A Light Scattering Study of the Hydrolytic Behavior of Zirconium(IV) and Niobium(V) in a Hydrochloric Acid Solution

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The hydrolytic behavior of zirconium(IV) and niobium(V) in a hydrochloric acid solution was studied using light scattering measurements. It is found that the species of zirconium(IV) have a degree of polymerization of 3 and a charge per monomer unit of 1.5 in a 1.5 M hydrochloric acid solution with $[Cl^-]=1.7$ M. Also, it was found that for a chloride ion concentration of 11 M, the species of niobium(V) are monomeric in 8—11 M hydrochloric acid and colloidal below 8 M. The effect of standing time of the hydrochloric acid solution of niobium(V) was also investigated.

The nature of hydrolysis and polymerization of metal ions in aqueous solutions has been clarified by Sillén and his co-workers.[1] They have employed accurate potentiometric measurements for a wide range of concentrations of reacting species and for a controlled, relatively high ionic strength. Alekseeva *et al.*[2] have studied potentiometrically the hydrolytic polymerization of zirconium(IV) and hafnium(IV) in perchloric acid solutions at pH 0.3—1.5. However, the state of the metal ions, which are highly hydrolyzable and have a strong tendency to precipitate, has been investigated in strong acid solutions. At high acidities, direct potentiometric measurements of hydrogen ions set free in the hydrolytic process are not possible. Norén[3] has employed an indirect technique using a fluoride membrane electrode in his investigation of the hydrolysis of zirconium(IV) and hafnium(IV).

However, interesting aspects of these metals in aqueous solutions have been also observed in other than potentiometric measurements. Yagodin *et al.*[4] pointed out that a part of the zirconium(IV) is in a form which can not extracted by tributyl phosphate (TBP), and that the amount of non-extractable substance corresponds to the amount of zirconium which could not be determined by the usual method using pyrocatechol violet. They also observed that in nitric acid solutions of zirconium there were two types of hydrolytic species, one being complexes with mobile equilibrium and the other stable ones without equilibrium. Suzuki and Inoue[5] have studied the stability of protactinium(V) in a perchloric acid solution employing thenoyl trifluoroacetone(TTA)–benzene extraction, ion exchange, filtration, and synergism of diisobutyl carbinol on the TTA–benzene extraction. It was observed that the method of preparation and concentration of protactinium both affected the behavior of the protactinium in a perchloric acid solution, a part of the protactinium being in a form which was not adsorbed by a cation exchange resin, and that the protactinium species extracted in the TTA–benzene solution were not stable. Mitsugashira[6] has also found that, in a perchloric acid solution of protactinium(V), non-extractable species were present in a di(2-ethylhexyl)phosphoric acid–benzene extraction study.

Therefore, in aqueous solutions of metal ions which are highly hydrolyzable and have a strong tendency to precipitate, species with irreversible processes are often present. Thus it is attractive to follow an approach from a view different from equilibrium analysis such as solvent extraction. It is also interesting to compare the results of this approach with that of equilibrium analysis. In the present work, the states of zirconium(IV) and niobium(V) in hydrochloric acid solutions were studied by means of Rayleigh light scattering measurements. These measurements are basically independent of equilibrium analysis such as solvent extraction. Therefore, this is a sensitive method for weighing the species in solution, and can therefore provide observations of the polynuclear complexes formed by the hydrolytic process.

Experimental

The zirconium obtained as $ZrOCl_2\cdot 8H_2O$ was recrystallized from concentrated hydrochloric acid. The salt was dissolved in the hydrochloric acid and finally the acidity of the zirconium solution was adjusted to 1.5 M and the chloride ion concentration to 1.7 M with sodium chloride.

A hydrochloric acid solution of niobium was prepared as follows. Niobium(V) oxide was fused with potassium bisulfate in the ratio of 1 gram of the oxide to 10 grams of the bisulfate. This melt was cooled and dissolved in a warm 4%-ammonium oxalate solution. The resulting solution was filtered and alkalized with 10% ammonia with vigorous stirring. The precipitate thus obtained was separated by centrifugation and washed with dilute hydrochloric acid solutions. This precipitate was dissolved in concentrated hydrochloric acid. Hydrogen chloride was passed through the resulting solution for several hours, initially at room temperature and finally in an ice bath. The solution was then diluted drop by drop with vigorous stirring to the desired concentration with respect to the hydrochloric acid using a hydrochloric acid solution of suitable concentration. The chloride ion concentration was adjusted to 11.0 M with lithium chloride, which was synthesized from lithium carbonate and hydrochloric acid.

The amount of zirconium was determined by EDTA utilizing back titration with copper(II) and niobium gravimetrically as an oxide, igniting niobium hydroxide precipitated by tannin. The acidity of the solution was determined by titration with a standard sodium hydroxide solution.

Light scattering measurements were made using a 4 cm semioctagonal or square cell at 436 nm with a Shimadzu PG-21 light scattering photometer modified in order to increase the sensitivity. The photometer was calibrated using benzene, so as to obtain 47.5×10^{-6} cm^{-1} for the total Rayleigh ratio. This benzene was washed with concentrated sulfuric acid, passed through an activated aluminium oxide column, and then carefully distilled prior to use. Measurements of the redistilled water gave reasonable values for the Rayleigh ratio $(2.70—2.90)\times10^{-6}$ cm^{-1}.

Refractive index increments were determined at 436 nm and at 25 °C using a Shimadzu DR-3 photoelectric differential refractometer calibrated with sodium chloride solutions.

Each sample was filtered through a Millipore MF filter having a pore diameter of 0.22 μm or a Fluorinert filter having a pore diameter of 0.2 μm, directly into cell, which had been previously rendered dust free. This clean solution was subjected to light scattering and then the refractive index increment was measured. During these procedures, the acidity of the solution remained unchanged.

Results

In a previous paper,[7] the present authors pointed out that the cross-term including the concentration scattering and density scattering, suggested by Bullough, does not need to be taken into account. Therefore, the relation between the Rayleigh ratio and the degree of polymerization, derived by Tobias and Tyree,[8] is valid. The weight-average degree of polymerization N is associated with the excess Rayleigh ratio R^* due to the zirconium or niobium species by

$$\frac{1}{N}=\frac{H\phi\psi^2m}{R^*}-\frac{z^2m}{2(m_3+m_5)} \qquad (1)$$
$$H=2000\pi^2n^2/\lambda^4N_A$$

where ϕ is the volume fraction of water, N_A Avogadro's number, n the refractive index of the solution, and λ the wave length of the light. The symblos m, z, and ψ denote the molarity, the absolute value of the charge, and the differential refractive index of the monomeric zirconium or niobium, respectively. The definition of ψ is

$$\psi=\left(\frac{\partial n}{\partial m}\right)-\frac{zm_3}{2(m_3+m_5)}\left(\frac{\partial n}{\partial m_3}\right)-\frac{zm_5}{2(m_3+m_5)}\left(\frac{\partial n}{\partial m_5}\right) \qquad (2)$$

where m_3 and m_5 are the concentrations of the acid and of the supporting electrolyte, respectively. Attention should be paid to the excess Rayleigh ratio expressed as a function of the degree of polymerization and charge.

Zirconium(IV). The influence of the zirconium concentration on the total Rayleigh ratio was investigated for a 1.5 M hydrochloric acid solution with [Cl$^-$]= 1.7 M, as is shown in Fig. 1. The Rayleigh ratio, obtained for a 1.5 M hydrochloric acid solution with [Cl$^-$]=1.7 M, was subtracted from the total Rayleigh ratio of the zirconium solution to give the excess Rayleigh ratio due to zirconium species. The excess Rayleigh ratio is also shown in Fig. 1. The results are reproducibile to within a few percent.

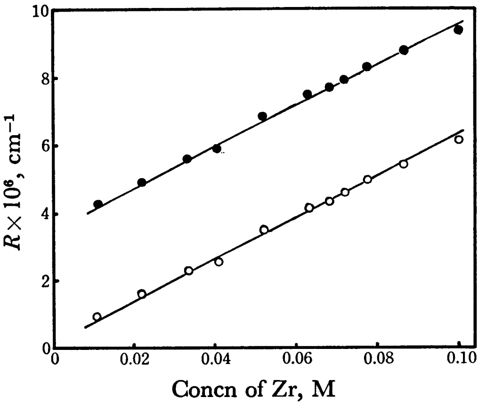

Fig. 1. Dependence of Rayleigh ratio on Zr concentration: ●, total Rayleigh ratio; ○, excess Rayleigh ratio.

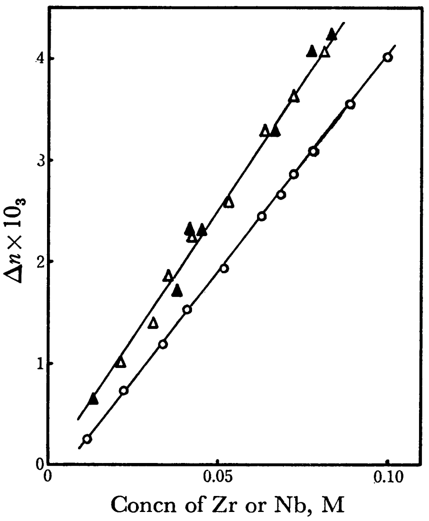

Fig. 2. Refractive index increment of Zr or Nb in HCl solutions: ○, Zr in 1.5 M HCl+0.2 M NaCl; △, Nb in 11 M HCl; ▲, Nb in 8.0 M HCl+3.0 M LiCl.

The refractive index increments of zirconium solutions were determined, as is shown in Fig. 2, where Δn is the difference of the refractive indices between the zirconium solution and a 1.5 M hydrochloric acid solution with [Cl$^-$]=1.7 M. The value found from the slope for $\partial n/\partial m$ is 4.02×10^{-2} l/M. The refractive index increments for hydrochloric acid solutions were also determined, as is shown in Fig. 3. In this figure, Δn is the difference in the refractive indices between a hydro-

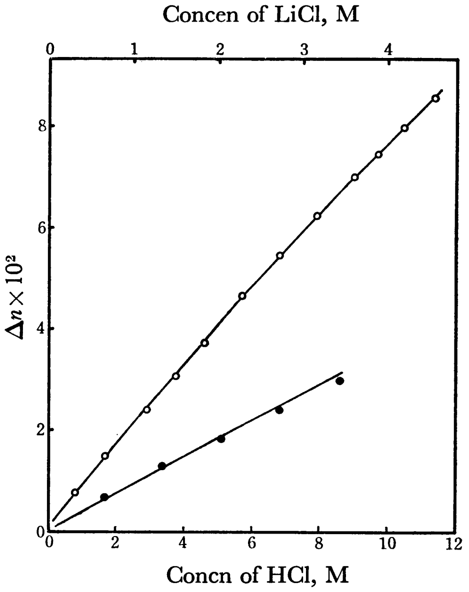

Fig. 3. Refractive index increment of HCl and LiCl solutions: ○, HCl; ●, LiCl.

chloric acid solution and redistilled water and is expressed as

$$\Delta n = -1.03\times10^{-4}m_3^2 + 8.77\times10^{-3}m_3 + 1.68\times10^{-4}. \tag{3}$$

The refractive index increments of sodium chloride solutions were taken from Ref. 9. The value found for $\partial n/\partial m_3$ is 8.46×10^{-3} l/M and that for $\partial n/\partial m_5$ is 1.01×10^{-2} l/M. The volume fraction of water in zirconium solutions was taken to be approximately that of a 1.7 M hydrochloric acid solution and was calculated from the density of the hydrochloric acid solution at 20 °C. The value found is 0.967.

The procedure[8] for applying Eq. 1 is to consider the charge z to be a parameter. A plot of the degree of polymerization, N, *vs.* the zirconium concentration, m, is made for the various values assumed for z. The value of z for which N is independent of m is the correct value for the charge, and the corresponding value of N yields the proper degree of polymerization. Figure 4 indicates that the weight-average degree of polymerization is 3 and that the average charge per zirconium atom is 1.5.

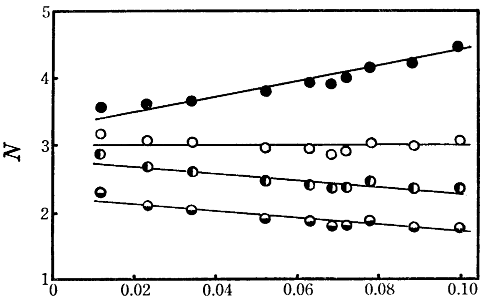

Fig. 4. Plot of the degree of polymerization *vs.* concentration of Zr with the charge as a parameter: ⊖, $z=0$; ◐, $z=1$; ○, $z=1.5$; ●, $z=2$.

Niobium(V). The effect of the hydrochloric acid concentration of the niobium solutions on the excess Rayleigh ratio was examined at niobium concentrations of 0.05 M. As is shown in Fig. 5, no appreciable change could be found in the range of acidity from 8 to 11 M, whereas below 8 M a rapid increase is observed.

The effect of the niobium concentration on the total Rayleigh ratio was investigated in two series of experiments. One is for the 11 M hydrochloric acid solution of niobium and the other is for the 8 M solution. The reproducibilities of these experiments were poor and thus the total Rayleigh ratio shown in Fig. 6 is approximately equal to the mean value of the measured ratio. The Rayleigh ratio obtained for the 11 M hydrochloric acid solution, or the 8 M solution with [Cl⁻]=11 M, was subtracted from the total Rayleigh ratio for a niobium solution in order to obtain the excess Rayleigh ratio due to the niobium species.

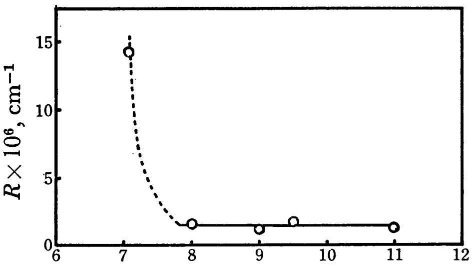

Fig. 5. Dependence of excess Rayleigh ratio on HCl concentration; [Nb(V)]=0.05 M; [Cl⁻]=11 M.

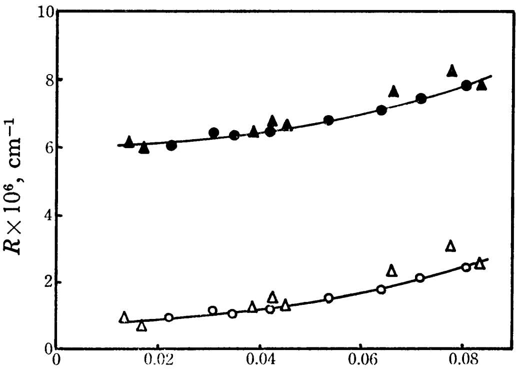

Fig. 6. Dependence of Rayleigh ratio on Nb concentration: ●, total Rayleigh ratio of Nb in 11 M HCl; ○, excess Rayleigh ratio of Nb in 11 M HCl; ▲, total Rayleigh ratio of Nb in 8.0 M HCl+3.0 M LiCl; △, excess Rayleigh ratio of Nb in 8.0 M HCl+3.0 M LiCl.

The refractive index increments of the niobium were determined in two series of experiments, as is shown in Fig. 2, where Δn is the difference in the refractive index between the niobium solutions and an 11 M hydrochloric acid solution or an 8 M solution with [Cl⁻]=11 M. The value found for $\partial n/\partial m$ is 5.18×10^{-2} l/M for both experiments. The refractive index increments of lithium chloride solutions were also determined, as is shown in Fig. 3. The value found for $\partial n/\partial m_5$ is 8.62×10^{-3} l/M and the values for $\partial n/\partial m_3$ were calculated using Eq. 3. The volume fraction were calculated from the density of the hydrochloric acid and lithium chloride solutions at 20 °C. For the 11 and 8 M series, the value found are 0.755 and 0.766, respectively.

Figure 7 shows the plots of the degree of polymerization *vs.* the concentration of niobium with the charge as a parameter in 11 and 8 M hydrochloric acid solutions

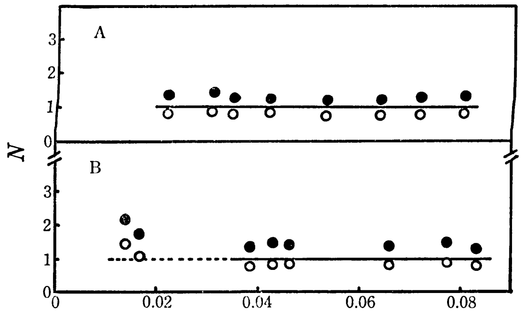

Fig. 7. Plots of the degree of polymerization *vs.* concentration of Nb with the charge as a parameter: ○, $z=0$; ●, $z=3$.
Series A, Nb in 11 M HCl.
Series B, Nb in 8.0 M HCl+3.0 M LiCl.

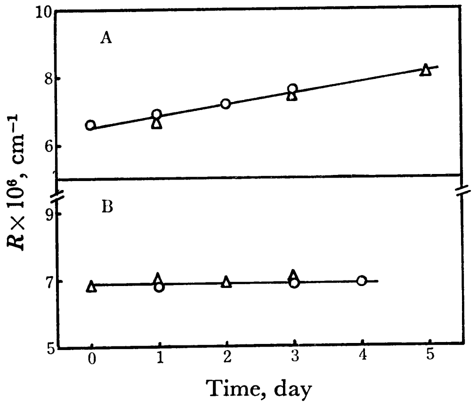

Fig. 8. The effect of standing time on the total Rayleigh ratio of Nb solutions.
Series A, Nb in 8.0 M HCl+3.0 M LiCl: ○, 0.0396 M Nb; △, 0.0430 M Nb.
Series B, Nb in 9.5 M HCl+1.5 M LiCl: ○, 0.0381 M Nb; △, 0.0409 M Nb.

of niobium. There is little difference in the degree of polymerization between the plots for $z=0$ and those for $z=3$. Considering both the poor reproducibility for the total Rayleigh ratios and the impossiblity of a species carrying four or five charges per niobium atom in the solution, we may estimate the degree of polymerization to be unity for the two series. However, it is not all possible to estimate the charge.

The relation between the total Rayleigh ratio of a niobium solution and the standing time after preparation was examined for 8 and 9.5 M hydrochloric acid solutions, as is shown in Fig. 8. At an acidity of 8 M, the total Rayleigh ratio changes appreciably, but it does not change at 9.5 M over several days. Also, the effect of a longer standing time on 8 M hydrochloric acid solutions was examined. However, no reproducible results could be obtained. In these solutions, thehydrolytic precipitation was observed within about ten days after the preparation, and thus, the poorly reproducible results may be related to the precipitation.

Discussion

Zirconium(IV). Assuming species to have constant charge, the weight-average degree of polymerization was found to be 3 and the charge per zirconium atom to be 1.5 in a 1.5 M hydrochloric acid solution. This result is qualitatively consistent with that obtained by ultracentrifugation[10] and with that obtained by spectrophotometry.[11]

From TTA–benzene extraction and spectrophotometric measurements, Zielen and Connick[12] found polynuclear complexes of $Zr_3(OH)_4{}^{8+}$ and $Zr_4(OH)_8{}^{8+}$, and also evaluated their hydrolytic constants, as is shown in a footnote to Fig. 9. In this footnote, additional data[13] for the formation of mononuclear complexes are listed. Using these constants, the distribution of these complexes at a hydrogen ion concentration of 1.5 M was calculated, as is shown in Fig. 9a, and as was the weight-average degree of polymerization and the charge per zirconium atom, which is shown in Fig. 9b. These results for a 1.7 M chloride solution are assumed to be valid, though these constants were evaluated with respect to a 2 M perchlorate solution. No appreciable error should be introduced, at least in the degree of polymerization, from this assumption, since Babko and Gridchina[14] have found that the degree of polymerization is the same in perchloric, hydrochloric and nitric acid solutions using a dialysis method. The degree of polymerization and the charge shown in Fig. 9b are consistent with the present results, except for a slight discrepancy of the charge. This discrepancy may be explained by experimental errors and/or by the diminishing charge for the coordination of chloride ions in the present chloride solutions.

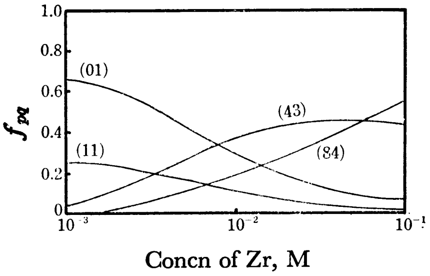

Fig. 9(a).

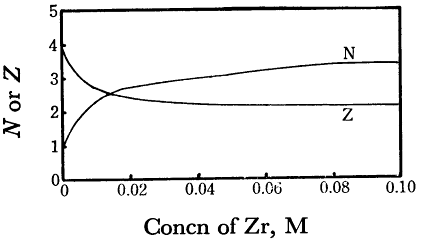

Fig. 9(b).

Fig. 9. Distribution f_{pq}, degree of polymerization N, and charge per one atom Z of Zr solution at $[H^+]=1.5$ M, which are calculated by hydrolytic constants, $\log\beta_{11}=-0.22$, $\log\beta_{21}=-0.84$, $\log\beta_{31}=-1.88$, $\log\beta_{41}=-3.05$, $\log\beta_{43}=5.39$, and $\log\beta_{84}=8.24$. In the (pq) p and q denote the composition of complex $Zr_q(OH)_p{}^{4q-p}$ and f_{pq}, N, and Z are defined as follow: $f_{pq}=q[Zr_q(OH)_p{}^{4q-p}]/[Zr]_{tot}$, $N=\sum_{p,q}q f_{pq}$, and $Z=\sum_{p,q}(4-p/q)f_{pq}$

The agreement between the results obtained by the solvent extraction and spectrophotometric method and that by the light scattering method is interesting from two point of view. One is concerned with the assumptions used in the experimental method and the other with the existence of species with irreversible processes. Now, the experimental methods based on different principles, such as solvent extraction and light scattering, were conducted under individual and separate assumptions. This agreement suggests that these assumptions are appropriate, at least in this case. However, in a zirconium solution there are often species with irreversible processes, as mentioned before. Thus, this agreement suggests that these species only slightly contribute to the behavior of these solutions.

Niobium(V). A hydrochloric acid solution of niobium is less stable than a solution of zirconium. Hydrolytic precipitation appears even in 10 M hydrochloric acid solutions with a niobium concentration of 0.01—0.1 M within a few hours after the preparation. However, maintaining the chloride ion concentration at 11 M, as is shown in Fig. 5, the precipitation does not appear for an 8 M hydrochloric acid solution of niobium. Below hydrochloric acid concentrations of 8 M, the rapid increase of excess Rayleigh ratio must be related to the formation of hydrolytic colloidal particles. The constancy of the excess Rayleigh ratio for acidities of 8—11 M suggests that monomeric species are predominant. These species may be forms of $\mathrm{Nb(OH)}_m\text{-}\mathrm{Cl}_n^{5-m-n}$, as has been suggested by Kanzelmeyer *et al.*[15]

It is interesting to note that a species in an 8 M hydrochloric acid solution of niobium is transformed into a colloidal particle for a 7 M solution. This transformation suggests that the intermediate polymer of niobium is unstable or that it can exist only in a narrow range of hydrochloric acid concentrations. This phenomenon is extremely different from the case of a zirconium solution, in which the polymer can exist stably over a wide range of concentrations. On the other hand, some investigations have indicated the existence of a niobium polymer.[16—18] This discrepancy may be explained by the different conditions of solutions and/or of the preparations of the solutions.

As is shown in Fig. 8, a standing effect is perceived for an 8 M hydrochloric acid solution of niobium but no effect was found for a 9.5 M solution a few days after the preparation of solution. This effect on the Rayleigh ratio must be associated with an increase in the degree of polymerization, because the Rayleigh ratio depends only slightly on the charge. The difference in the standing effect between 8 and 9.5 M solutions suggests that some species which are present in the 8 M solution and are hardly present in the 9.5 M solution, may be related to the polymerization process.

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