlet and outlet, the glass electrode, and the salt bridge J tube of the measuring cell. Cell potentials, accurate to within ±0.1 mV, were rapidly obtained in all, other than hydrolysis, regions during a particular run.

Results and Discussion

In all the work described in this paper, the potentiometric titrations were conducted in a similar fashion to

(15) A. J. Zielen, Ph.D. Dissertation, University of California, 1953.
(16) G. Biedermann, *Ark. Kemi*, **9**, 277 (1956).
(17) S. Hietanen, *Acta Chem. Scand.*, **8**, 1626 (1954).
(18) R. Nasanen, *Suom. Kemistilehti B*, **30**, 61 (1957).
(19) W. Forsling, S. Hietanen, and L. G. Sillén, *Acta Chem. Scand.*, **6**, 901 (1952).

that described by Intorre and Martell;[10] *i.e.*, no attempt was made to maintain a constant metal chelate concentration in the titration cell during a particular run. This concentration, in fact, progressively decreased throughout the run due to the dilution of the contents of the cell through addition of titrant. In this respect, the runs described here, and by Martell, *et al.*, differ from those employed by Sillén and his coworkers, where the metal concentration is kept constant during a hydrolysis run through the addition of appropriate aliquots of metal stock solution to the contents of the cell.

Examples of the results obtained in this present study are given in Figures 1 and 2, respectively, where Figure 1 depicts the influence of initial metal chelate concentration in the system at a fixed Tiron/Zr(IV) ion ratio, while Figure 2 depicts the effect of varying this ratio at a fixed initial metal chelate concentration.

It will be seen that varying the initial metal chelate concentration, within the limits depicted in Figure 1, has little effect on the nature of the titration curves obtained. Although the curves for dilute solutions show less sharp breaks than those for more concentrated solutions, they all exhibit these breaks at the same molar ratio of OH$^-$/metal chelate, m, in the system. However, if it is assumed that the initial buffer region corresponds to chelation while the second buffer region corresponds to hydrolysis of the chelate, it will be seen that while the curves for the dilute solutions lie above those for more concentrated solutions during the chelation process, during hydrolysis the order is reversed. This behavior is somewhat unusual. In most other reported potentiometric studies of the formation and hydrolysis of chelated metal ions in aqueous solution the titration curves in the hydrolysis region have shown the same concentration dependence as that observed during chelation. A similar effect to that reported here, however, has been observed by Murakami and Martell[20] in their investigation of the Th^{IV}–Tiron system, where they established the presence of Tiron-bridged thorium species.

The results depicted in Figure 2, where data for the highest initial metal concentration studied are presented, indicate that varying the Tiron/Zr(IV) ion ratio in the system has a considerable influence on the titration curve obtained. Where this ratio is less than 2.5:1, *i.e.*, where the proportion of Tiron in the system is relatively small, the titration curves for each ratio appear to be unique, and both the position of the first steep inflection and the length of the subsequent buffer region are unrelated to the metal ion/ligand ratio in any simple way. Furthermore, over the range 1.5 < Tiron/Zr(IV) ion ratio < 2.5 the experimental results indicate that chelation and hydrolysis occur simultaneously during the initial buffer region, since the length of the latter is greater than can be accounted for solely on the basis of the number of protons released by the ligand in the system. Thus, at a Tiron/Zr(IV) ion ratio of 1.5, the data indicate that a species of empirical

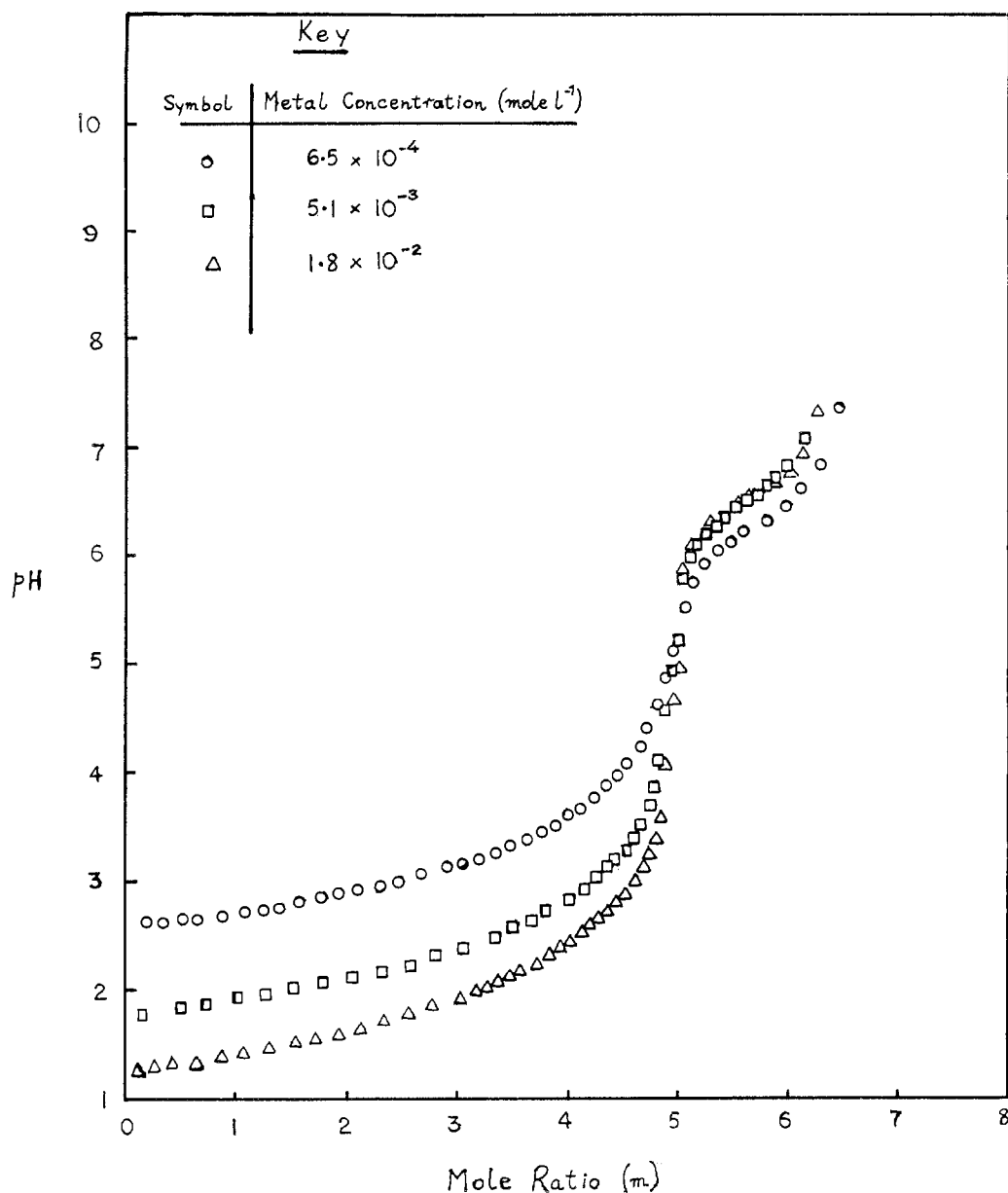(20) Y. Murakami and A. E. Martell, *J. Amer. Chem. Soc.*, **82**, 5605 (1960).

Figure 1.—The influence of initial metal chelate concentration at a fixed Tiron/Zr(IV) ion ratio (2.5:1) on the formation and hydrolysis of zirconium(IV)-Tiron chelates in 3 M sodium perchlorate medium.
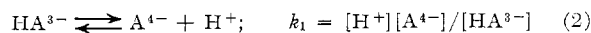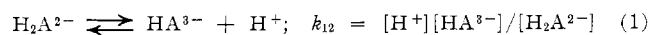
formula $ZrA_{1.5}(OH)_{1.25}$ (where A = Tiron) is initially formed and that this species is subsequently hydrolyzed further to $ZrA_{1.5}(OH)_{2.5}$, while at a Tiron/Zr(IV) ion ratio of 2.0 the initial species formed is of formula $ZrA_{2.0}(OH)_{0.5}$ and is subsequently hydrolyzed to $ZrA_{2.0}$-$(OH)_{2.0}$.

Where the Tiron/Zr(IV) ion ratio is equal to or greater than 2.5, however, the first steep inflection in the titration curves always appears at $m = 5$, and at a pH of approximately 4, suggesting the formation of a definite species, although possibly of complex structure. Since the length of the initial buffer region in this case is either equal to or less than the number of moles of base required to neutralize the protons released by the ligand, it is suggested that this species is unhydrolyzed and possesses the empirical formula $ZrA_{2.5}$.

For ratios greater than 2.5:1 there is a further buffer region between pH values of 4.0 and 5.5 whose length

depends on the amount of Tiron in excess of a ratio of 2.5:1 in the system. Some idea of the nature and behavior of the species present in the system over this buffer range may be obtained if the assumption that the initial species present is unhydrolyzed $ZrA_{2.5}$ is accepted and the equations developed by Richard, Gustafson, and Martell[21] are applied to this particular case.

Thus, for a diprotonated ligand H_2A^{2-}, such as Tiron, ionization proceeds according to the equations

$$H_2A^{2-} \rightleftharpoons HA^{3-} + H^+; \quad k_{12} = [H^+][HA^{3-}]/[H_2A^{2-}] \quad (1)$$

$$HA^{3-} \rightleftharpoons A^{4-} + H^+; \quad k_1 = [H^+][A^{4-}]/[HA^{3-}] \quad (2)$$

and if it is assumed that the free ligand base, A^{4-}, reacts with metal ion to form chelates according to the general process

$$x_iM^{n+} + y_iA^{4-} \rightleftharpoons M_{x_i}A_{y_i}{}^{(nx_i - 4y_i)+} \quad (3)$$
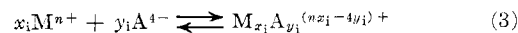
(21) C. F. Richard, R. L. Gustafson, and A. E. Martell, *J. Amer. Chem. Soc.*, **81**, 1033 (1959).
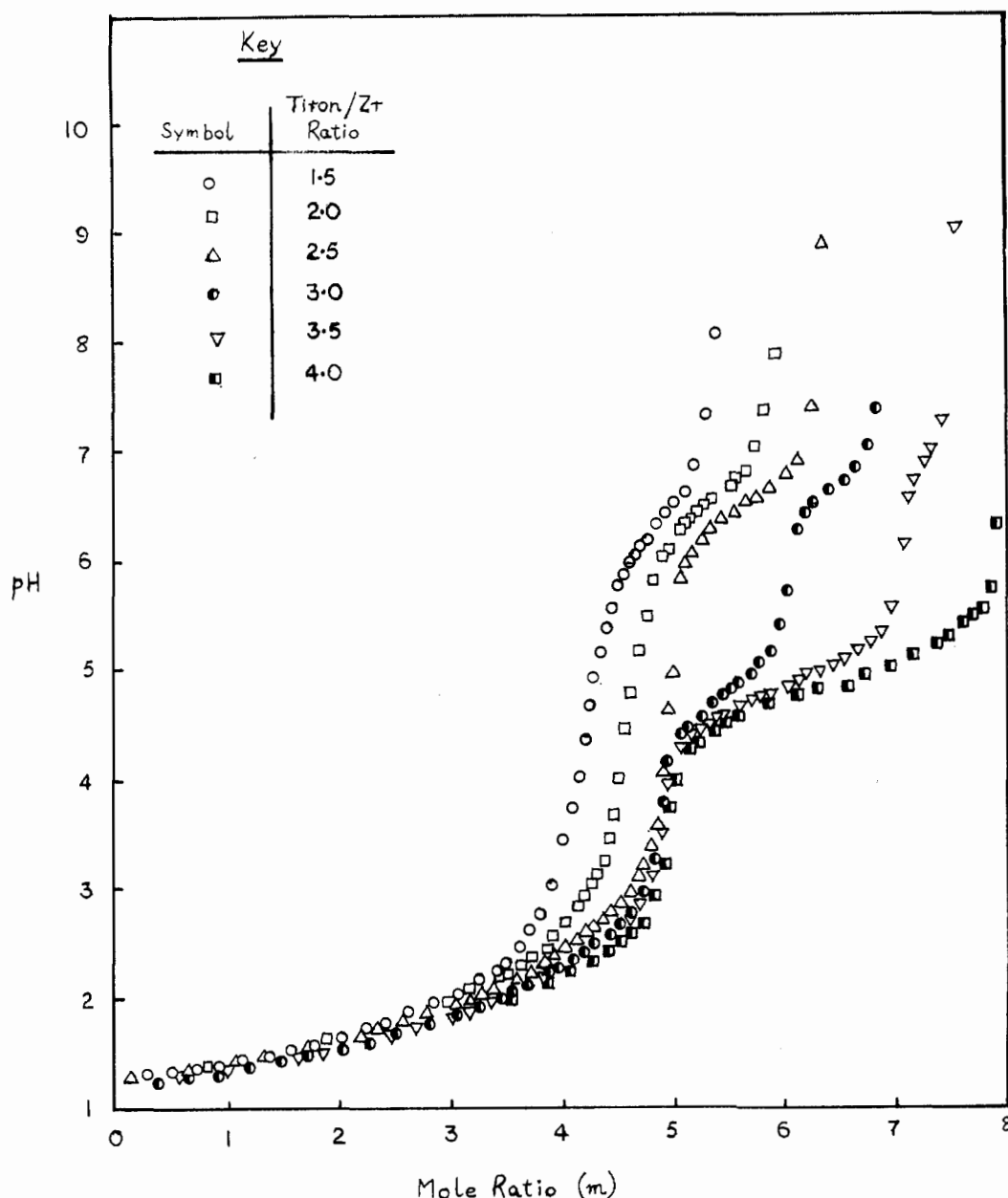
Figure 2.—The influence of varying Tiron/Zr(IV) ion ratio at a fixed initial metal chelate concentration ($1.8 \times 10^{-2}M$) on the formation and hydrolysis of zirconium(IV)-Tiron chelates in 3 M sodium perchlorate medium.

then it may be shown that

$$[A^{4-}] = \frac{(2 - a)T_A - [H^+] + [OH^-]}{\dfrac{2[H^+]^2}{k_{12}k_1} + \dfrac{[H^+]}{k_1}} \quad (4)$$

where a is the number of moles of base added per mole of ligand and T_A is the total concentration of the various ligand species in the solution.

Furthermore, if the Bjerrum formation function is defined as $\bar{n}$, then

$$\bar{n} = \frac{1}{T_M}(T_A - X[A^{4-}]) \quad (5)$$

where T_M is the total metal ion concentration in the system and X is defined by the equation

$$X = \frac{[H^+]^2}{k_{12}k_1} + \frac{[H^+]}{k_1} + 1$$

Using values of $\bar{n}$ and $[A^{4-}]$ obtained *via* (5) and (4),

respectively, it is possible to construct a Bjerrum formation curve from the data over the range $2.5 \leqslant$ Tiron/Zr(IV) ion $\leqslant 4.0$ in the system. Such a curve is shown in Figure 3 and indicates that if the assumptions mentioned above regarding ZrA$_{2.5}$ are accepted, then the formation of this species is represented as a definite step in the formation curve. What is more important, however, is that the curve indicates that addition of further Tiron to the ZrA$_{2.5}$ species results in the conversion of the latter to a ZrA$_4$ species. Thus, at ratios greater than 2.5:1, the additional buffer region noted above is due to this conversion process, the extent of conversion depending on the excess amount of Tiron in the system.

In summary, therefore, the results reported in this study suggest that at Tiron/Zr(IV) ion ratios equal to or greater than 2.5 the formation and behavior of the
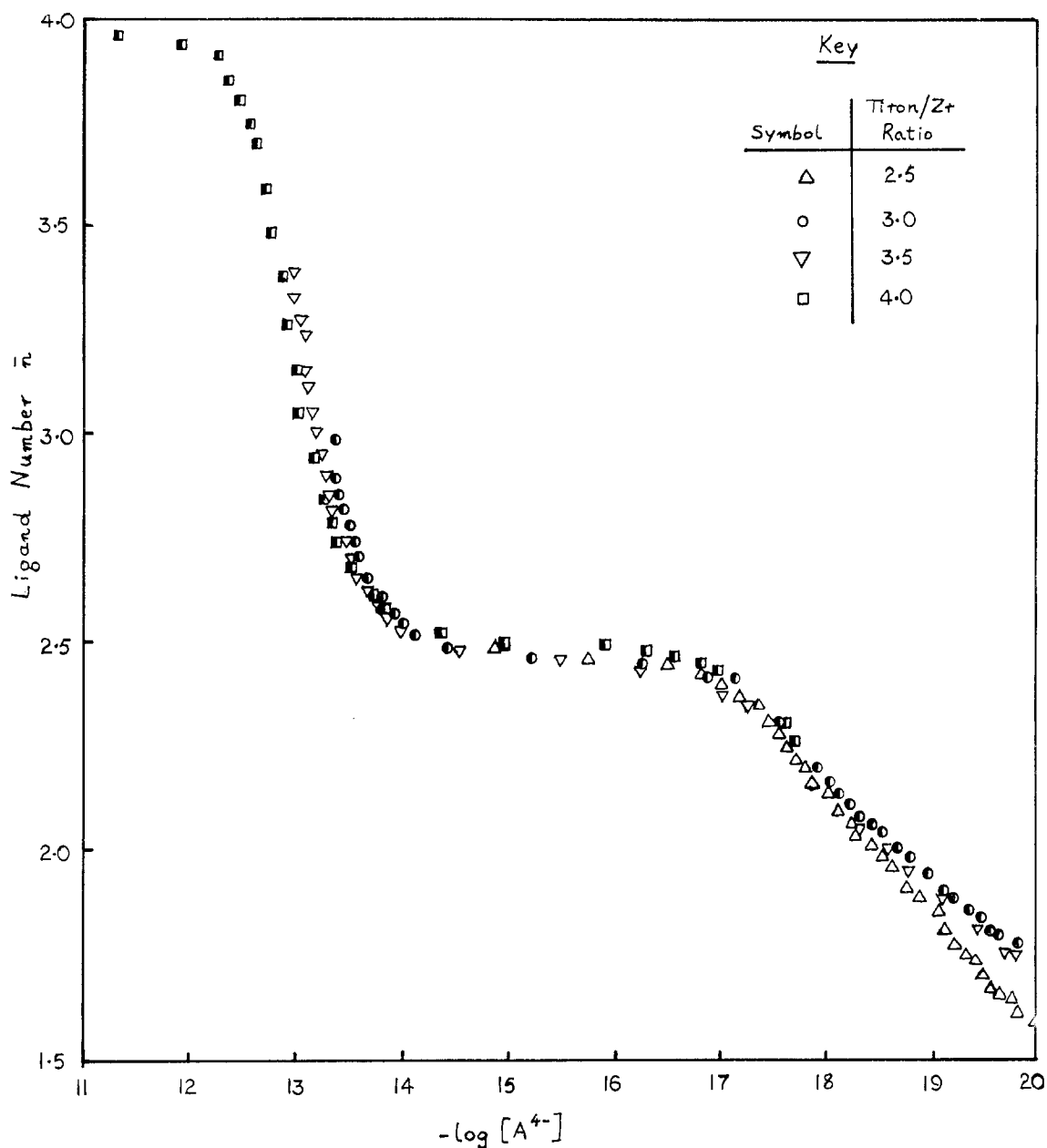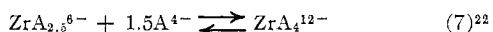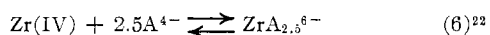
Figure 3.—Formation curves for the zirconium(IV)–Tiron system in 3 M NaClO$_4$ at Tiron/Zr(IV) ion ratios equal to or greater than 2.5 and at a fixed initial metal chelate concentration of 1.8×10^{-2} M.

species in the system may be depicted by the equations

$$Zr(IV) + 2.5A^{4-} \rightleftharpoons ZrA_{2.5}^{6-} \qquad (6)^{22}$$

$$ZrA_{2.5}^{6-} + 1.5A^{4-} \rightleftharpoons ZrA_4^{12-} \qquad (7)^{22}$$

Of these species, the potentiometric data depicted in Figure 2 show that the ZrA$_{2.5}$ entity undergoes hydrolysis, taking up 1.5 mol of base per mole of Zr(IV) ion. ZrA$_4$ is not hydrolyzed and since the "complexes" formed by the addition of Tiron to ZrA$_{2.5}$ are best regarded as mixtures of ZrA$_{2.5}$ and ZrA$_4$, the hydrolytic behavior of the system within the range $2.5 \leq$ Tiron/Zr(IV) ion ≤ 4.0 may be explained in terms of the hydrolysis of the ZrA$_{2.5}$ component while the ZrA$_4$ component remains unchanged.

(22) Although the species ZrA$_{2.5}$ and ZrA$_4$ are depicted as possessing very large negative charges, in 3 M NaClO$_4$ solution many of these charges are probably neutralized by counterions from the medium.

Several important questions remain unanswered, however. First, although suggesting the conversion of the ZrA$_{2.5}$ species to the ZrA$_4$ species at high Tiron ratios in the system, this study offers no positive proof of the correctness of this suggestion. Such proof is supplied by the results reported in part II of this series,[23] where it is also shown that the ZrA$_{2.5}$ species possesses a binuclear structure.

Second, the results reported here allow no explanation of the apparently unique hydrolytic stability of the ZrA$_{2.5}$ species at low pH values in the system. The three titration curves at ligand/metal ion ratios of 1.5:1, 2.0:1, and 2.5:1 in Figure 2 are very similar in appearance and could logically suggest that similar reactions are involved in each case. Whether these reactions are

(23) B. H. Massey and F. G. R. Gimblett, *Inorg. Chem.*, **9**, 2043 (1970).

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.

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]

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.

(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.