Zirconium(IV) Tetramer/Octamer Hydrolysis Equilibrium in Aqueous Hydrochloric Acid Solution

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Abstract: Small-angle X-ray scattering measurements were performed on zirconium acidic aqueous solutions to investigate the structure and the size of polynuclear species larger than the previously identified tetrameric species. Solutions with $[H^+]_{added}$ and $[OH^-]_{added}$ ranging from 0.0 to 1.0 M and 0.0 to 0.02 M, respectively, were analyzed. This study demonstrates that an octameric species, $Zr_8(OH)_{20}(H_2O)_{24}Cl_{12}$, exists in equilibrium with the tetrameric species, $Zr_4(OH)_8(H_2O)_{16}Cl_6^{2+}$, such that, for 0.05 M Zr(IV) in highly acidic solutions ($[H^+]_{added} \geq 0.6$ M), the tetramer is the dominant species; and at conditions with $[H^+]_{added} \leq 0.05$ M, the octameric species becomes predominant. The estimated value of the equilibrium quotient obtained for the tetramer/octamer equilibrium is 0.20 ± 0.05 M^3. The tetramer and octamer have radii of gyration of 3.8 and 5.1 ± 0.2 Å and a hydrolysis ratio of 2.0 and 2.5, respectively. The octamer forms by stacking two tetramers on top of each other. At conditions where small amounts of NaOH are added, unidentified polymeric Zr(IV) species larger in size than the octameric species appear.

Introduction

Metal ion hydrolysis has been an important subject of study[1] for more than a century due to the significant role which it plays in metal ion aqueous chemistry. We are particularly interested in the hydrolysis chemistry of heavy-metal ions due to their importance in aqueous nuclear fuel processing operations. The hydrolysis chemistry of Th(IV), Pu(IV), and Zr(IV) has been of particular concern in this laboratory because these tetravalent ions occur (especially zirconium and plutonium) in processing situations. Although there are similarities in their chemical behavior which merit considering them as a group, extensive differences distinguish their hydrolysis chemistry. In particular, Th(IV) and Pu(IV) hydrolyze and aggregate immediately to form large polymer networks while Zr(IV) hydrolyzes in acidic solutions to first form the tetrameric unit,[3] $[Zr_4(OH)_8(H_2O)_{16}]^{8+}$, prior to more extensive aggregates of the tetrameric unit.[2]

The hydrolysis of zirconium in aqueous solutions has been previously investigated using various techniques that include Raman spectroscopy,[4] wide and small-angle X-ray scattering (SAXS),[3,5−7] and ultracentifugation.[8] The existence of the zirconium tetramer $[Zr_4(OH)_8(H_2O)_{16}]^{8+}$ in highly acidic aqueous solutions has been confirmed both by hydrolysis studies[3,7] and by comparison with the crystal structure of $ZrOCl_2 \cdot 8H_2O$,[9,10] which contains discrete tetrameric units. Clearfield[11] has described that either on refluxing or on increasing the pH of the solution, these tetrameric units aggregate as two-dimensional sheets to eventually form gels or precipitates. Fryer et al.[12] conducted electron microscopy studies on zirconium oxychloride dried solutions and supported Clearfield's theory of the formation of two-dimensional tetrameric sheets. Johnson and Kraus[8] observed that 0.05 M $ZrOCl_2$ solutions, with ≤0.2 M added acid, contain polydisperse zirconium species having an average degree of polymerization of ∼10. Hannane, Bertin, and Bouix[4] studied $ZrOCl_2$ solutions with different zirconium concentrations and varying hydrolysis ranges using Raman spectroscopy and proton NMR. They have also reported that the tetramer $[Zr_4(OH)_8(H_2O)_{16}]^{8+}$ is the major species in aqueous solutions. The addition of the OH^- ions to the tetrameric solution leads to formation of large species in which double hydroxyl bridging bonds, Zr−(OH)$_2$−Zr, are converted to Zr−O−Zr bonds through aging and loss of water. They have further suggested that the predominant species before the gel formation contains eight zirconium atoms which are bridged with an oxygen atom to each other. Ohtsuka, Hayashi, and Suda[13] found three zirconium polynuclear species in zirconium oxychloride solutions in their study of microporous clay intercalation compounds prepared by the cation exchange on clays swollen with the aqueous zirconium polynuclear ionic species. It was postulated that the major species is the tetramer that exists as an intercalation compound with a 7 Å interlayer spacing. The other two species formed by the hydrolytic polymerization of the tetramer are intercalation compounds with 12 and 14 Å layer spacing. These two polynuclear species are three-dimensional clusters based upon the tetramer in contrast to two dimensional sheets of tetramers suggested by the electron microscopy study[12] on zirconium aqueous solutions. However, they did not attempt to describe any relationships such as chemical equilibria between the tetramer and these two polymeric species. Other studies on zirconium aqueous solutions have been undertaken using ^{17}O nuclear magnetic resonance,[14] extended X-ray adsorption fine structure (EXAFS),[15] spectroscopy and SAXS.[5,6]

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Aberg and Glaser[14] in an ^{17}O and ^{1}H NMR study found that the zirconium tetramer formula in aqueous solutions can be written as $[Zr_4(OH)_8(H_2O)_8I(H_2O)_8II]^{8+}$ in which there are two inert and two labile water molecules per zirconium atom. SAXS investigation by Jutson et al.[6] on refluxed zirconium oxychloride solutions led them to postulate that rod-like particles of varying length but constant cross-sectional radius are produced. Their conclusions were in contrast to Clearfield's theory for the aggregation mechanism for tetramers.

From the above discussion, it can be seen that while the tetramer is quite well established in the literature, the chemical mechanism of aggregation of these tetramers to form other discrete species apart from the tetramer is still not clearly understood. In our earlier work,[5] we reported on the small-angle X-ray scattering from aqueous zirconium nitrate solutions which were believed to contain predominantly tetrameric species based on the reported[1] hydrolysis equilibrium. However, on extending this work to other acidities and examining the aggregation process, it was apparent that other relatively simple species could also grow in as had been indicated by some of the previous investigators. Therefore, the purpose of this study was to extend the zirconium oxychloride solutions as a function of the pH using the SAXS technique to identify other species in equilibrium with the tetramer in solution.[23] From SAXS measurements, it is possible to determine the electronic radius of gyration of particles (i.e. root-mean-square distance of all scattering elements (electrons) from the center of gravity) and the absolute intensity at zero angle (a measure of the molecular weight of particles) which was not provided by previous experimental studies. With these two physical quantities, we can obtain new structural information about the zirconium polymeric species in the solution.

Experimental Procedure

The aqueous stock Zr(IV) solution of 0.2 M concentration was prepared by dissolving $ZrOCl_2{\cdot}8H_2O$ crystalline material (99% pure and supplied by EM Chemicals) in water. Solutions with an added H^+ concentration, $[H^+]_{added}$, were prepared by mixing an appropriate amount of 1.8 M HCl and zirconium stock solution to form the solutions having $[H^+]_{added}$ ranging from 0.0 to 1.0 M. In another set of experiments, an appropriate amount of 0.1 M NaOH (Fisher Scientific Reagent) and zirconium stock solutions were mixed to obtain a $[OH^-]_{added}$ value for solutions ranging from 0 to 0.02 M. The final concentration of zirconium in all solutions was 0.05 M. Scattering measurements were made on solutions aged between 1 and 8 days at room temperature.

The pH was measured with a glass combination electrode. Because the pH electrode gives a measure of the activity when the NBS standards are used rather than the concentration of H^+ ions, the following method was used to determine the $[H^+]$ from the pH measurements. A standard KCl solution with known H^+ concentration was prepared from stock hydrochloric acid and was used to calibrate the pH scale. The pH and the ionic strength of this solution were close to those of the zirconium solution. This procedure has the uncertainty represented by the difference in activity coefficient, γ_{H^+}, in zirconium and KCl solutions of the same ionic strength and also from the changing liquid junction potentials in the standardization and measurement steps. The measured $[H^+]$ from pH measurements should equal the $[H^+]_{added}$ most of the time because the concentration of Zr(IV) is so low.

SAXS data were obtained from the aqueous samples contained in a titanium metal cell fitted with mica (0.0003-in.-thick) windows. The sample path length ranged from 0.7 to 0.75 mm (determined by the thickness of a Teflon spacer measured at the termination of each experiment) with a resulting X-ray transmission that varied from 30 to 40% depending on chloride ion concentration and thickness of the Teflon spacer.

The SAXS experiments were conducted on the 10-m SAXS instrument at Oak Ridge National Laboratory.[16] The X-ray source was a 12-kW Rigaku rotating anode generator operated at 40 kV and 100 mA with a copper target and a graphite crystal monochromator. The SAXS system also uses a pinhole collimator and a 20×20 cm^2 two-dimensional position-sensitive counter of 64×64 virtual channels. A 1-cm diameter lead beam stop was used to absorb the scattered X-rays close to the zero angle. The sample-to-detector distance was set at 1.069 m, which gave a scattering vector, $q = 4\pi \sin \theta/\lambda$, of 0.03 to 0.5 Å^{-1}, where 2θ is the scattering angle and λ is the wavelength of the X-ray. The sample scattering was corrected for detector sensitivity, dark current, and the background solvent. The background scattering using hydrochloric acid solvent was measured in the same cell with the same concentration of hydrochloric acid as that in the sample. The measured scattering intensity, I, was calibrated in absolute units using a porous-vitreous-carbon secondary standard previously calibrated by Russell, Lin, Spooner, and Wignall.[17] Therefore, it is possible to convert all the measured intensities to absolute units of cm^{-1}. It is estimated that the error for individual $I(0)$ data points is approximately ±10% and is the basis for error bars shown in Figures 2 and 6.

Numerical Analysis of Scattering Data

The X-ray scattering depends on the number of particles, the electron contrast between the particle and the medium, and the size of the particles.[18]

$$I(q) = I_e(q)N_p(\Delta\rho v)^2 \exp(-q^2 R_g^{\ 2}/3) \tag{1}$$

where v is the volume of the particle, N_p is the number of particles per unit volume, R_g is the radius of gyration, I_e is the scattering from a single electron, $\Delta\rho$ is the electron density difference between the particle and the medium, and q is the scattered wave vector, $q = 4\pi \sin \theta/\lambda$, with 2θ the scattering angle and λ the wavelength of X-rays.

From eq 1, it is clear that the plot ln I vs q^2 will be linear and the R_g of the particle can be determined from the slope of this line. The Guinier law is at least valid for $q \le 1/R_g$, and it is not the function of the particle shape for this range of q.

The intensity at zero angle, $I(0)$, obtained by the extrapolation of Guinier's law to $q = 0$, gives information about the number of particles and the number of electrons in each particle:

$$I(0) = I_e(0)N_p(\Delta\rho v)^2 \tag{2}$$

Equations 1 and 2 were developed originally for monodisperse particles. In the case of polydisperse systems, the observed radius of gyration and the intensity at zero angle can be expressed as follows[18,19]

$$R_g^{\ 2} = \frac{\sum_{i=1}^{N}(N_{p,i}(\Delta\rho_i v_i)^2(R_{g,i})^2)}{\sum_{i=1}^{N} N_{p,i}(\Delta\rho_i v_i)^2} \tag{3}$$

$$I(0) = I_e(0)\sum_{i=1}^{N} N_{p,i}(\Delta\rho_i v_i)^2 \tag{4}$$

where $N_{p,i}$ is the number density of the ith particle, v_i the volume

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of the particle, $R_{g,i}$ the radius of gyration of the ith particle and $\Delta\rho_i$ the difference in electron density of the particle and the medium.

The Guinier law does not give any information about the shape of the particle. Therefore, to determine the shape of the particle, a complete scattering curve should be calculated. The scattering of a particle in the gas phase can be written as follows:[19]

$$I(q) = \overline{F}^2(q) = \sum_{i=1}^{n} f_i^2(q) + \sum_{i=1}^{n} \sum_{i \neq j} f_i(q) f_j(q) \frac{\sin(qr_{ij})}{qr_{ij}} \tag{5}$$

where r_{ij} is the distance between two atoms, q is the scattering vector, *F(q)* is the structure factor, and f_i is the atomic scattering factors and is calculated by

$$f(q) = \sum_{j=1}^{4} a_j \exp\left[-b_j\left(\frac{q}{4\pi}\right)^2\right] + c \tag{6}$$

The coefficients a_j, b_j and c for each kind of atom are listed in the X-ray International Table 1.[21]

The electron density of the gas phase is, of course, negligible. However, in the case of polynuclear clusters or complex ions in solutions, such as in zirconium aqueous solutions, the particles must be treated as embedded in a medium of finite electron density. To correct for the medium, one can calculate the number of electrons in the volume of the medium displaced by the particle and divide that by the total number of atomic scattering centers to arrive at an effective number of electrons, $f_b(q)$, to be subtracted from each atom. The $f_b(q)$ was considered to be proportional to $f_i(q)$ since the q dependence of $f_i(q)$ is very small at small angles. The scattering function for polynuclear clusters can be expressed as[22]

$$I(q) = \sum_{i=1}^{n} (f_i(q) - f_b(q))^2 + \sum_{i=1}^{n} \sum_{i \neq j} (f_i(q) - f_b(q))(f_j(q) - f_b(q)) \frac{\sin(qr_{ij})}{qr_{ij}} \tag{7}$$

where,

$$f_b(q) = \left(\frac{\upsilon\rho_m}{n}\right)\left(\frac{f_i(q)}{f_i(0)}\right) \tag{8}$$

where υ is the volume of the particle, ρ_m the electron density of the medium, and n is the total number of atoms in the particle. From eq 7, the scattering curve of a polynuclear species can be calculated if the relative atomic positions of each atom in the species and the electron density of the solvent are known.

In case the particle volume in solution is uncertain, eq 2 can be rewritten as follows

$$I(0) = I_e(0)N_p(Z_p - \upsilon\rho_m)^2 \tag{9}$$

where Z_p is the number of electrons in the particle. Therefore, the volume of the particle can be calculated by eq 9 if one knows the number density of particles in solution, the Z_p, and the $I(0)$ in absolute unit cm^{-1}.

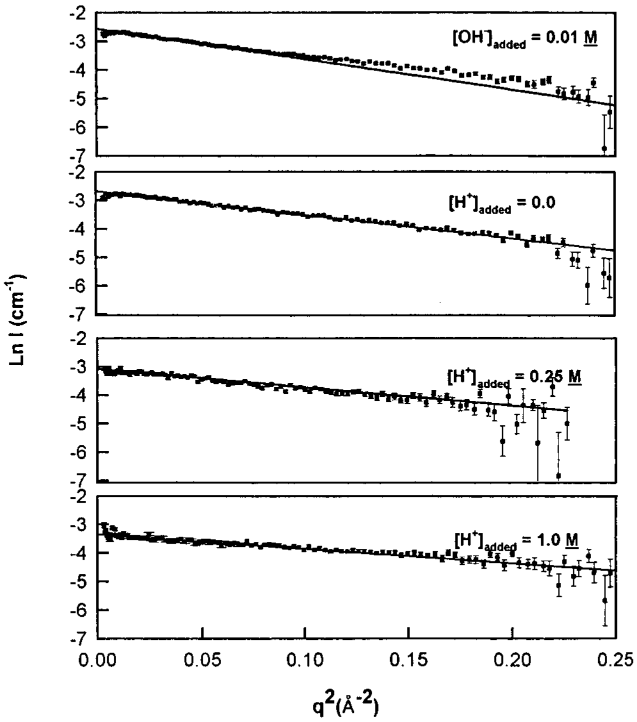

Figure 1. The Guinier plot for solutions with different acidities.

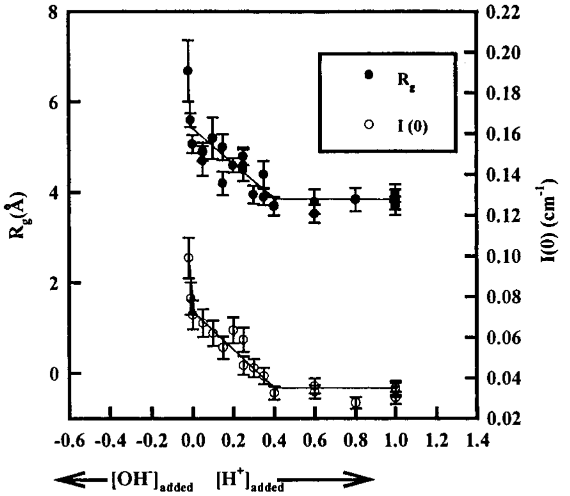

Figure 2. The R_g and $I(0)$ plotted as a function of $[H^+]_{added}$ and $[OH^-]_{added}$.

Results and Discussion

Solutions having a range of $[H^+]_{added}$ from 0.0 to 1.0 M were studied. A few solutions were also studied by adding various amounts of NaOH to zirconium oxychloride solutions. The Guinier plots, ln I vs q^2, where I is the measured absolute intensity of some of the solutions with different acidities are shown in Figure 1. All of the scattering data are shown along with the error bars. As seen from eq 1, the linearity of the plots in the Guinier region is indicative of a relatively monodisperse system at higher acidity and thus permits the determination of R_g. The linearity that extends well beyond the Guinier region is unusual for these hydrous polymeric systems. With decreasing acidity of the solution, the increase in the slope of the line suggests that larger species are forming. The R_g and $I(0)$ values determined in the Guinier region for various solutions are shown in Figure 2. For $[H^+]_{added}$ ranging from 1.0 to 0.4

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(23) In the Zr(IV) system, the initial species are relatively small by colloidal standards and represent an important transition from the solution condition to colloidal aggregates. We shall refer to these species in the aqueous system as *solutions*, but there is little to distinguish these from large polymeric sols other than size.

M, both R_g and $I(0)$ do not change significantly. This suggests that the species in solutions is largely unchanged for $[H^+]_{added}$ of 0.4 to 1.0 M, and in earlier studies,[2,3] this species was identified as the tetramer $[Zr_4(OH)_8(H_2O)_{16}]^{8+}$.

It is instructive to fit the scattering data to a chemical model. In order to fit the scattering intensities at high acidities to a tetrameric model, it should be realized that any chloride ions associated with the species will have a relatively large effect on the intensities because of their high electron density and, therefore, must be included in the scattering model. (However, the nature of this bond has only been thought of previously as "partial".[1,7]) Two possible coordination extremes can be used to represent the tetrameric species, one with and one without associated chloride ions $Zr_4(OH)_8(H_2O)_{16}Cl_8$ and $[Zr_4(OH)_8(H_2O)_{16}]^{8+}$, respectively. In the $Zr_4(OH)_8(H_2O)_{16}Cl_8$ species, chloride ions are arranged in the second coordination sphere of the zirconium atoms, probably bonded by electrostatic forces to the tetramer $[Zr_4(OH)_8(H_2O)_{16}]^{8+}$. Crystal structure studies[9,10] on $ZrOCl_2 \cdot 8H_2O$ single crystals have demonstrated two different sites for chloride ions around the tetramer designated as Cl_1 and Cl_2, respectively. The chloride ions on site Cl_1 are likely not part of the tetramer in the solution, probably due to the high dielectric constant of the water. A plausible geometry for the zirconium tetramer can be derived from the crystal structure data of the $ZrOCl_2 \cdot 8H_2O$ single crystal[9] using the atomic positions as found in the crystal structure data, and this geometry, in turn, can be used to calculate the radius of gyration of the tetramer.

The calculated R_g values for the $[Zr_4(OH)_8(H_2O)_{16}]^{8+}$, $[Zr_4(OH)_8(H_2O)_{16}Cl_6]^{2+}$, and $Zr_4(OH)_8(H_2O)_{16}Cl_8$ species are 3.2, 3.8, and 3.95 Å, respectively, neglecting the scattering from the hydrogen atoms due to their low atomic number. (The schematic of the tetramer is shown in several references[1-3,7,9,10] with the geometery of the three tetrameric species considered here differing only in the number of chloride ions in the second coordination shell.) The observed R_g for the solution with a $[H^+]_{added}$ of 1.0 M is 3.8 ± 0.2 Å, which is close to the R_g of two species: $[Zr_4(OH)_8(H_2O)_{16}Cl_6]^{2+}$ and $Zr_4(OH)_8(H_2O)_{16}Cl_8$. This analysis leads to the conclusion that the species $[Zr_4(OH)_8(H_2O)_{16}Cl_x]^{(8-x)+}$ is to be considered as the scattering entity in these solutions instead of $[Zr_4(OH)_8(H_2O)_{16}]^{8+}$. The previous wide-angle X-ray scattering studies[3,7] on zirconium oxychloride aqueous solutions also concluded that the tetramer is associated with chloride ions. This conclusion is consistent with the realization that the high electron density associated with the chloride ions contributes significantly to the scattering and therefore must be considered in the species identification.

The scattering curve of each tetrameric species ($[Zr_4(OH)_8(H_2O)_{16}]^{8+}$, $[Zr_4(OH)_8(H_2O)_{16}Cl_6]^{2+}$, and $Zr_4(OH)_8(H_2O)_{16}Cl_8$) was calculated using eq 7 to test the effect of chloride ions on the scattering intensity and, if successful, to thus demonstrate that SAXS measurements can be used to deduce the constituents of such small species. The calculated scattering curves of species $Zr_4(OH)_8(H_2O)_{16}Cl_8$, $[Zr_4(OH)_8(H_2O)_{16}Cl_6]^{2+}$, and $[Zr_4(OH)_8(H_2O)_{16}]^{8+}$ were adjusted to the experimental curve at an $[H^+]_{added}$ of 1.0 M using a scaling factor which scales the theoretical intensity unit, e^2, to the laboratory unit, cm^{-1}. Figure 3 shows that the scattering curve from the $[Zr_4(OH)_8(H_2O)_{16}Cl_6]^{2+}$ fits the data best, while the scattering curve of $[Zr_4(OH)_8(H_2O)_{16}]^{8+}$ does not fit the data at all and also χ^2 (i.e., the residual) for the fit is smaller for the $[Zr_4(OH)_8(H_2O)_{16}Cl_6]^{2+}$ species in comparison to $Zr_4(OH)_8(H_2O)_{16}Cl_8$ species.[24]

Until now we have only discussed solutions having $[H^+]_{added}$ greater than 0.4 M. On further decreasing the acidity ($[H^+]_{added} < 0.4$ M), both R_g and $I(0)$ increase. At an $[OH^-]_{added}$ value greater than zero, the R_g as well as $I(0)$ increase very rapidly suggesting that larger molecular weight species have also formed. The radius of gyration increases from 3.8 to 5.1 Å as the $[H^+]_{added}$ decreases from 0.4 to 0.0 M while the $I(0)$ increases in a systematic manner. Since the scattering intensity is proportional to the square of electrons, the observed R_g and $I(0)$ will be dominated by the larger species. For example, if two species with R_g's of 8.0 and 5.0 Å exist in the solution, the observed R_g will be close to 8.0 Å rather than 5.0 Å. This suggests that smaller polynuclear species (tetramers) are forming larger polynuclear species as the pH increases. This is also supported from the Guinier plots (Figure 1) that a monodisperse tetrameric species system at an $[H^+]_{added}$ of 1.0 M converts to another monodisperse polymeric species system at no added acid with a larger size than the tetramer.

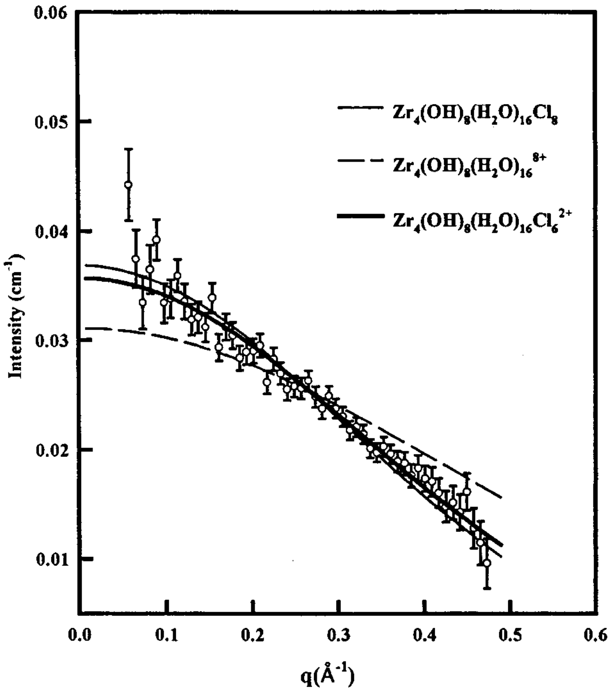

Figure 3. The calculated scattering curves for three species, namely $Zr_4(OH)_8(H_2O)_{16}Cl_8$, $[Zr_4(OH)_8(H_2O)_{16}]^{8+}$, and $[Zr_4(OH)_8(H_2O)_{16}Cl_6]^{2+}$- are compared with the experimental curve at $[H^+]_{added} = 1.0$ M.

Johnson and Kraus[8] have postulated that for this pH range, the average degree of polymerization increases from 4.0 to 10.0, but they did not propose any specific species appearing in addition to the tetramer. However, the current SAXS data can be explained by the appearance of a species having a radius of gyration close to 5.1 Å and an OH/Zr ratio more than 2.0. The octamer $[Zr_8(OH)_{20}(H_2O)_{24}Cl_{12}]$ is just such a moiety, and there are two possible configurations that should be considered for an octamer (Figure 4). In Figure 4a, two tetramers are attached in sheet-like fashion through two double hydroxyl bridges between matching edges, while in Figure 4b, they are stacked on top of each other attaching themselves with four single OH^- bridges. The calculated R_g values in the two cases are 5.4 and 5.0 Å,[25] respectively. (The two octamer geometeries were based on the crystal structure data of the $ZrOCl_2 \cdot 8H_2O$ single crystal.[9])

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(24) The $f_b(0)$ (equal to 6.4) required in eq 7 was calculated using eqs 8 and 9. The tetrameric species $[Zr_4(OH)_8(H_2O)_{16}Cl_6]^{2+}$ has been considered for the $f_b(0)$ calculations for the observed $I(0)$ at 1.0 M $[H^+]_{added}$ solution. Considering $Zr_4(OH)_8(H_2O)_{16}Cl_8$ instead of $[Zr_4(OH)_8(H_2O)_{16}Cl_6]^{2+}$ for the $f_b(0)$ calculation introduces an error of 10% in $f_b(0)$. However, this error does not significantly affect the calculated scattering curve for the tetrameric species.

(25) The average bond length for Zr–OH is 2.15 Å.[9] Therefore, the Zr–OH–Zr bond length was considered 4.3 Å in the radius of gyration calculation.

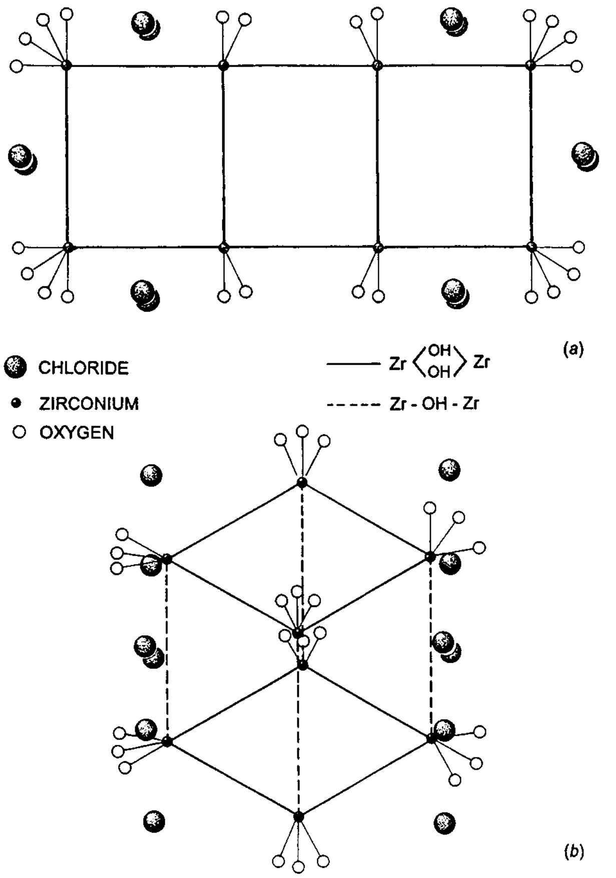

Figure 4. The representation of two octamer configurations: (a) sheet octamer and (b) stacked octamer.

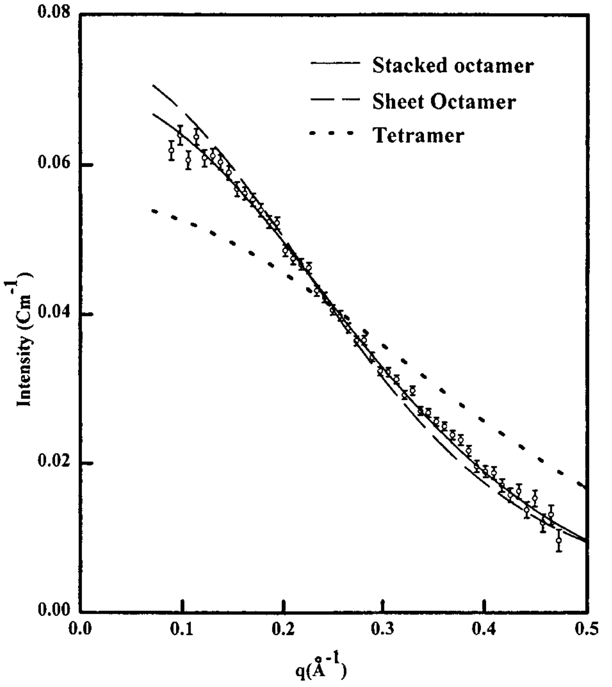

Figure 5. The calculated scattering curves for both geometries of the octamer and the tetramer $[Zr_4(OH)_8(H_2O)_{16}Cl_6]^{2+}$ compared with the experimental curve at no added acid.

Due to small differences in the calculated radii of gyration for the two octameric structures, we cannot distinguish between the two based on R_g consideration alone.

As was done for the tetrameric species, the scattering curves of both octameric species (stacked and sheet like) were calculated using eq 7 to compare with the experimental scattering curve at high pH and also determine which octameric species fits the data best. The calculated scattering curves of octameric species $[Zr_8(OH)_{20}(H_2O)_{24}Cl_{12}]$ and the tetrameric species $[Zr_4(OH)_8(H_2O)_{16}Cl_6]^{2+}$ were scaled to the experimental curve at no added acid. Figure 5 shows the calculated curve along with the previously determined $[Zr_4(OH)_8(H_2O)_{16}Cl_6]^{2+}$ superimposed on the data. It is clear octameric species fit the data best and the tetramer $[Zr_4(OH)_8(H_2O)_{16}Cl_6]^{2+}$ does not fit the data at all. The scattering curve calculated for the sheet-like octamer deviated at small as well as large *q*. From the analysis, it appears that the octamer forms by stacking two tetramers on top of each other rather than by connecting them in sheet like fashion.

Increasing the $[H^+]_{added}$ of solution causes a progressive shift to all tetrameric species and the degree of control between these two species suggests they occur in equilibrium. Therefore, to explain our scattering results, we have developed an equilibrium model for the tetramer/octamer distribution and have used this model to fit the experimentally observed R_g and the $I(0)$. The equilibrium between these species is described in the following paragraphs.

Equilibrium Model between Tetramer and Octamer. The equilibrium between the two species is described as follows:

$$2[Zr_4(OH)_8(H_2O)_{16}Cl_6]^{2+} \rightleftarrows [Zr_8(OH)_{20}(H_2O)_{24}Cl_{12}] + 4H^+ + 4H_2O \tag{10}$$

$$Q = [Zr_8(OH)_{20}(H_2O)_{24}Cl_{12}][H^+]^4/[(Zr_4(OH)_8(H_2O)_{16}Cl_6)^{2+}]^2 \tag{11}$$

In addition to eq 11, there is a mass balance equation because of the fixed zirconium concentration of 0.05 M in the solution.

$$4[Zr_4(OH)_8(H_2O)_{16}Cl_6]^{2+} + 8[Zr_8(OH)_{20}(H_2O)_{24}Cl_{12}] = 0.05 \tag{12}$$

Although in the equilibrium equations chloride ions have been included, we believe that the chloride ions are part of both species and affect only the SAXS results, not the chemical equilibrium between the tetramer and the octamer since free chloride ions do not appear in eq 10. The two simultaneous eqs 11 and 12 can be solved for the concentration of both species, assuming that the $[H^+]$ can be obtained from the measured pH of the solution. The distribution of the tetramer and the octamer can be calculated as a function of pH of the solution from eqs 11 and 12 if the equilibrium quotient, Q, for the octamer formation is known. From the concentration of these two species, the apparent R_g and the $I(0)$ that would be observed in the SAXS experiments can be calculated from eqs 3 and 4. It is evident from eqs 3 and 4 that the calculation of the average values of R_g and $I(0)$ for a specific distribution requires knowledge of the electron density difference of each species from that of the medium. Therefore, the average number of solvent electrons, $f_b(0)$ (for each atom in the particle which is equal to 6.4), was subtracted from the scattering of each atom in the species. The effective radius of gyration and number of excess electrons in each species are listed in the Supporting Information.

From the above equations, we can fit the experimentally observed R_g and $I(0)$ with the calculated R_g and $I(0)$ as a function of the pH, using the equilibrium quotient and the scaling factor which converts the calculated intensity in electron units, e^2/cm^3, to the laboratory scale, cm^{-1}. A nonlinear least-squares fit was performed, using statistical weighting of both R_g and $I(0)$ with Q and the scale factor as fitting parameters. In the fitting procedure, the R_g of octamer formed by stacking two tetramers was considered. The agreement between the experi-

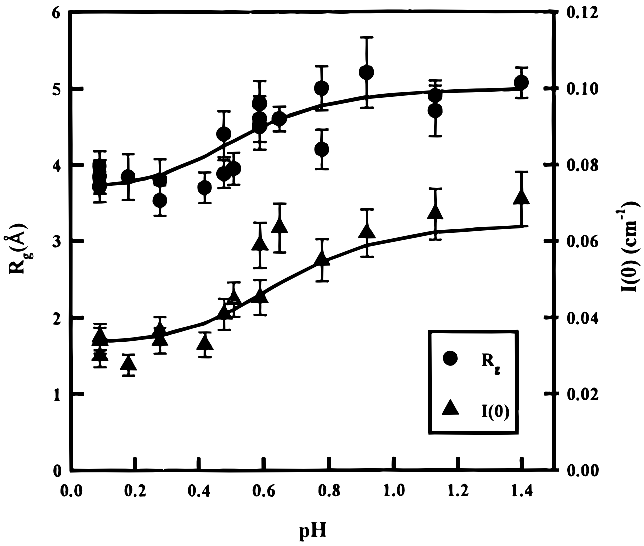

Figure 6. The experimental R_g and $I(0)$ values are fit with those calculated from the tetramer/octamer equilibrium model as a function of the pH of the solution.

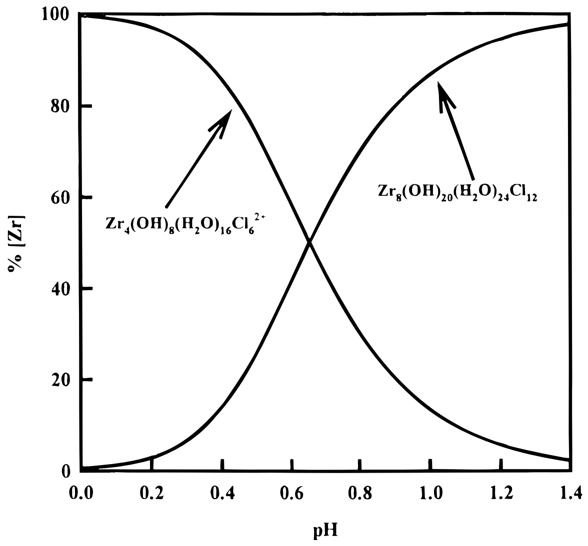

Figure 7. The distribution of zirconium ions in the tetramer $Zr_4(OH)_8(H_2O)_{16}Cl_6 2+$and in the octamer $Zr_8(OH)_{20}(H_2O)_{24}Cl_{12}$ as a function of the pH of the solutions.

mentally measured radius of gyration and the intensity at zero angle over the pH range studied is quite good (Figure 6). The estimated value of the equilibrium quotient, Q, is 0.20 ± .05 M.[26] The scaling factor of 7.96×10^{-26} obtained from the fit is satisfactorily in agreement with the Thomson scattering factor, 7.8×10^{-26}.

The species distribution calculated from the fitted value of the equilibrium quotient as a function of the pH is shown in the Figure 7. For the initial pH of solutions (≤ 0.3), most of the zirconium is present as the tetramer, while upon further increasing the pH, the octamer starts to form. At pH close to 1.4, most of the zirconium exists as the octamer.

Conclusions

SAXS measurements have enabled the determination of the *z*-averaged radius and the intensity at zero angle (a measure of the molecular weigh of the species) which was not possible from other experimental techniques used in the past on aqueous zirconium chloride solutions. This study concludes that there are at least two equilibrium species that exist in zirconium oxychloride solutions: the tetramer $[Zr_4(OH)_8(H_2O)_{16}Cl_6]^{2+}$ and the octamer $Zr_8(OH)_{20}(H_2O)_{24}Cl_{12}$. These data give substantial definition to the chemical process only indicated previously in earlier work. The radius of gyration of the tetramer is 3.7 Å and the hydrolysis ratio is 2.0, while the octamer has a radius of gyration close to 5.0 Å and a hydrolysis ratio of 2.5. The geometry of the octamer is close to that of the stacked octamer. The tetramer is a predominant species in solutions having $[H^+]_{added}$ greater than or equal to 0.6 M. On decreasing the $[H^+]_{added}$ (<0.6 M), the octameric species begins to appear, and at $[H^+]_{added} \leq 0.05$ M, most of the zirconium is present as the octamer.

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Supporting Information Available: A table on the calculated values of R_g and the number of electrons in the tetramer and the octamer (1 page). See any current masthead page for ordering and Internet access instructions.

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(26) The error of the equilibrium quotient was estimated on the basis of errors in the pH measurements.