[CONTRIBUTION FROM THE OAK RIDGE NATIONAL LABORATORY, CHEMISTRY DIVISION]

Hydrolytic Behavior of Metal Ions. VI. Ultracentrifugation of Zirconium(IV) and Hafnium(IV); Effect of Acidity on the Degree of Polymerization[1,2]

BY JAMES S. JOHNSON AND KURT A. KRAUS

RECEIVED JANUARY 12, 1956

Polymerization of zirconium and hafnium (*ca.* 0.05 *M*) has been investigated by equilibrium ultracentrifugation. Hf(IV) at this concentration is probably polymerized in 5 *M* HCl. There is definite polymerization in 3 *M* HCl. In the range 0.5–2 *M* HCl, Hf(IV) is probably either a trimer or tetramer and the degree of polymerization is relatively independent of Hf(IV) and HCl concentrations. At acidities 0.2 *M* and less, Hf(IV) is more highly polymerized and polydisperse. Polymerization of Zr(IV) is similar. The principal difference is that Zr(IV) is more highly aggregated than Hf(IV) at the lower acidities. Centrifugation of solutions containing varying concentrations of Zr(IV) and of supporting electrolyte in 1 *M* HCl indicate that the polymers, like those of hafnium, are trimeric or tetrameric at this acidity and carry charges of *ca.* plus one per monomer unit. The same degree of polymerization was found for Zr(IV) in 1 *M* $HClO_4$. Decrease of temperature from *ca.* 25° to *ca.* 5° markedly lowers the degree of polymerization in 0.08 *M* HCl, in contrast to the small effect observed in 1 *M* HCl. Aging of $ZrOCl_2$ solutions, or heating, increased the degree of polymerization significantly but did not produce very large polymers.

The hypothesis that Zr(IV) polymerizes on hydrolysis is of long standing,[3] but descriptions of the process inferred from different methods are somewhat contradictory. Workers in the field seem to have abandoned the idea[4] that a monomeric ZrO^{++} ion predominates in aqueous solutions over a wide range of acidity. Polymerization of Zr(IV) is suggested by many types of results, including slow conductivity changes[5,6]; freezing point depressions and potentiometric studies[7]; and titrations of $ZrCl_4$ with base.[8] From diffusion measurements, Jander and Jahr[9] concluded that Zr(IV) in perchlorate solution forms low molecular weight polymers and that the degree of polymerization is unchanged over a wide range of acidity. Small polymers were also postulated from measurements of hydrolysis of $ZrCl_4$[10] in acidic solutions and from the rate of Zr(IV) uptake by ion-exchange resin from nitric acid solutions.[11]

On the other hand, Connick and Reas[12] measured the extraction of Zr(IV) from one to two molar $HClO_4$ into benzene–thenoyltrifluoroacetone (TTA) solutions, and analyzed their results by the continuous polymerization hypothesis of Sillén.[13] Their interpretation indicated a mixture of species, considerably more highly aggregated and more polydisperse than postulated by the earlier workers. Later, however, spectrophotometric studies of Zr(IV)–TTA complexes, carried out in the same laboratory, were interpreted on the basis of zirconium trimers and tetramers under these conditions.[14]

Larsen and Wang[15] recently reported results of cation exchange of mixed Zr(IV)–Hf(IV) solutions (total metal concentrations 10^{-5} to 10^{-2} *M*) in 0.5–2.0 *M* $HClO_4$. They concluded that in the aqueous phase Zr(IV) and Hf(IV) are present as Zr^{+4} and Hf^{+4} ions at their lowest metal concentration and that the species in the resin are hydrolyzed. In chloride solutions, ultracentrifugations have indicated that in solutions 0.0075–0.1 *M* in Hf(IV) and 1 *M* in HCl, most of the Hf(IV) is found in one or a few species having a weight average degree of polymerization, N_w, of 3 or 4.[1]

Other studies of the solution chemistry of hafnium are rare. It is generally believed that it is similar to that of Zr(IV). The solubilities of $ZrOCl_2$ and $HfOCl_2$ as a function of HCl concentration are indeed much alike.[16] Larsen and Gammill[17] found evidence in a study of precipitation of the hydroxides that hafnium is somewhat less hydrolyzed than zirconium.

In this paper a study of the effect of acidity on the polymerization of Zr(IV) and Hf(IV) in aqueous solutions, principally by equilibrium ultracentrifugation, is presented.

Experimental

Details of centrifugation procedure have been described earlier.[1,18] Briefly, solutions were centrifuged in a Specialized Instrument Corporation Model E ultracentrifuge. Observation of sedimentation is based on refractive index gradients with radius resulting from concentration gradients induced by the centrifugal field. The quantity used for interpretation is Z^*, a number proportional to the refractive index gradient attributable to the presence of the polymeric solute.

The solutions were contained in cells of approximately 12 mm. thickness in the direction of the optical path. The

---

[1] This document is based on work performed for the U. S. Atomic Energy Commission at the Oak Ridge National Laboratory. Previous paper: J. S. Johnson, K. A. Kraus and R. W. Holmberg, THIS JOURNAL, **78**, 26 (1956).

[2] Presented in part, 126th ACS Meeting, New York, September, 1954, Abstracts, p. 60-R. preliminary report, K. A. Kraus and J. S. Johnson, *ibid.*, **75**, 5769 (1953).

[3] W. B. Blumenthal, *Ind. Eng. Chem.*, **46**, 528 (1954). This paper reviews zirconium literature and has a more complete set of references than presented here. Earlier literature is reviewed by F. P. Venable, "Zirconium and Its Compounds," ACS Monograph Series, Chemical Catalog Co., Inc., New York, 1922.

[4] See *e.g.*, (a) E. Chauvenet, *Ann. chim.*, **13**, 59 (1920); (b) W. M. Latimer, "The Oxidation States of the Elements and Their Potentials in Aqueous Solutions," Second Edition, Prentice-Hall, Inc., New York, N. Y., 1952, p. 271.

[5] R. Ruer, *Z. anorg. Chem.*, **43**, 282 (1905).

[6] F. P. Venable and D. H. Jackson, THIS JOURNAL, **42**, 2531 (1920).

[7] M. Adolf and W. Pauli, *Kolloid-Z.*, **29**, 173 (1921).

[8] H. T. S. Britton, *J. Chem. Soc.*, **127**, 2120 (1925).

[9] G. Jander and K. F. Jahr, *Kolloid-Beih.*, **43**, 295 (1936).

[10] K. A. Kraus and S. Y. Tyree, Chem. Div. Quarterly Report ORNL-499, September 30, 1949, p. 26.

[11] B. A. J. Lister and L. A. McDonald, *J. Chem. Soc.*, 4315 (1952).

[12] R. E. Connick and W. H. Reas, THIS JOURNAL, **73**, 1171 (1951).

[13] (a) F. Granér and L. G. Sillén, *Acta Chem. Scand.*, **1**, 631 (1947); (b) L. G. Sillén, *ibid.*, **8**, 299 (1954); (c) **8**, 318 (1954).

[14] A. J. Zielen, U. S. A.E.C., UCRL-2268, July, 1953.

[15] E. M. Larsen and P. Wang, THIS JOURNAL, **76**, 6223 (1954).

[16] G. v. Hevesy, *Kgl. Danske Videnskab. Selskab, Mat.-fys. Medd.*, **6**, No. 7, 1 (1925).

[17] E. M. Larsen and A. M. Gammill, THIS JOURNAL, **72**, 3615 (1950).

[18] J. S. Johnson, K. A. Kraus and T. F. Young, *ibid.*, **76**, 1436 (1954).

TABLE I

ULTRACENTRIFUGATION OF ZIRCONIUM(IV) AND HAFNIUM(IV) IN CHLORIDE SOLUTION

Expt. no. and conditions[a]		Medium	Initial molarity				S'_e[d]	α'_e[e]		Temp., °C.
			Hf(IV)	Zr(IV)	HCl	MCl		x = 6.3	x = 6.9	
1	B-5	HCl	0.049		5	0	0.0224	0.80	1.18	33.2
2	B-4	HCl	.049		3	0	.0256	1.28	1.53	29.1
3[b]	B-5	HCl		0.043	3	0	.0248	0.88	1.14	29.0
4	B-4	HCl	.050		2	0	.0357	1.82		25.9
5[b]	C-5	HCl-NaCl	.048		1	1	.0517	1.88		32.2
6[b]	B-5	HCl-NaCl		.047	1	1	.0344	1.25		33.1
7	B-5	HCl-CsCl		.050	1	1	.0244	0.89		34.0
8	B-4	HCl-CsCl		.052	1	1	.0168	.88		33.8
9	B-5	HCl-LiCl		.049	1	1	.0354	1.29		33.0
10	B-5	HCl-LiCl		.023	1	1	.0371	1.35		33.3
11	B-5	HCl		.050	1	0	.0348	1.27		34.5
12	B-4	HCl-LiCl	.050		0.5	1.5	.0384	1.96		26.7
13[b]	B-3	HCl-NaCl	.048		.2	1.9	.0271	1.88	2.09	30.0
14[b]	B-5	HCl-NaCl		.043	.2	1.9	.0502	1.77	2.32	29.7
15	A-2	HCl-LiCl	.050		.08	1.9	(f)	3.71	4.59	27.2
16	A-2	HCl-LiCl	.050		.08	1.9	(f)	2.75	3.39	8.5
17	C-4	HCl-LiCl		.051	.08	1.9	(f)	2.90	4.85	26.2
18	B-4	HCl-LiCl		.051	.08	1.9	(f)	2.20	2.96	0.9
19[c]	B-1	LiCl		.05	0	2	(f)	10.0	13.2	28.4
20[c]	B-1	LiCl		.05	0	2	.0496	13.2	18.3	26.5

[a] Bar angle: A, 35°: B, 45°; C, 55°. Approximate speed of rotation (r.p.m.): 1, 9250; 2, 17,980; 3, 20,410; 4, 23,150; 5, 27,690. [b] Zr(IV) or Hf(IV) introduced as $ZrCl_4$ or $HfCl_4$. All other experiments, introduced as oxychloride. [c] Experiment 19 on unheated $ZrOCl_2$ solution; Experiment 20 on $ZrOCl_2$ solution heated for one hour at 100°. [d] Values of S'_e used to compute Fig. 1. [e] $\alpha'_e = 10^6 S'_e T/\omega^2$. Single values of α'_e apply to average radius of solutions ($x \approx 6.6$ cm.) and indicate that S'_e was either constant or decreased slightly with x. [f] Equilibrium not attained.

cells were located at a radius of about 65 mm. Most solutions attained equilibrium distribution in the field after about a week of centrifugation. In a few cases, at lower acidities, slow changes of Z^* with time were observed after considerably longer periods. Apparently polymerization was still occurring in these solutions. In these cases, the results reported were computed from the photographs made at the termination of the experiments as though equilibrium had been attained. The degrees of polymerization obtained in this way probably represent fairly well the aggregation of the solute at the end of the centrifugation.

Zirconium(IV) and hafnium(IV) were usually introduced as the oxychlorides, though the tetrachlorides were used in a few cases. The hafnium compounds were essentially zirconium free and, along with the other chemicals used, have been discussed earlier.[1] Commercial $ZrOCl_2$ was used after recrystallization from 9 M HCl. Zirconium tetrachloride was supplied to us by Dr. S. Y. Tyree of the Univeristy of North Carolina.[19] Spectroscopic analysis of both compounds showed negligible impurities except for 1.4 to 2.5 weight per cent. hafnium.[20] Metal–chloride mole ratios determined by gravimetric analysis of the oxychlorides were equal to the theoretical values within accuracy of the analyses.

Densities of the solutions were determined with a pycnometer and with gradient tubes.[21]

Results and Discussion

Solutions of Hf(IV) at stoichiometric acidities 0.08–5 M HCl in excess of the oxychloride were studied by equilibrium ultracentrifugation. The (acid) range for zirconium was 0–3 M excess HCl. The initial concentration of Hf(IV) or Zr(IV) was about 0.05 M except for a series in 1 M excess HCl, for which the effect of concentration was studied. The effect of temperature on polymerization in the range 0–30° was investigated for solutions 0.08 M in HCl. A solution of $ZrOCl_2$ with no excess acid, which had been heated at 100° for an hour, was also centrifuged in order to correlate the changes in chemistry observed by Ruer with possible differences in degree of polymerization.

The conditions for the equilibrium centrifugations are summarized in Table I. The experiments with Hf(IV) in 0.5–2 M HCl have been reported earlier,[1] but are included for comparison. Two centrifugations in 1 M $HClO_4$ will be discussed (section 7) but are not included in Table I. A few velocity centrifugations were also carried out to obtain information on polymerization of freshly prepared solutions.

The new equilibrium centrifugation results for chloride solutions are summarized in Fig. 1, which is a plot of the difference ($\log (Z^*/x) - S'_e x^2$) *vs.* x^2. This difference should be independent of x^2 for an ideal monodisperse solute. The values of $S'_e = d \log (Z^*/x)/d(x^2) = S_e/2.303$ were selected to give the minimum range of ordinate in Fig. 1 and are listed in Table I. Only those centrifugations for which equilibrium was attained are included in the figure. The symbols and equations used in this paper have been discussed more fully earlier.[1]

1. **Method of Interpretation.** (a) **Monodisperse Systems.**—The polymers studied are probably charged, and the magnitude of the charge is unknown. Since equilibrium distribution is affected by charge as well as by molecular weight,[22] even though centrifugations are carried out at a high concentration of light supporting electrolyte, estimation of the degree of polymerization in principle requires knowledge of charge. For systems having an essentially constant weight average degree of polymerization, N_w, (*i.e.*, $d \ln N_w/d(x^2) \approx 0$), and

---

(19) W. S. Hummers, S. Y. Tyree and Seymour Yolles, in "Inorganic Syntheses," Vol. 4, McGraw-Hill Book Co., New York, N. Y., 1953, p. 121.

(20) We are indebted to C. Feldman and M. Murray of the ORNL Spectroscopic Laboratory for the analyses.

(21) K. Linderstrøm-Lang and H. Lanz, *Compt. rend. trav. lab. Carlsberg*, **21**, 315 (1938).

(22) O. Lamm, *Arkiv Kemi, Mineral. Geol.*, **17A**, paper 25 (1944).

obeying certain other restrictions, simultaneous evaluation of N_w and of z', the charge per monomer unit, is possible by carrying out centrifugations under a variety of conditions.[1,23]

The equations for computing N_w and z' from experimental results were derived[23] on the assumption that charge z', activity coefficient ($y_{\pm i}$), partial specific volume ($\bar{v}_i$), and specific refractive index increment ($\partial n/\partial w_i$) are constant for each species, and that solution density (ρ) is also constant. The weight average degree of polymerization is given by the equation

$$N_w = \frac{S/A'_2}{1 - \dfrac{z'^2c'_2}{2c_3A'_2}(S - \sigma)} \tag{1}$$

In this equation $S = \mathrm{d}\ln c'_2/\mathrm{d}(x^2)$; $\sigma = \mathrm{d}\ln c_3/\mathrm{d}(x^2)$; $A'_2 = M'_2(1 - \bar{v}_2\rho)\omega^2/2RT$; ω is the angular velocity; R the gas constant; T the absolute temperature; c'_2 the concentration of the polymer component (component 2) expressed as monomer; and c_3 the concentration of the supporting electrolyte (MX, component 3). The polymer component is defined as ($PX_z - (z/2)$ MX) where P^{+z} is the polymeric cation and X^- the anion. The polymer component has the molecular weight $M_2 = NM'_2$, the charge $z = Nz'$, and the partial molal volume $\bar{V}'_2$ appropriate to its definition.

Equation 1 is in terms of $S = \mathrm{d}\ln c'_2/\mathrm{d}(x^2)$, rather than the experimentally obtained $\mathbf{S}_e = \mathrm{d}\ln(Z^*/x)/\mathrm{d}(x^2)$. The relation between these quantities is given by the equation[1]

$$S - S_e = \frac{\dfrac{z'^2c'_2}{2c_3A'_2}(S - \sigma)^2}{1 + \dfrac{z'^2c'_2}{2c_3A'_2}\sigma} \tag{2}$$

and the assumption that $\mathbf{S}_e$ is equal to $\mathrm{d}\ln(\mathrm{d}c'_2/x\mathrm{d}x)/\mathrm{d}(x^2) = S_e$.

By equations 1 and 2 values of N'_z may be computed and plotted for the plausible range of z'. A series of centrifugations are carried out at different ratios of c'_2/c_3. The intersection of these curves or the point where they approach closest to each other then gives N_w (or N) and z'.

Equations 1 and 2 are for systems of the three components, water, supporting electrolyte and polymeric solute. If more than one supporting electrolyte is present and if the supporting electrolytes differ greatly in $M(1 - \bar{v}\rho)$, so that an average value is not adequate, more elaborate though similar equations must be used.[1]

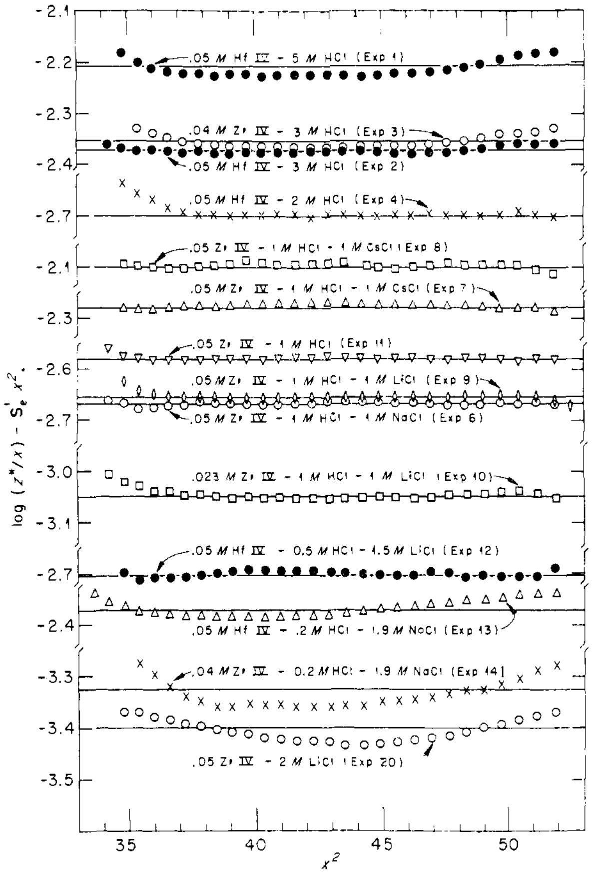

Fig. 1.—Test of constancy of $\mathbf{S}'_e$.

(b) **Polydisperse Systems.**—For those polydisperse systems where N_w does not change greatly in any single experiment, equations 1 and 2 may be used directly without introducing significant errors.[1] These systems are characterized by essential invariance of the difference $\log Z^*/x - \mathbf{S}'_e x^2$ as a function of x or by a downward curvature of this function (charge effect). However, some of the systems studied here showed upward curvature of this function, which implies considerably greater polydispersity. For these, $\mathrm{d}\ln N_w/\mathrm{d}(x^2)$ is not constant and equations 1 and 2 are not directly applicable. However, if the analog of equation 2 is derived without neglect of $\mathrm{d}\ln N_w/\mathrm{d}(x^2)$, the equation

$$S - S_e = \frac{\dfrac{z'^2c'_2}{2c_3A'_2}(S - \sigma)^2}{1 + \dfrac{z'^2c'_2}{2c_3A'_2}\sigma} - \left(\frac{1 - \dfrac{z'^2c'_2}{2c_3A'_2}(S - \sigma)}{1 + \dfrac{z'^2c'_2}{2c_3A'_2}\sigma}\right)\frac{\mathrm{d}\ln N_w}{\mathrm{d}(x^2)} \tag{3}$$

is obtained. A rather cumbersome iteration is required to obtain c'_2 as a function of x and such effort does not appear justified in the present work, in the light of the limited experimental accuracy and the uncertainties in many of the assumptions. Thus, it is unlikely that the individual polymeric species are hydrolyzed to the same degree, and the assumption that they all have constant properties, *e.g.*, constant specific refractive index increments, is probably not as good for highly polydisperse solutes as for solutes distributed in a narrow range of molecular weights. Treatment of results for obviously polydisperse systems, therefore, will be by the less ambitious procedure of setting $z' = 0$.

Lansing and Kraemer[24] have shown that for uncharged polymer systems, for which species activity coefficients $\bar{v}_i$ and ($\partial n/\partial w_i$) are constant, the Z-average molecular weight M_z is directly obtained

---

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

[24] W. D. Lansing and E. O. Kraemer, THIS JOURNAL, **57**, 1369 (1935).

from observations based on refractive index gradients. Thus

$$M_Z = \frac{\sum M_i^2 w_i}{\sum M_i w_i} = \frac{2RT}{(1 - \bar{v}\rho)\omega^2} S_e \qquad (4)$$

$$M_Z/M_2' = N_Z \qquad (5)$$

where w_i is the weight of species i in a given volume of solution.

If the data were in terms of concentrations, rather than refractive index gradients (*i.e.*, if equation 4 were in terms of S rather than S_e), the weight averages, M_w and N_w, would be obtained. Weight averages defined by the equation

$$N_w = \frac{M_w}{M_2'} = \frac{\sum M_i w_i}{M_2' \sum w_i} \qquad (6)$$

tend to be lower than Z-averages, since the latter emphasize heavier species. If we compute an average degree of polymerization N_e from the observed slopes $\mathbf{S}_e$ by equations 4 and 5 without considering possible charge on the polymers, the computed degree of polymerization will be equal to or lower than the Z-average. Actually, if the charge on the polymer is large, N_e might even become smaller than a weight average N_w. A rough estimate of this effect was made for one of the more unfavorable cases, Experiment 19, Table I. If the polymer had $z' = 1$, the maximum plausible value, N_e would be 45% lower than N_w. At the other extreme, for $z' = 0$, N_e would be equal to N_Z and 40% higher than N_w. Since it is unlikely that z' is either as high as one or as low as zero in this medium, N_e should not differ greatly from N_w and in any event may be used for semi-quantitative estimation of aggregation and for comparison of Zr(IV) with Hf(IV).

2. **Monomer Unit and Partial Specific Volume.**—Computation of degree of polymerization requires evaluation of M_2' and $\bar{v}_2$, for which an estimate of the degree of hydrolysis **n** is needed. From solubility[16] and hydrolysis data,[10] $2 \leqslant \mathrm{n} \leqslant 2.3$ was estimated for the monomer unit for Hf(IV) in HCl. The same arguments apply to Zr(IV). For $ZrOCl_2$, the partial molal volume was computed from the experimentally determined $\bar{V}_{ZrCl_4}$ = *ca.* 39 cc. (in 1 *M* HCl–1 *M* NaCl) by the equation

$$\bar{V}_{ZrOCl_2} = \bar{V}_{ZrCl_4} - 2\bar{V}_{HCl} + \bar{V}_{H_2O} \qquad (7)$$

with the assumption that $\bar{V}_{H_2O}$ = 18 cc. and $\bar{V}_{HCl}$ = 19.9 cc. From this, $\bar{v}_{ZrOCl_2}$ = 0.096 cc./g. was obtained, with 92 as the atomic weight of the metal (Zr adjusted for Hf content). Earlier, $\bar{v}_{HfOCl_2}$ = 0.06 cc./g. had been found. The degree of hydrolysis undoubtedly varies with acidity. However, the effect on the computed degree of polymerization is small. For example, if the monomer unit were $Zr(OH)_3Cl$, rather than $ZrOCl_2$, then for $z' = 0$, $\rho = 1.05$, $M_2'(1 - \bar{v}_2\rho)$ would be 12% lower and the computed degree of polymerization 12% higher. The percentage error for Hf(IV) would be less. Since details of hydrolysis are unknown, $ZrOCl_2$ and $HfOCl_2$ were assumed to be the monomer units in all computations.

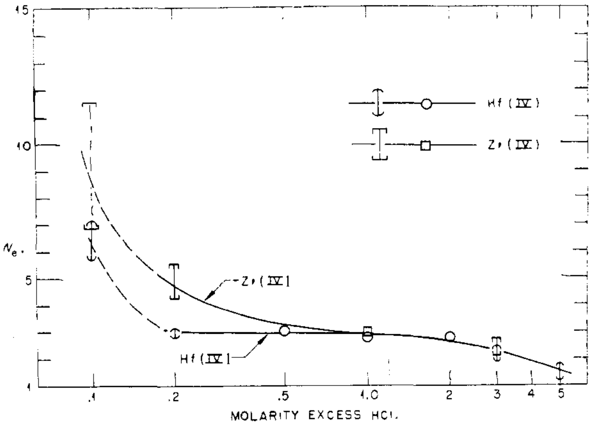

Fig. 2.—Polymerization of Zr(IV) and Hf(IV) as a function of acidity.

The apparent molal volume of $ZrCl_4$ in a solution containing 0.0365 *M* $ZrCl_4$ and 1 *M* NaCl was 42 cc. For present purposes this is not much greater than the value found in 1 *M* HCl–1 *M* NaCl, where polymerization is less. It appears that errors from assuming $\bar{v}_2$ independent of acidity are not great.

3. **Polymerization of Hf(IV) as a Function of Acidity.**—The results for Hf(IV) are presented in Fig. 2 as a plot of N_e *vs.* excess acidity (in excess of the composition $ZrOCl_2$). The range of N_e given for each acidity was computed from $\mathbf{S}_e'$ at radii 6.3 and 6.9 cm., points approximately 3 mm. from the edges of the cell. Concentrations, c_2', at the radii selected, bracket the initial concentrations of the solution. Closed symbols are used, if $\mathbf{S}_e'$ either did not vary as a function of x or decreased slightly with increasing x, in the direction expected for a charge effect.

Hf(IV) at *ca* 0.05 *M* is apparently somewhat polymerized even in 5 *M* HCl (N_e = 1.2 and 1.8). Some doubt results from the fact that sedimentation of HCl at this concentration is accompanied by appreciable increase in its activity coefficients with increasing radius. If the effect on the activity coefficients of the polymers is in the same direction, the computed values of N_e should be too low. In 3 *M* HCl, Hf(IV) is polymerized and polydisperse (N_e = 2.0 and 2.4). In the range 0.2 to 2 *M* HCl, N_e is *ca.* 3 and essentially independent of *M* HCl. This flatness suggests monodispersity and, as mentioned earlier, detailed study[1] of polymerization in 1 *M* HCl, with consideration of charge, indicated that the species was probably either a trimer or tetramer, and that z' = *ca.* 1. An indication of slight polydispersity in 0.2 *M* excess HCl became definite in 0.08 *M* acid, where N_e is also considerably greater. The curve is dotted in this range to indicate that equilibrium was not reached (centrifugation time *ca.* 10 days). Since $\mathbf{S}_e'$ was still increasing, though slowly, when the experiment was terminated, the values of N_e = 5.7 and 7.1 given for this acidity are minimal.

4. **Polymerization of Zr(IV) as a Function of Acidity.**—The results for zirconium are similar to those for hafnium, though fewer centrifugations were carried out. The curve (Fig. 2) was drawn with the same general shape as that for Hf(IV).

In 3 *M* HCl, the solution is obviously polydisperse (N_e = 2.1 and 2.7). For the 1 *M* HCl solutions, discussed more fully in section 6, $\mathbf{S}'_e$ was constant or decreased with x^2, and about the same value of N_e was found as for Hf(IV). In 0.2 *M* excess acid, Zr(IV) is clearly more polymerized and polydisperse (N_e = 4.2 and 5.5) than in 1 *M* HCl. In 0.08 *M* excess acid, equilibrium was not attained in ten days, but the minimum values (N_e = 6.9 and 11.6) indicate that N_e is larger than in 0.2 *M* HCl.

5. **Comparison of the Polymerization of Zr(IV) and Hf(IV).**—The results confirm the expected similarity in the behavior of Zr(IV) and Hf(IV). However, significant differences exist. Although the slight difference in N_e in 3 *M* HCl is of questionable significance, Zr(IV) is definitely more polymerized than Hf(IV) in 0.2 *M* excess HCl. Similarly, though equilibrium was not reached in 0.08 *M* HCl, the values of N_e were higher and seemed to be rising faster at termination of centrifugation for Zr(IV) than for Hf(IV).

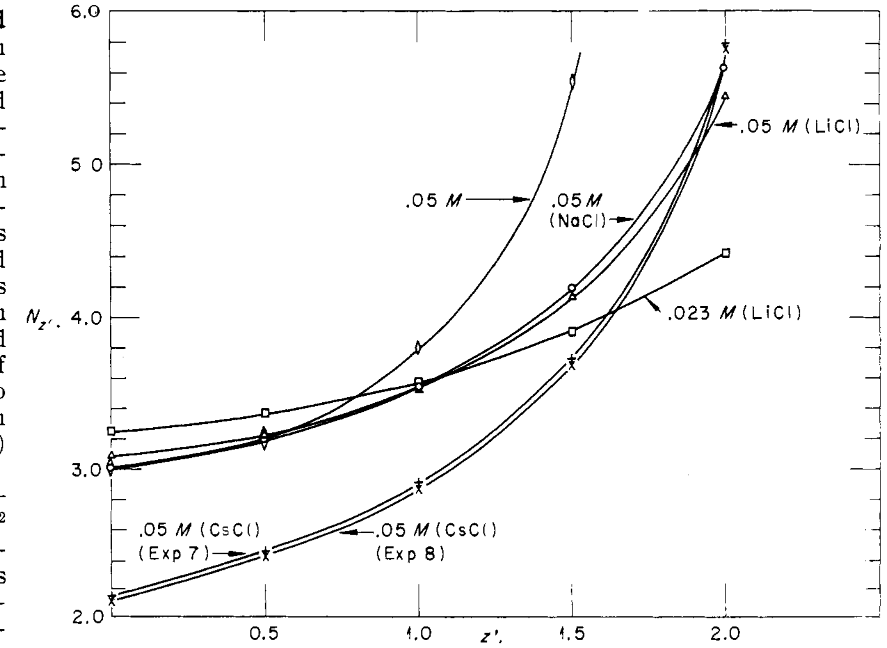

Fig. 3.—Degree of polymerization of Zr(IV) computed as a function of charge: all solutions 1 *M* in HCl and at molarity of Zr(IV) indicated; additional supporting electrolyte, when present, at 1 *M*.

6. **Zr(IV) in 1 *M* HCl.**—The constancy of $\mathbf{S}'_e$ with x^2 for Zr(IV) in 1 *M* HCl solutions suggests that at this acidity an analysis by equations 1 and 2 would be profitable. Centrifugations were, therefore, carried out at different initial concentrations of Zr(IV), at different total chloride concentrations, and in the presence of different supporting electrolytes. The complete equations 12 and 13, ref. 1, were used to interpret the experiments in HCl–CsCl. The results are summarized in Fig. 3 as a plot of the degree of polymerization $N_{z'}$ computed as a function of assumed z'. The curves appear closest to each other at z' = *ca.* 1 and $N_{z'}$ = *ca.* 3.5.[25] These values are very similar to the corresponding results for Hf(IV)[1] ($N_{z'}$ = *ca.* 3.2, z' = *ca.* 1). The uncertainty in the values of $N_{z'}$ and z', however, is considerably greater than in the Hf(IV) study. As in the earlier work, the curve for the experiment in 1 *M* chloride is higher than those in 2 *M* chloride, *i.e.*, opposite to what would be expected if changes in complexing of the poly mer by chloride ions were an overriding effect.

The large discrepancy between the experiment in HCl–CsCl solution and those in other media is puzzling. This centrifugation was repeated on a new solution, and virtually the same result was obtained. A lower speed was also tried (23,150 r.p.m. instead of 27,700), and the values of $N_{z'}$ obtained were almost the same as for the higher speed. The discrepancy thus does not seem to result from experimental error. It may, in part, result from the fact that in this system $(\partial n/\partial c'_2)$ is not constant as assumed, since it is a function of the ratio c_{HCl}/c_{CsCl}. This ratio decreases with radius and the resulting error is in the right direction to account for the discrepancy. The error is expected to be less for Hf(IV), but it is not clear why it was not observed at all.[1]

In spite of the poor coherence of the data in Fig. 3, the similarity between the present data on Zr(IV) and the earlier data on Hf(IV) is striking. Apparently both elements form a low molecular weight polymer (probably trimer or tetramer) with charge z' = *ca.* +1 per monomer unit.

7. **Zr(IV) in 1 *M* HClO$_4$.**—Two centrifugations of Zr(IV) in 1 *M* HClO$_4$–1 *M* NaClO$_4$ have been carried out with (initially) 0.049 and 0.12 *M* Zr(IV). Both were carried out at *ca.* 27,700 r.p.m. The equilibrium temperature for centrifugation of 0.049 *M* Zr(IV) was 24° and for 0.12 *M* Zr(IV), 29°. The monomer unit was assumed to be $ZrO(ClO_4)_2$, and its partial molal volume estimated by adding to $\bar{V}_{ZrOCl_2}$ twice the difference $(\bar{V}_{NaClO_4} - \bar{V}_{NaCl})$.[26]

The results were then treated in the same way as those in 1 *M* HCl. A plot similar to Fig. 1 showed concavity downward, as expected for charged species of constant N_w. On a graph similar to Fig. 3, a crossover was found at $N_{z'}$ = *ca.* 3.7 and z' = *ca.* 1.75. These values are not considered accurate, but they do indicate that there is no major difference between the degree of polymerization of Zr(IV) in 1 *M* HClO$_4$ and in 1 *M* HCl.

8. **Effect of Temperature.**—Temperature change from *ca.* 30° to *ca.* 0° was shown to have only a minor effect on polymerization of Hf(IV)

---

(25) In a preliminary report (ref. 2) of some of this work, the degree of polymerization for Zr(IV) under these conditions was given as 3.0. This figure must now be revised in view of a more extensive analysis.

(26) (a) H. E. Wirth and F. N. Collier, THIS JOURNAL, **72**, 5292 (1950); (b) T. F. Young and M. B. Smith, *J. Phys. Chem.*, **58**, 716 (1954).

in 1 M HCl.[1] A much larger effect was observed for the obviously polydisperse solutions of lower acidity.

Hafnium(IV) and zirconium(IV) solutions were prepared at room temperature. They both were then centrifuged at room temperature (experiments 15 and 17, Table I) and at low temperature (experiments 16 and 18). In both cases, centrifugation at the lower temperatures brought about the usual initial rise in Z from sedimentation. However, this was followed by a decrease in Z, presumably the result of depolymerization. In the Hf(IV) experiment, the values of Z were still falling at the end of five days. At this time, the values of N_e computed were 4.3 and 5.2 (maximum) at $x = 6.3$ and 6.9 compared with 5.7 and 7.1 (minimum) at termination of centrifugation at 27°. For Zr(IV), N_e was 5.3 and 7.1 (maximum) at the same values of x at termination of the low temperature experiment (1°) after 11 days. The corresponding values at 26° were 6.9 and 11.6 (minimum).

Since equilibrium was not attained, the values have only relative significance, but the direction of the changes leaves no doubt that the over-all reaction is endothermic (ΔH is positive). Whether the observation is explained by a predominating positive ΔH of hydrolysis, or indicates a positive ΔH of aggregation, or both, cannot be established from these results.

9. **Aged and Heated Solutions.**—Relatively little is known about the polymers formed on aging or heating Zr(IV) and Hf(IV) solutions. There is good evidence, *e.g.*, from conductivity changes,[5,6] that hydrolysis continues for a long time in $ZrOCl_2$ solutions. Such slow hydrolysis is also implied, of course, by the slow aggregation which occurs in weakly acidic solutions (see Sections 3 and 4). Marked changes in chemical behavior which have been noted on heating $ZrOCl_2$ solutions for long periods led Ruer to refer to them as solutions of "metazirconic acids," by analogy with metastannic acids.[5,27] He also reported that solutions heated for shorter times showed properties different from those freshly prepared. For example, heated solutions gave precipitates with sulfates, soluble in excess sulfate; the unheated solutions gave no precipitate. Some inferences have been made about the species in solution from the empirical formulas of precipitates obtained from them (see *e.g.*, ref. 3 and 27), but such a procedure is, of course, uncertain.

Since equilibrium ultracentrifugation is not applicable to a study of unaged (freshly prepared) solutions, a few sedimentation velocity measurements were carried out. These measurements will not be interpreted quantitatively since the polymers were polydisperse, since the peaks (boundaries) were not clearly separated from the meniscus, and since frictional coefficients are unknown. However, the measurements may be used for purposes of comparison. A freshly prepared 0.05 M $ZrOCl_2$ solution in 2 M LiCl (no excess acid) had an apparent sedimentation constant (25°) $s = ca.\ 1.5 \times 10^{-13}$. A similar solution which was aged for a year at room temperature and which showed sulfate precipitation behavior similar to Ruer's heated solution, gave $s = ca.\ 3 \times 10^{-13}$. Although some increase in aggregation seems to occur with aging, the change is rather small. The molecular weight range of these solutes can be inferred from the results of an attempted equilibrium ultracentrifugation on a similar two-month-old 0.05 M Zr(IV)–2 M LiCl solution (expt. 19, Table I). When this experiment was terminated after two weeks, the computed values of N_e were 24 and 31 at $x = 6.3$ and 6.9.

Similar degrees of polymerization were, surprisingly, observed in heated Zr(IV) solutions. A 0.25 M $ZrOCl_2$ solution was heated at *ca.* 100° for one hour (to approximate Ruer's conditions). It could then be precipitated and redissolved by sulfate. The solution was mixed with a LiCl solution to give 0.05 M Zr(IV)–2 M LiCl. Centrifugation equilibrium was attained in a week (expt. 20, Table I), and values of $N_e = 31$ and 43 at $x = 6.3$ and 6.9, respectively, were obtained. The same solution gave $s = ca.\ 3 \times 10^{-13}$ in a velocity sedimentation. It is tempting to conclude from these results that the degree of polymerization reaches an asymptote with aging or heating. This does not seem to be the case, however, since a 0.25 M Zr(IV) solution heated at 100° for several days, until cloudy, then treated to give 0.05 M Zr(IV)–2 M LiCl, had a higher s ($ca.\ 6 \times 10^{-13}$) for the unprecipitated portion. Apparently the growth of the polymers is rather slow, but the present results give no indication that the process reaches a definite limit.

10. **General Discussion.**—The results reported here show in general increasing polymerization with decreasing acidity for both Zr(IV) and Hf(IV), with relatively minor differences between these elements. The most marked difference is the greater tendency of Zr(IV) to polymerize at low acidities. Since polymerization presumably parallels hydrolysis, this result seems to agree with the observation of Larsen and Gammill[17] that Zr(IV) precipitates hydrolytically at higher acidity than Hf(IV). The complex distribution of polymeric species makes interpretation of solubility data in terms of simple ions uncertain.[28] This is especially true of the hydroxides,[4b] for which solubility products such as $(ZrO^{+2})(OH^-)^2$ or $(Zr^{+4})(OH^-)^4$ may be inadequate for most conditions.

The great complexity of the polymerization reactions and the relatively narrow range of conditions covered preclude presentation of a detailed picture of the course of hydrolysis at present. Thus, the question of the identity of the species predominating in strongly acidic solution (*e.g.*, *ca.* 9 M HCl where both hafnium and zirconium oxychlorides have minimum solubility) remains unanswered. In 5 M HCl, the highest acidity studied here, and 0.05 M Hf(IV), polymeric species apparently still exist. The fact that N_e was less than two does not necessarily indicate that monomers are present to an important extent, since the reported degree of polymerization is probably a lower limit. Predominance of the species Zr^{+4} at low concentrations ($<$ *ca*

---

(27) See also: E. H. Rodd, *J. Chem. Soc.*, **111**, 396 (1917).

(28) Presumably such difficulties arise in general in the hydrolysis of ions which tend to form hydrolytic polymers.

10^{-3} *M*) of Zr(IV) in 1 *M* and 2 *M* $HClO_4$ solutions has been postulated by Connick and McVey[29] on the basis of an approximate fourth power dependence of solvent extraction on TTA concentration. A similar conclusion was drawn by Larsen and Wang[15] and Zielen.[14] Although this is the simplest interpretation, their results could conceivably be explained by other species at low metal concentrations, *e.g.*, $(Zr(OH)_2)_2^{+4}$. The preparation by Larsen, Terry and Leddy[30] of the compound $Zr(TTA)_4$ from the benzene phase of a benzene–water system makes such an alternate species unlikely. The centrifugation results, though for higher Zr(IV) concentrations, also argue for the unhydrolyzed monomer at low metal concentrations. Zielen's results indicate that the polymers at higher Zr(IV) concentration are three to four times as large as the species at low concentrations. If the low concentration species were not monomeric, the degree of polymerization at 0.05 *M* Zr(IV) would have to be considerably higher than that found by ultracentrifugation. This discussion, of course, refers to perchlorate solutions and does not necessarily apply to chloride solutions. Lister and McDonald[11,31] measured the charge of Zr(IV) in nitric acid by cation exchange and found indication of hydrolysis even in 4 *M* HNO_3. Their zirconium concentrations (*ca.* 0.04 *M*), however, were higher than those for which predominance of Zr^{+4} is reported.

A remarkable feature of the centrifugation results at moderate acidities is a polymerization plateau, which indicates low molecular weight species, probably trimers or tetramers, of surprising stability. The charge per monomer unit in this region appears to be about one for Hf(IV) and about the same for Zr(IV). The acidity range for the plateau is roughly the same as for the plateau of diffusion coefficients found by Jander and Jahr[9] for 0.1 *M* Zr(IV) in perchlorate media, and their estimate of molecular weight agrees with the present results about as well as could be expected. They found stability over a somewhat wider range of acidity (1 *M* $HClO_4$ to 0.01 *M* NaOH in excess of $ZrO(ClO_4)_2$) but this may stem from differences between chloride and perchlorate media and differences in temperature (their measurements were at 10°). Lister and McDonald[11] also found evidence for a plateau of low molecular weight polymers for Zr(IV) in nitric acid solutions.

The disagreement between the ultracentrifugation results at high acidity (low molecular weight polymer) and the solvent extraction results of Connick and Reas[12] (large degree of polymerization, highly polydisperse systems) was discussed previously.[2] In any case, Zielen's subsequent spectrophotometric studies[14] of Zr(IV)–TTA complexes, which were carried out in Connick's laboratory, have apparently resolved most of these differences.

Polymeric reactions of Zr(IV) and Hf(IV) become complicated at low acidities. Not only does formation of higher molecular weight products occur but slow equilibria seem to be involved, in contrast to behavior in the more acidic solutions (polymerization plateau). Interestingly, the molecular weights of the bulk of the polymers existing in Zr(IV) solutions of low acidities, even after aging or heating (degrees of polymerization in the range 20 to 40) do not seem to be extremely large compared to those in "unaged" solutions (N_e *ca.* 10). Even heating solutions to onset of visible precipitation seems to increase the degrees of polymerization by only a factor of five or so over "unaged" solutions. It seems unlikely that the marked differences in precipitation properties (*e.g.*, precipitation with sulfate) between unaged and aged or heated solutions results from such modest differences in size of polymers alone. More likely, structural changes of the polymers occur on aging and heating. Since the polymers are presumably held together by hydroxide or oxide bridges, a change from one type to the other might be responsible for the differences in precipitation properties. Changes in coördination number (*e.g.*, six to eight) might also occur. Since aging is presumably also accompanied by an increase in the degree of hydrolysis of the polymers (hydroxyl number), the extent of which is not known, further speculations on the structural differences between aged and freshly prepared polymers seems at present unwarranted.

Sillén,[13] among others, has visualized hydrolytic polymers in solution as fragments of the metal–oxygen sheets or chains often found in precipitates of hydrous oxides or basic salts. His model leads to a continuous series of polymers, no one much more stable than the others. Polymerization of Zr(IV) and Hf(IV) at low acidities may be of this type, but the existence of the plateau region implies special structures which are not necessarily fragments of infinite sheets or chains. Recently, Clearfield and Vaughan[32] have shown by X-ray diffraction that Zr(IV) exists in discrete tetrameric units in the crystal $ZrOCl_2 \cdot 8H_2O$. That the polymers found in *ca.* 1 *M* HCl solutions have the same basic structure is an interesting possibility, though such a conclusion is by no means established at present.

OAK RIDGE, TENN.

---

[29] R. E. Connick and W. H. McVey, THIS JOURNAL, **71**, 3182 (1949).

[30] E. M. Larsen, G. Terry and J. Leddy, *ibid.*, **75**, 5107 (1953).

[31] See also B. A. J. Lister in report of Conference on "Ion Exchange and Its Applications," Society of Chemical Industry, London S.W.I., 1955, p. 112.

[32] P. A. Vaughan private communication.