Chapter 4
CHAPTER 4

Hydrolysis and Polymerization of Zirconium(IV) in Aqueous Nitric Acid Solutions

4.1. Introduction

Hydrolysis and polymerization of zirconium in aqueous solutions have found renewed interest mainly for its application in sol gel processes, ceramic engineering and also due to the fact that zirconium has high yield among the uranium fission products of fast neutron spectrum and it is considered as a high priority element for the assessment of radioactive nuclear waste repositories [21]. Zr(IV) is mainly taken as an analogue for Pu(IV) to understand its hydrolytic behavior. This is due to its similar tendency towards hydrolysis [151]. The first hydrolysis constant for M(OH)$_3^+$ are $\beta_{1,1}^{0}$=14.3 [152] and $\beta_{1,1}^{0}$=14.0 [153] for Zr(IV) and Pu(IV) also matches.

Zr$^{4+}$ is stable only at very acidic condition and the onset of hydrolysis starts even at pH $< 0$ similar to Pu(IV) [92]. Mononuclear species dominates only at low concentration of Zr ($< 10^{-5}$ M) [154]. For increasing pH, degree of polymerization increases leading to the formation of polynuclear species such as tetramers, pentamers, octamers. They are found to exist in concentrated solutions of zirconium salts ([Zr] $> 10^{-5}$ M) even at high acidities [155]. Close to the solubility limit large
polymers are also formed which is yet another parallel to Pu(IV) [92]. Figure 4.1 compares the species distribution in dilute solutions when polynuclear complexes are not present in the system.

![Graph showing species distribution](image)

*Fig. 4.1. Calculated distribution of mononuclear hydroxide complexes (HCl/NaCl solutions of I=0.5 M) in the absence of polynuclear species, at very low metal ion concentration [30]*

Polymerization of zirconium can be identified by slow conductivity changes in the solution and freezing point depression [156-157], potentiometry, titration with base or by using desktop ESI-MS [158]. Earlier works reported the existence of trimeric \([\text{Zr}_3(\text{OH})_4^{8+}\text{ or Zr}_3(\text{OH})_5^{7+}]\) and tetrameric \([\text{Zr}_4(\text{OH})_8^{8+}]\) solution species. X-ray scattering studies have shown that \([\text{Zr}_4(\text{OH})_8(\text{H}_2\text{O})_{16}]^{8+}\) species is the major form present in solutions and tetramers are stable even at high concentration ((Zr) = 2M) [159-162]. Various studies were performed to elucidate the structure of these polymeric species. Some of the important results are as follows.

Computational study on tetrameric species indicates a planar form comprising eight-coordinated \(\text{Zr}^{4+}\) ions with an antiprism/irregular dodecahedron ligand arrangement in an aqueous environment [163]. Studies also reported that these tetrameric units aggregate as two dimensional sheets [164]. SAXS measurements
performed on zirconium acidic aqueous solutions also identified tetrameric species
and in addition they have also demonstrated that octameric species also exists in
equilibrium with tetrameric species. These octamers are formed by stacking two
tetramers on top of each other [165]. Nanoelectrospray mass spectrometry combined
with XAFS investigation also confirmed the same results [154]. The two plausible
configurations for the octameric species are shown in figure 4.2.

![Diagram of two octamer configurations](image)

**Fig. 4.2. Representation of two octamer configurations** A) Sheet octamer B) Stacked octamer [160]

These layers further aggregate and form a three dimensional fluorite structure by a
condensation process that result in loss of water from the structure [166]. Another
mechanism also supported the two dimensional sheet like structure [167]. SAXS
measurements made on ZrOCl₂ solutions heated to elevated temperatures showed that
the shape of clusters at earlier stages of growth is close to rod rather than sheet [168].
EXAFS on samples of oligomeric and polymeric species postulates that the structure
of these solution species is not a simple ZrO₂; it has neither the monoclinic, cubic,
orthorhombic, nor tetragonal ZrO₂ structure. Its structure cannot be derived from
simple stacking of tetrameric $[\text{Zr}_4(\text{OH})_8(\text{H}_2\text{O})_{16}]^{8+}$ units as discussed earlier. The species are built up of primarily $\text{ZrO}_8$ building blocks. The $\text{ZrO}_8$ building blocks can take on different geometries and related polyhedra being cube, square antiprism, dodecahedron and hendecahedron [169].

But there are very limited information available related to polymers and colloids formed due to hydrolysis of zirconium. Thus the present chapter deals with the conditions of colloids formed, ageing effect and determining the molecular weight of freshly prepared and polymers aged at different time intervals.

4.2. Experimental work

4.2.1. Preparation of standard solution for determination of Zr(IV)

- Four solutions of 0.025, 0.05, 0.075 and 0.1 mg of zirconium per ml were prepared in 1 N nitric acid. The solutions were prepared by dissolving required amount of zirconium nitrate in 1 N nitric acid to avoid hydrolysis.

- Standard phosphate solution was prepared by dissolving 0.05 g of sodium dihydrogen phosphate in distilled water and diluting it to 100 ml.

- A 10% solution of ammonium molybdate was prepared by dissolving 5 g of ammonium molybdate in distilled water, filtered and diluted to 50 ml.

- 10 N sodium hydroxide solution and 2.8 N nitric acid was prepared freshly by dissolving desired amount and diluted to 50 ml with distilled water.

4.2.2. Preparation of colloidal Zr(IV) solutions

- Formation of polynuclear species and colloids must be investigated in an environment extremely clean with respect to crystallization germs/impurities
which could cause premature precipitation and formation of colloids. Thus prior to the investigation, the sample cells were thoroughly cleaned and in order to ensure that the solutions are colloid free, the following procedure was followed,

- The sample cell was thoroughly cleaned with conc. HNO₃.
- The stock solution was always prepared in 1M HNO₃ to avoid any initial hydrolysis which can lead to colloid formation.
- The solutions are then centrifuged at a speed of 20,000 rpm.
- Finally scattering measurements were performed to ensure there is no signal corresponding to the presence of colloid.

Zirconium solutions of various concentrations (0.0125 to 0.05 gml⁻¹) were prepared from zirconyl nitrate monohydrate in 1 M nitric acid in order to avoid initial hydrolysis. 0.1 M sodium hydroxide and 0.1 M nitric acid was added to adjust pH and light scattering measurements were performed to determine the onset of colloid formation. All the measurements were performed at 27±1°C.

4.3. Results and discussions

4.3.1. Procedure for determination of micro-level Zr(IV) in aqueous solutions

Solutions of zirconium salts can contain Zr⁴⁺, ZrO²⁺ and several polymerized ions if the concentration of metal is higher and also depending on the acidity of the solution. The Zr⁴⁺ ion reacts with many reagents much faster and this fact is used for determining microquantities of the metal ion. Several organic reagents were used as complexing agents such as xylenol orange [170], Arsenazo I and III
[171], pyrocateechol violet [172] for trace determination of Zr and have certain limitations with sensitivities and they will be stable only at particular pH. The gravimetric determination of zirconium as zirconium phosphate is another most widely used method for determining zirconium but it is applicable only for macro amounts of Zr. Hence a method to determine micro-level zirconium in aqueous solution at high acidities is required in order to avoid the interference of its hydrolyzed species.

In the present method, zirconium is precipitated as zirconium phosphate by the addition of standard phosphate solution and the remaining concentration of phosphate in the supernatant solution is determined by converting it into molybdiphosphoric acid which has a characteristic yellow colour. The concentration of zirconium in the present investigation ranges about 25-100 ppm. A 20 ml of the prepared zirconium solution is transferred to 50 ml beaker and 5 ml of concentrated nitric acid is added to it. To that, 10 ml of standard phosphate solution is added and the solution is allowed to stand for about 4 hours. The treatment of acidic solution of zirconium ions with excess of phosphate solution results in the precipitation of zirconium as zirconium phosphate. The resultant solution is centrifuged for 15 min. About 25 ml of the supernatant solution is transferred into 50 ml beaker and neutralized with 10 N sodium hydroxide solution. 5 ml of concentrated nitric acid is added to it and then diluted to the mark with distilled water. 5 ml of the molybdate solution is added to the above solution. Yellow colour develops. Ammonium molybdate solution is used as blank. For different concentration of zirconium solutions the maximum absorbance is measured at $\lambda_{\text{max}} = 369$ nm. As the concentration of zirconium in the solution increases the phosphate ions in the solution
decreases because large amount of zirconium will be precipitated as zirconium phosphate. Hence the intensity of the colour which is the characteristic of molybdiphosphoric acid will decrease. This results in the decrease of absorbance at higher concentration of zirconium. Figure 4.3 a & b shows the absorption spectra and calibration graph of zirconium(IV). It shows that the molybdiphosphoric acid system confirms the Beer’s law. That is a definite relationship exists between the concentration of zirconium and the removal of phosphate ions from the solution. For the determination of microamounts of zirconium, the proposed method is simple and sensitive. Therefore this procedure assumes significant importance in view of scarcity of good methods available for determining zirconium.

Fig. 4.3.(a). UV-visible absorption spectra of Zr(IV) (b). Plot showing a linear relationship between zirconium concentration and removal of phosphate ions from the solutions
4.3.2. Light scattering studies on hydrolysis of zirconium(IV)

4.3.2.1. Formation of Zr(IV) colloids

Light scattering measurements were performed for different concentrations between \([\text{Zr(IV)}]_{\text{tot}} = 0.1 – 0.5\) M. The hydrolysis of Zr species is a continuous process which leads to charge compensation through the sequential substitution of water molecules by hydroxide ligands close to the solubility of \(\text{Zr(OH)}_4(\text{am})\) leading to polymers of colloidal dimensions. The general equilibrium reaction for hydrolysis of Zr(IV) is shown in figure 4.4.

\[
m\text{Zr}^{n+} + 2n\text{H}_2\text{O} \rightleftharpoons \text{Zr}_m(\text{OH})_{n(4m-n)} + n\text{H}_3\text{O}^+\n\]

*Fig. 4.4. General equilibrium reaction for hydrolysis of Zr(IV)*

The formation of colloids after exceeding the solubility limit was observed by DLS as described in section 2.2.6. The onset of colloid formation starts at pH = 0.3 for initial concentration of 0.1 M Zr and the pH of onset of colloid formation still decreases with increase in the concentration of zirconium. The intensity data of DLS is taken as the average size of the particle and it is found to be 255 nm (figure 4.5) formed in 0.1 M Zr(IV) solution of pH~2.0 at 27°C. The size of the particle is not constant and it
increases with increase in Zr concentration. The polydispersity index of the polymer is 0.1. For decreasing Zr concentration (i.e. [Zr] < 0.1 mM) it was difficult to observe colloid formation because DLS technique is restricted to suspensions of large colloids. At [Zr]_{tot} = 0.1 mM diluted to pH > 3.0 small number of colloids of >1μm was observed. The summary of the peak is given in table 4.1.

Fig. 4.5. Intensity distribution curve of Zr(IV) polymer formed in aqueous nitric acid solution ([Zr(IV)] = 0.1 M)

Table 4.1. Peak summary for Intensity distribution curve of Zr(IV) hydrous polymer

<table>
<thead>
<tr>
<th>Particle Diameter (nm)</th>
<th>Volume %</th>
<th>Width</th>
</tr>
</thead>
<tbody>
<tr>
<td>255.0</td>
<td>100</td>
<td>168.10</td>
</tr>
</tbody>
</table>

The polymeric species are considered to be linked through hydroxyl bridges. There are many reports available in order to support this assumption. For instance, the
structure of the tetrameric unit is believed to be a ring of four zirconium atom each linked to its neighbor through a pair of hydroxyl bridges. These tetrameric species are composed of two dimeric units \((\text{Zr(OH)}_2\text{Zr})\) bridged by hydroxyl groups [173]. A hard sphere model was proposed for polynuclear hydrolysis species of Zr(IV). It was considered to follow the same trend as tetravalent actinides, i.e polymers are bridged by hydroxide ions and not by oxygen bridges.

### 4.3.2.2. Effect of pH on size of Zr(IV) colloidal polymer

Figure 4.6 shows the effect of pH on size of the polymer formed at constant concentration of zirconium. The initial concentration taken for investigating the pH

![Graph showing the effect of pH on size of Zr(IV) colloidal polymer](image)

**Fig. 4.6. Increasing colloidal size with increasing pH for 1 M Zr(IV) solution**

Figure 4.6 shows the effect of pH on size of the polymer formed at constant concentration of zirconium. The initial concentration taken for investigating the pH
dependent size variation is 1 M Zr(IV) solution. In the present case, the size of the colloids formed initially is \(~25 \text{ nm}\) at pH<0.1. The size of the initially formed colloids are very small when compared to colloids formed in 0.1 M Zr(IV) solution. This may be due to the microcrystalline nature of colloids. This can also be understood from the scattering solubility data due to existence of different phases. It exists as microcrystalline phase of very small size at low pH and less ordered amorphous phase of larger particles at high pH [92, 174]. This is similar to Pu(IV), whose amorphous Pu(IV) hydroxide colloid formed has weighted mean colloid size of 12 – 25 nm which is much bigger than the 2 nm crystalline PuO\(_2\) colloids.

When pH of the solution is increased, the size of the colloids also increases. With increase in the pH of the solution, the reaction for the deprotonation step required in the condensation process increases. Thus, creation of a larger number of OH sites on the polymer increases the probability of contact in other direction leading to the increase in growth rate of the polymer. Polymerization of Zr(IV) hydrolyzed species proceeds more slowly at low pH than at high pH due to limited number of OH groups available and hence it is considered that colloids formed at lower pH has more ordered structure [167]. In figure 4.6, beyond pH~1.5, the size of the colloid immediately increases and reaches 256 nm at pH 1.7. This shows that there is rapid aggregation at higher pH. A further increase in pH i.e. pH > 1.7 results in lower number of colloids and colloids smaller than 200 nm were not detected at all due to size screening effect i.e., decrease in signal proportional to \(d^6\). In other words large particles if present in even small quantities will be accounted during data analysis.
4.3.2.3. Size of Zr(IV) colloidal polymer aged at different time intervals

0.1 M Zr(IV) solution diluted to pH = 0.3 was aged for around 7 days. Further growth of colloids was observed with ageing. The colloid growth was accompanied by a slight increase in acidity due to release of H⁺ into the solution which can be understood from the following equation 4.1.

\[
\text{Zr(OH)}_2^{2+} + 2\text{H}_2\text{O} \rightarrow \text{Zr(OH)}_4\text{(coll)} + 2\text{H}^+ \tag{4.1}
\]

Colloids of two different sizes were obtained at ~215 nm and another at ~402 nm for solutions aged for 3 days (figure 4.7(a)). The particle size corresponding to 215 nm may be due to the primary particle that was formed initially in the system. On ageing the solution, the primary particles form large aggregates. Peak corresponding to 402 nm may be due to larger aggregates formed. This on further ageing for 7 days gave a similar size distribution pattern. But there is a slight shift in the 402 nm peak (figure 4.7(b)). This is due to more aggregation with increase in time. Figure 4.7(c) depicts the overall growth process. Zirconium oxychloride solutions prepared at different pH were heated at elevated temperature for various aging periods to gain understanding of growth mechanism and structure of zirconium hydrous polymers. SAXS (Small angle X-ray scattering) measurements were made on these solutions. The scattering data indicated that a rod shaped primary particle is formed at pH 1.2 and on increase in pH, the primary particles become more branched. On aging more than 1250 min at 95°C, these primary particles form large aggregates. These aggregates restructure while growing in size and eventually transform into dense particles [164].
Fig. 4.7. Intensity size distribution of Zr(IV) colloid
(a) Aged for 3 days
(b) Aged for 7 days
(c) Schematics of growth process of Zr polymeric species forming rod-like particles [164]
4.3.2.4. Molecular weight of Zr(IV) hydrous polymer

4.3.2.4.1. Freshly prepared polymer

Figure 4.8 shows the refractive index increment for different concentrations of Zr. As the concentration of the solute increases the refractive index of the solution also increases giving a positive slope with $\frac{dn}{dC} = 0.1278 \text{ mlg}^{-1}$. This value has been used as an input for generating the Debye plot. A value of $3.25 \text{ gcc}^{-1}$ was used for particle density which corresponds to hydrous ZrO$_2$.

![Refractive index increment of different concentration of Zr(IV) solution](image)

**Fig. 4.8. Refractive index increment of different concentration of Zr(IV) solution**

Shape of the particle is an important parameter to determine molecular weight of polymers. As mentioned in earlier investigations, Zr polymer at its earlier stages of growth is rod shape. Hence molecular weight measurements were done considering the shape of the system as irregular. Following are the steps followed to obtain Debye plot.
• Preparation of different concentrations of Zr(IV) polymer solutions.

• Concentration of the solution and differential refractive index values were given as input in the software.

• For each individual concentration, the KC/R₀ was obtained.

• Finally a plot of KC/R₀ Vs C (g/ml) was generated.

• The Molecular weight (Mₐ) is determined from the intercept point on the Y axis. i.e. KC/R₀ = 1/Mₐ in Daltons.

• The 2nd Virial Coefficient (A₂) is determined from the gradient of the Debye plot.

The weight average molecular weight of the freshly prepared polymer was determined as 1,610 Da from the intercept of the Debye plot shown in figure 4.9. The calculated parameters from the Debye plot are shown in table 4.2. The negative value of second virial coefficient (A₂) indicates that the intermolecular interaction i.e. solute-solute interaction dominates over solute-solvent interaction. Thus there is aggregation in the system. Degree of polymerization is calculated from the ratio of weight average molecular weight and molecular mass of monomer.

\[
\text{Degree of polymerization} = \frac{\sum w_i M_i}{m}
\]

In the present case, \(\sum w_i M_i = 1,610\), \(m = 125\). It shows that around 10 atoms of Zr are present in the freshly prepared polymeric unit which is similar to Pu(IV) polymer whose molecular weight is 4,000 Da if freshly prepared containing around 10 Pu atoms in the polymer unit [73].
Fig. 4.9. Debye plot for freshly prepared Zr(IV) hydrous polymer

Table 4.2. Calculated parameters from the Debye plot for freshly prepared Zr(IV) hydrous polymer

<table>
<thead>
<tr>
<th>Substance</th>
<th>Measured at $\lambda = 780$ nm</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>$M_w$ (Da)</td>
</tr>
<tr>
<td>Zr(IV) hydrous polymer (freshly prepared)</td>
<td>1,610</td>
</tr>
</tbody>
</table>

4.3.2.4.2. Aged polymer

The colloidal solution was kept to age for 7 days and growth of colloids was observed. Figure 4.10 shows the refractive index increment for different concentrations of Zr. As the concentration of the solute increases the refractive index of the solution also increases giving a positive slope with $dn/dC = 0.1278$ ml g$^{-1}$. 
Fig. 4.10. Refractive index increment of different concentration of polymeric Zr(IV) solution aged for 7 days

Fig. 4.11. Debye plot for 7 days aged Zr(IV) hydrous polymer
Table 4.3. Calculated parameters from the Debye plot for 7 days aged Zr(IV) hydrous polymer

<table>
<thead>
<tr>
<th>Substance</th>
<th>Measured at $\lambda = 780$ nm</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>$M_w$ (Da)</td>
</tr>
<tr>
<td>Zr(IV) hydrous polymer (aged for 7 days)</td>
<td>3,000</td>
</tr>
</tbody>
</table>

The weight average molecular weight of the polymer aged for seven days was determined as 3,000 Da from the intercept of the Debye plot shown in figure 4.11. The positive value Second virial coefficient ($A_2$) is positive which indicates that the intermolecular interaction i.e. solute-solvent interaction dominates over solute-solute interaction. Thus after few days, the colloids are stable and there was no settling or precipitation. It shows that Zr form larger aggregates after the solubility limit is exceeded and these colloids do not dissolve for longer time. The growth of the colloid continues until equilibrium is reached [169]. Recent studies have also suggested that ageing of freshly prepared amorphous zirconium hydroxide polymers leads to phase transformation towards a more crystalline phase [169]. The calculated parameters from the Debye plot are summarized in table 4.3. Weight average molecular weight of the polymer shows that ~ 30 atoms of Zr are present in the polymeric unit aged for 7 days which is similar to Pu(IV) polymer whose molecular weight is $10^{10}$ Da for aged polymer with 100 - 1000 Pu atoms in the polymer unit [73].
4.4. Conclusions

- The gravimetric determination of zirconium as zirconium phosphate is one of the most widely used macro-methods for determining zirconium. The present method was to develop a spectrophotometric method applicable to the micro determination of zirconium.

- At a given Zr(IV) concentration, and with increasing pH, the degree of polymerization increases.

- The size of initially formed colloids at lower concentration is much higher than that of the colloids formed at higher concentration due to existence of different phases.

- Close to the solubility limit, continuous growth of the polymers was found which leads to the formation of large polynuclear species and colloids of ~1,600 Da.

- On further ageing for 7 days, the weight average molecular weight of the polymers increases to ~3,000 Da. This shows that the ageing of the polymer is accompanied by addition of more monomeric unit to the polymer.

- Second virial coefficient indicates that there was aggregation during the initial formation of polymer and the colloids become stable in the solution with increase in time.

- The molecular weight of Zr(IV) polymers formed in acidic solution has not been reported in the literature. The present study provides an insight to
determine molecular weight of colloidal polymers and also the nature of interaction of the solute with the solvent.

- Molecular weight determination of polymers by light scattering is simple and sensitive than other proposed techniques.

- It is also clear that the aqueous chemistry of Zr(IV) is similar to Pu(IV) and serves as an excellent homologue.