Study of Speciation for Zirconium(IV) Compounds in Aqueous Solution

by

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Monomeric \([\text{Zr(CO}_3\text{)}_4]^{4-}\) Complex in an Ammonium Zirconium Carbonate Aqueous Solution

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Chapter 1

General Introduction

Zirconium chemicals are used today in a wide range of industries and with advances in modern technology the diversity of their applications is constantly increasing.\(^1\) Zirconium chemicals have been manufactured in commercial quantities for upwards of half a century and with developments in processing techniques the volume and range of products continues to grow.\(^1\) In terms of raw material supply, zirconium is a fairly common element, ranking 20th in order of abundance in the earth’s crust, and is widely distributed, especially as its most abundant mineral, zircon.\(^1\) Thus, there is no reason to worry about lacking in the resources of zirconium chemicals.

Zirconium salt aqueous solutions have been used in a wide industrial uses, which are paper, paint, metal surface treatment, etc.\(^1-5\)

Toxicity of zirconium salts is low or absent.\(^6-8\) This is an advantage of zirconium salts in industrial uses. It verifies the safety of zirconium salts that zirconium chloride have been used for antiperspirant as a main component\(^9\) and FDA (Food and Drug Administration) has approved applying of ammonium zirconium carbonate (AZC) to paper and board products for packaging of foods.\(^10\) Since the safety management of chemicals and intention of reduction of environmental load have been strengthened by enforcement of Registration, Evaluation, Authorization and Restriction of Chemicals (REACH), recently, much attention has been paid to the safety of industrial materials. Consequently, it is expected that need of the zirconium salts, being secure, expands in the future.

In the industrial uses, one of the most important ability of zirconium salts is cross-linking for water-soluble macromolecules, e.g. poly-vinyl alcohol (PVA). Zirconium salts are superior to major cross-linking agents, for instance glyoxal, glutaraldehyde, etc. on the point of view of low toxicity and environmental resistance.
On the other hand, in industrial field of metal surface treatment, hexavalent chromium(VI) salts, which was reasonable and could apply to all kinds of metal substrate, had been heavily used until their harmfulness had been considered in the 1970s. Then, since hexavalent chromium(VI) salts contained products were regulated by End-of Life Vehicles (ELV) directive and Restriction of Hazardous Substances (RoHS) directive in the 2000s, try of disuse of hexavalent chromium(VI) salts has been accelerated. Thus, application of zirconium salts providing high performance metal surface coating and low toxicity has been expanded in the field. Improvement of applied performance of zirconium salts is certainly required to further expand the use of zirconium. The improvement is also an important theme for the industries of paper, paint, metal surface treatment, etc., from point of view of supply of low toxic and high performance products.

For instance in earlier work, McAlpine reported that rheology of coating compound for paper containing AZC solution and its cross-linking activity against water-soluble macromolecules could be controlled by addition of tartaric acid to the AZC solution. Since it is considered that cross-linking reaction between water-soluble macromolecules and zirconium species in solution is a substitutive reaction between hydrophilic group of the macromolecules and ligand coordinating zirconium ion, it is guessed that degree of polymerization (DP) and structure of the zirconium species are important factors for activity of the cross-linking reaction.

On the other hand, in industrial field of metal surface treatment hurrying disuse of hexavalent chromium(VI), recently, applications of zirconium salts have been studied well. Although an advantage of metal surface coating of zirconium salts is a function of barrier against corrosive factors, so as halide ions, in environment, since the coating is formed by eduction of zirconium species on surface of metal substrate, it is conjectured that the structure of zirconium species in solutions directly affect the structure of metal...
surface coating, causing its corrosion resistance.

Because of intricate and various structure of zirconium species in solutions, analyzing it is hard. Consequently, even if there are problems in the practical use depending on the structure of zirconium species, any studies of application based on structural analysis of zirconium species in solutions have been not performed. Therefore, a technology to improve applied performance based on the structure of zirconium species in solution has potential to provide novel high performance in the application of zirconium salts, so as cross-linking, metal surface coating, etc.

Since zirconium(IV) ion have the features which are high-valent, spherical orbital of electron and short ionic radius, it has high activity against ligand of oxoacid anion. Because of the activity, zirconium species are oligomerized via mainly oxoacid anion, so that various structures of zirconium species were generated depending on chemical composition of zirconium salt solution.

The structure of zirconium species in solutions were investigated by various methods. By the methods of ion-exchanging, UV-vis absorption spectrometry, super centrifugation, X-ray scattering and electron-migration, confirmation of oligomer in zirconium salt solutions and change of DP of it depending on chemical composition of the solutions were revealed. The results of these studies agree with each other qualitatively, however, quantitative discussions could not be performed.

In contrast, extended X-ray absorption fine structure (EXAFS) analysis give a signal influenced more directly than old methods of the above by the structure surrounding certain element. EXAFS analysis is available to zirconium salt solutions. For the first time, EXAFS analysis was applied to zirconium salt aqueous solutions by Ogawa et al. and they confirmed that change of structure of zirconium species in zirconium chloride solutions depending on chemical composition of the solutions. Since then, EXAFS analysis
was also employed for structural analysis of zirconium salts, so that more definite speciation of zirconium in various chemical composition have been understood.\textsuperscript{23-25} Since in the energy region of K shell absorption edge of zirconium atom, which is around 18 keV, the influence of absorption by light element, e.g. carbon, nitrogen, oxygen and chlorine, is little enough to perform quantitative EXAFS analysis on Zr-K edge. Thus, EXAFS analysis is suitable for structural analysis zirconium salts.

We assume that structure of zirconium species in zirconium salt solutions is a critical factor of applied performance of the solutions, for instance cross-linking for water-soluble macromolecules. Based on the assumption, we aim that more suitable structure for higher applied performance is clarified and it can be produced industrially as final targets. In order to achieve them, detail of the structure depending on chemical composition and aging condition of them must be resolved. In this study, the structure of zirconium species in zirconium salts solutions was investigated by EXAFS analysis as a main experimental method, which is suitable one for structure of zirconium salt solutions. Particularly, zirconium chloride and ammonium zirconium carbonate solution were analyzed in this study, being major materials in industries of paper, paint, metal surface treatment, etc. and used more than other zirconium salts.
References


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Chapter 2
Experimental

2-1 Experimental methods

In this study, X-ray absorption fine structure analysis was employed as a main analytical method to investigate structure of zirconium species in aqueous solutions. The other methods that were dynamic light scattering measurement by Zetasizer Nano ZS (Malvern Instruments), scanning transmission electron microscopy by HD-2700 (Hitachi High-Technologies), Raman spectrometry by LabRam HR-800 (HORIBA), UV-vis absorption spectrometry by V550 (JASCO) were used.

Theory of extended X-ray absorption fine structure (EXAFS) analysis

The absorption coefficient of a certain material in X-ray region generally decreases monotonously as the energy of the photon is increased. When the energy reaches a certain critical value, the absorption coefficient increases abruptly. This discontinuity corresponds to the threshold of the ejection of a core electron from an atom in the material and is called the absorption edge. In addition, the absorption coefficient often exhibits oscillations extending to as much as 1000 eV above the absorption edge. This variation is named X-ray absorption fine structure, XAFS. In general, XAFS is separated in two regions. The near edge part, up to about 50 eV above the absorption edge, is called X-ray absorption near-edge structure, XANES, and the other from about 50 to 1000 eV extended X-ray absorption fine structure, EXAFS. XAFS have been widely used as a tool of structural analysis, because the X-ray absorption spectrum can be measured irrespective of the state of the sample material, e.g. gas, liquid, solution, etc.

EXAFS reflects a final state interference involving scattering of the outgoing photoelectron at the neighboring atoms. The probability of absorption of an X-ray photon by a core electron depends on both the initial and the final state of the electron. The electron of the
initial state stays at the localized core level corresponding to the absorption edge. Its final state consists of an ejected photoelectron. It can be represented as an outgoing spherical wave originating from the X-ray absorbing atom. If the atom is surrounded by other atoms, the outgoing photoelectron wave will be back-scattered by the neighboring atoms, thereby producing an incoming wave. The final state is then affected by the interference between the outgoing and the incoming waves that gives rise to the sinusoidal variation of absorption coefficient versus X-ray energy known as EXAFS. The frequency of the EXAFS depends on the distance between the absorbing atom and the neighboring atom, while the amplitude of the EXAFS depends on the number and the back-scattering power of the neighboring atom. Therefore, the analysis of the EXAFS gives the distance and the number of atoms surrounding the absorber.

**EXAFS measurement**

All measurements of EXAFS were performed by quick scan of transmission method at Beam line BL14B2 of the SPring-8. The composition of BL14B2 for the measurements by transmission method in this study is shown in Fig. 1.

![Fig. 1 The composition of BL14B2 for the EXAFS measurements by quick scan of transmission method. *) Form of samples is explained as follows.](image)
The preparation of gas proportions in ion chambers and the optical setting were regulated by an optical control program “Optics” equipped with BL14B2.

The measured samples were set between ion chambers $I_0$ and $I_1$, intersecting the optical path of X-ray. Intensity of incident and transmitted X-ray were counted by the chambers $I_0$ and $I_1$, respectively. In the measurements, sample solutions were sealed into a polyethylene bag, and then the package and a spacer were sandwiched between a pair of plastic boards with window by clips or it was set into a plastic box holder with windows. In order to gain suitable intensity of X-ray absorption coefficient, optical path length was adjusted by the thickness of the spacer or the box holder. Fig. 2 shows the solution sample packages for the EXAFS measurements of which optical path length were changed with the various holders. On the other hand, powder samples, e.g. zirconium oxychloride octahydrate ($\text{ZrOCl}_2 \cdot 8\text{H}_2\text{O}$) and ammonium zirconium carbonate dehydrate ($\text{(NH}_4\text{)}_3\text{Zr(OH)(CO}_3\text{)}_3\cdot 2\text{H}_2\text{O}$), were diluted by boron nitride (Aldrich) and were molded into pellet form, of which diameter was 10 mm and thickness was 1 mm. The pellet was sealed a polyethylene bag and the package was locked on the plastic board with window by clips. Fig. 3 shows the pellet package for the measurement.

![Fig. 2 The solution samples packages of which optical path length were adjusted for the EXAFS measurements.](image)
2-2 Reagents

In order to prepare zirconium chloride and ammonium zirconium carbonate solutions, zirconium oxchloride octahydrate (special grade agent, Mitsuwa Chemicals, Japan), zirconium basic carbonate (42 mass% as $\text{ZrO}_2$, $\text{Zr(OH)}_a(\text{CO}_3)_b\cdot n\text{H}_2\text{O}$, $a \approx 3.2$, $b \approx 0.4$, $n \approx 6.9$, Daiichi Kigenso Kagaku Kogyo), perchloric acid (special grade agent, 70.5 mass%, Sigma Aldrich Japan), Sodium chloride (special grade agent, Katayama Kagaku Kogyo), ammonium hydrogen carbonate (purity $\text{NH}_3$: 20-23 mass%, special grade agent, Kishida Chemical), and aqueous ammonia (purity $\text{NH}_3$: 25 mass%, special grade agent, Sigma Aldrich Japan), ammonium L-(-)-tartarate (special grade agent, Kishida Chemical), citric acid anhydrate (special grade agent, Kishida Chemical), gluconic acid (1st agent, Sigma Aldrich Japan), triethanolamine (special grade agent, Kishida Chemical) were used.

References

Chapter 3
Zr(IV) Structure in Aqueous Zirconium Chloride Solution from X-ray Absorption Fine Structure Analysis

Abstract

Zirconium salt solutions have been used for a wide variety of industrial applications and it is important to control the structure of the zirconium species in solution to ensure appropriate performance during various processes. To assist in understanding the relationship between structure and performance, X-ray absorption fine structure analyses of zirconium chloride solutions with varying values of [Zr], [H+] and [Cl−] were performed to examine the Zr structures formed in solution. In these solutions, the Zr-Zr coordination number exhibited an obvious change from 4 to 2, regardless of [Zr], as [HCl] was changed from 0.03 to 0.5. In contrast, the coordination number remained relatively steady when the [H+] value was modified by the addition of perchloric acid, and also changed very little when [Cl−] was varied at low [H+] values. Furthermore, since the Zr-Zr coordination number was stable in solutions with a [Cl−]/[Zr] ratio of 0.7, regardless of changes in the concentrations of the other components, it was concluded that stable Zr structures exist at that ratio. The residual ratios of polyvinyl alcohol films formed from solutions with various [Cl−]/[Zr] ratios were measured following extraction with hot water and the data showed that a maximum residual was obtained at a [Cl−]/[Zr] ratio of 0.7. The enhanced extent of cross-linking at this [Cl−]/[Zr] ratio is believed to be caused by the high degree of polymerization and chemical stability of the zirconium species in this particular solution.
3-1 Introduction

Zirconium chloride solutions are often applied as helpful cross-linking agents, since they exhibit resistance to environmental factors and various chemicals and confer superior stability when used with water-soluble polymers. They also serve as important starting materials for the manufacture of various zirconium compounds, such as stabilized zirconia and mixed rare-earth oxides.\textsuperscript{1-6} It is well known that zirconium in aqueous solution can adopt a wide variety of structures, due to the significant charge, large size and ready ligand acceptance of the zirconium ion.\textsuperscript{7} Although the existence of the monomeric species Zr\textsuperscript{4+} has been demonstrated under specific conditions in which [Zr] is low and [H\textsuperscript{+}] is high, it is believed that zirconium more often adopts a polymeric rather than monomeric form in solution.\textsuperscript{8,9} Additionally, it has been shown that the structure of zirconium in solutions will vary depending on [H\textsuperscript{+}] as well as the nature of the accompanying anion and its concentration. As an example, the tetrameric species [Zr\textsubscript{4}(OH)\textsubscript{8}16H\textsubscript{2}O]\textsuperscript{8+} (Fig. 1)\textsuperscript{10} normally present in crystals of zirconium oxychloride hydrate (ZrOCl\textsubscript{2} \cdot 8H\textsubscript{2}O) is the predominant form in zirconium oxychloride aqueous solutions in which [Zr] = 2 M.\textsuperscript{11}

![Fig. 1. Structure of the zirconyl chloride octahydrate tetramer.](image-url)
In addition, an equilibrium between the tetrameric and octameric forms of \( (\text{Zr}_8(\text{OH})_{19}^{13+}) \) which varies with the pH of a chloride solution has been suggested by Singhal et al. and Walther et al.\textsuperscript{12,13} Since the properties of zirconium chloride solutions associated with practical applications, such as cross-linking ability, are changed by variations in \([\text{H}^+]\) and \([\text{Cl}^-]\), zirconyl chloride solutions in which \([\text{Cl}^-]/[\text{Zr}]\) is about 0.7 are typically preferred in industrial applications.\textsuperscript{1,14} It is assumed that the observed variations in cross-linking of zirconium solutions are due to changes in the structures of the zirconium species, however, to date there have been no detailed studies of these structural changes. Extended X-ray absorption fine structure (EXAFS) analysis represents a suitable technique for examining the structure of zirconium species in solutions because it can be applied to both the amorphous phase and solutions over a wide range of concentrations of various chemical components. Previously, EXAFS analysis has demonstrated the existence of tetrameric species in an oxychloride solution in which \([\text{Zr}]\) was 1.0 M as well as the polymerization of this tetrameric species in a 0.1 M solution.\textsuperscript{15} In the present study, the structures of zirconium species under conditions including a wide range of \([\text{Zr}], [\text{H}^+]\) and \([\text{Cl}^-]\) were investigated using EXAFS analyses. The results revealed changes in the polymeric structure over a wider range of concentrations of chemical components than were investigated in previous studies.\textsuperscript{15}

### 3-2 Experimental

**Preparation of samples**

The chemical compositions of the zirconium chloride solutions applied in this study are shown in Table 1. The solutions were made by first dissolving zirconium basic carbonate (42 mass% as \( \text{ZrO}_2 \), \( \text{Zr(OH)}_a(\text{CO}_3)_b\cdot n\text{H}_2\text{O} \), \( a\approx3.2 \), \( b\approx0.4 \), \( n\approx6.9 \), Daiichi Kigenso Kagaku Kogyo) in hydrochloric acid (special grade agent, 36.2 mass%, Sigma Aldrich...
Japan) with agitation until a transparent solution was observed. In this manner, solutions with various \([\text{Cl}^-]/[\text{Zr}]\) ratios and in which \([\text{Zr}]\) ranged from 2 to 2.5 M were prepared. These mixtures were subsequently diluted with deionized water to produce solutions 1 to 46 as shown in Table 1.

Perchloric acid (special grade agent, 70.5 mass%, Sigma Aldrich Japan) was added to solutions in which \([\text{Zr}] = 1.0\) M and \([\text{Cl}^-] = 0.65\) M, prepared in the same manner as above, in order to obtain solutions 47 to 51. These samples differed from each other only in terms of the \([\text{H}^+]\), since \([\text{Zr}]\) and \([\text{Cl}^-]\) were kept constant at 0.1 M and 0.065 M, respectively. In addition, sodium chloride (special grade agent, Katayama Kagaku Kogyo) was added to the previously prepared solution in which \([\text{Zr}] = 0.1\) M and \([\text{Cl}^-] = 0.65\) M and these solutions were diluted with deionized water to prepare samples 52 to 54. The \([\text{H}^+]\) of samples were determined using a pH meter (HORIBA) with a glass electrode (9677), except in the case of solutions 24 to 28, 35, 36, 40 to 42 and 46, for which \([\text{H}^+]\) was estimated from the quantity of hydrochloric acid used to prepare the samples.
Table 1 Chemical composition of zirconium chloride solutions

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<tr>
<th>Sample No.</th>
<th>[Zr] / mol L$^{-1}$</th>
<th>[Cl$^{-}$] / mol L$^{-1}$</th>
<th>[H$^{+}$] / mol L$^{-1}$</th>
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No.47-51: Perchloric acid was added to the sample solutions.
No.52-54: Sodium chloride was added to the sample solutions.
All samples were analyzed within 10 days of preparation because of the aging effect which occurs in zirconium solutions.\textsuperscript{15}

**EXAFS measurement**

The X-ray absorption spectra of samples 1 to 54 were acquired at beamline BL14B2 of the SPring-8 facility of the Japan Synchrotron Radiation Research Institute (JASRI), applying the quick scan transmission method. X-ray energy levels of 17.3 to 19.7 keV were applied during the measurements in conjunction with a double crystal Si(111) monochromator. During analyses, samples were sealed in polyethylene bags and both the bag and a spacer were sandwiched between a pair of boards containing a window or were set into a box holder incorporating a window.

Optical path lengths were set at: 1 mm ([Zr] = 1.0 and 2.0 M), 3 mm ([Zr] = 0.5 M), 15 mm ([Zr] = 0.1 M), 20 mm ([Zr] = 0.05 M) and 40 mm ([Zr] = 0.01 M) depending on the sample concentration. The scan times were set at: 1 min. ([Zr] = 0.5, 1.0 and 2.0 M), 3 min. ([Zr] = 0.1 M) and 10 min. ([Zr] = 0.05 and 0.01 M). All scans were performed twice for the [Zr] = 0.01 M solutions and the spectra were added prior to analysis.

**EXAFS analyses**

REX2000 software (RIGAKU) was used for EXAFS analysis. X-ray absorption spectra were converted to EXAFS spectra in terms of $\chi(k)$ as a function of the wave number of the photoelectron, $k$, and these spectra were amplified by the multiplier $k^3$. A Fourier transform was applied to EXASF spectra between $k = 27.5$ to 185 nm\textsuperscript{-1}. The secondary peaks in the Fourier transform spectra were attributed to Zr-Zr coordination and were extracted by the application of an inverse Fourier transform and these spectra were fit such that Zr-Zr coordination numbers and coordination distances were obtained. During the fitting process, the phase shift and backscattering amplitude associated with Zr-Zr coordination (distance: 0.3559 nm) as calculated by FEFF6L (through the application of simulating
photoelectron scattering)\textsuperscript{16} were used.

**Evaluation of cross-linking ability**

PVA solutions were prepared by dissolving 100 g aliquots of Gohsefimer Z-200 (PVA: polyvinyl alcohol, Nippon Synthetic Chemical Industry) in 900 g of deionized water, after which 10 ml of a zirconium chloride solution in which [Zr] = 0.1 M (samples 18 and 21 to 26) was added to 12.8 g of the PVA solution with stirring. After spreading 1.0 g of this mixture uniformly along the bottom of a glass 30 mm diameter Petri dish and allowing it to sit at room temperature for one week to dry, the sample was heat-treated at 343 K for 30 minutes to obtain a PVA film cross-linked by zirconium chloride. Plain PVA films to which 10 ml of deionized water was added instead of the zirconium solution were also prepared. After drying, each Petri dish along with its PVA film was soaked in hot (353 K) water and then removed and dried for 90 min at 343 K, following which the mass of residual PVA film was measured.

**3-3 Results and discussion**

The Zr-K edge X-ray absorption spectra of the 0.1 M solutions along with EXAFS spectra are presented in Figs. 2 and 3, respectively, while the corresponding Fourier transform spectra are shown in Fig. 4. To identify the peaks due to Zr-Zr coordination, the peak positions were derived by theoretical calculations with FEFF6, applying the known structural parameters of zirconium oxychloride octahydrate crystals (Zr-Zr coordination distance: 0.3559 nm, coordination number: 2), as included in Fig. 2. In these calculations, the square of the Debye-Waller factor was set to $3 \times 10^{-5}$ nm$^2$. 
Fig. 2 X-ray absorption spectra of zirconium chloride solutions ([Zr] = 0.1 M).

a: [Cl\(^-\)] = 4.0 M, [H\(^+\)] = 4.0 M, b: [Cl\(^-\)] = 2.0 M, [H\(^+\)] = 2.0 M, c: [Cl\(^-\)] = 0.72 M, [H\(^+\)] = 0.68 M, d: [Cl\(^-\)] = 0.34 M, [H\(^+\)] = 0.28 M, e: [Cl\(^-\)] = 0.14 M, [H\(^+\)] = 0.049 M, f: [Cl\(^-\)] = 0.065 M, [H\(^+\)] = 6.9×10\(^{-3}\) M

Fig. 3 EXAFS \(k^3 \chi(k)\) spectra of zirconium chloride solutions ([Zr] = 0.1 M).

a: [Cl\(^-\)] = 4.0 M, [H\(^+\)] = 4.0 M, b: [Cl\(^-\)] = 2.0 M, [H\(^+\)] = 2.0 M, c: [Cl\(^-\)] = 0.72 M, [H\(^+\)] = 0.68 M, d: [Cl\(^-\)] = 0.34 M, [H\(^+\)] = 0.28 M, e: [Cl\(^-\)] = 0.14 M, [H\(^+\)] = 0.049 M, f: [Cl\(^-\)] = 0.065 M, [H\(^+\)] = 6.9×10\(^{-3}\) M
Since the location of the absorption edge around 18 keV and the shape of the spectra in Fig. 2 are similar for all samples, the electronic states of the zirconium atoms were evidently not changed regardless of the chemical composition. All samples exhibited this phenomenon other than those for which [Zr] = 0.1 M and therefore the zirconium was in the tetravalent state in these solutions.

In Fig. 4 the locations of the secondary peaks of the samples are in good agreement with the theoretical position based on Zr-Zr coordination in the structural model of zirconium oxychloride octahydrate derived from theoretical calculations with FEFF6L. This was the case for all samples other than those which contained 0.1 M Zr. This result indicates that the Zr-Zr coordination structures in these solutions were based on bridging by...
two OH\(^{-}\) ions in a manner similar to the structure of the tetrameric species in the oxy-chloride crystal.

The Zr-Zr coordination numbers as a function of [H\(^{+}\)] at different [Zr] values are shown in Fig. 5 and structural models corresponding to each Zr-Zr coordination numbers are provided in Fig. 6. In this figure, the Zr-Zr coordination number of the trimeric model is 1.3 (Fig. 6a), while the tetrameric model has a coordination number of 2 (Fig. 6b) and the polymer consisting of \(n^2\) tetrameric units bonded with one another in a square sheet arrangement has a coordination number of \(4-2/n\) (Fig. 6c).

Fig. 5 Zr-Zr coordination number as a function of hydrogen ion concentration at various zirconium concentrations.

[Zr]: ○ = 0.01 M (samples 1-9), ● = 0.05 M (samples 10-17), △ = 0.1 M (samples 18-28), ▲ = 0.5 M (samples 29-36), □ = 1.0 M (samples 37-42), ■ = 2.0 M (samples 43-46), * = 0.1 M (samples 47-51)

*: Perchloric acid was used to control hydrogen ion concentration (samples 47-51)
Fig. 6 Structures of zirconium species and their expected Zr-Zr coordination number ($n_{Zr-Zr}$): a) Trimer ($n_{Zr-Zr} = 1.3$), b) tetramer ($n_{Zr-Zr} = 2.0$) and c) square shaped $n \times n$ polymer composed of tetramers ($n_{Zr-Zr} = 4-2/n$)

From Fig. 5, the Zr-Zr coordination number decreased with increases in [H$^+$] regardless of the [Zr] value. Although this correlation with [H$^+$] has been observed previously, $^8,13,17$ a particularly remarkable variation in structure induced by changes in the Zr-Zr coordination number in solution over the [H$^+$] range of 0.03 to 0.5 M was found in this study. Within this [H$^+$] range, the structural changes represented by Figs. 6(b) and (c) are believed to occur.

In the [H$^+$] range of 0.5 to 1.0 M, the Zr-Zr coordination numbers converge at approximately 2 regardless of the [Zr] value, indicating that the tetrameric species in Fig. 6(b) is dominant in this [H$^+$] range. Additionally, the Zr-Zr coordination number is below 2 when [H$^+$] is above 1.0 M, which demonstrates the generation of a species with a degree
of polymerization equal to 3 or less. This result is in agreement with indications of trimeric species in Ogawa’s study, in which the Zr-Zr coordination number of the zirconium chloride solution for which [Zr] = 0.2 M and [HCl] = 4 M was estimated to be 1.6 by EXAFS analysis.\textsuperscript{15} Since it has also been reported by Angstadt and Tyree that the trimeric species was dominant in 2.8 M HCl, its existence seems definite.\textsuperscript{18}

In addition, Southon et al. suggested a model consisting of a sheet-like structure composed of square tetrameric species arranged and bonded in two dimensions, based on the structural analysis of a gel obtained from colloidal zirconium hydroxide in nitric acid.\textsuperscript{19} Clearfield also reported sheet-like species similar to the above following the hydrolysis of aqueous zirconium chloride solution.\textsuperscript{20} The fact that the Zr-Zr coordination number plateaued at about 4 between [H\textsuperscript{+}] = 0.001 and 0.02 M in the present study agrees with the theories of previous researchers concerning sheet-like structures. If tetrameric species are arranged and bonded on a plane, such that the zirconium atoms are positioned at the nodes of a checkered pattern, the Zr-Zr coordination number will approach 4 as the degree of polymerization of the sheet-like polymer increases, resulting in the structural model shown as Fig. 6(c) when \( n \) is sufficiently large.

In Fig. 5, for the group in which [Zr] = 0.1 M (samples 19-24), the Zr-Zr coordination numbers are 4.2 and 2.0 at [Cl\textsuperscript{−}] = 0.085 M, [H\textsuperscript{+}] = 0.024 M and [Cl\textsuperscript{−}] = 0.72 M, [H\textsuperscript{+}] = 0.68 M, respectively. In contrast, in the case of the group to which perchloric acid was added to increase [H\textsuperscript{+}] (samples 47-51), holding [Zr] at 0.1 M and [Cl\textsuperscript{−}] at 0.065 M, the Zr-Zr coordination numbers stay between 4.0 and 3.6 over the [H\textsuperscript{+}] range of 0.021 to 0.65 M. These data indicate that the Zr-Zr coordination number does not depend solely on [H\textsuperscript{+}].

Fig. 7 shows the Zr-Zr coordination numbers as a function of [Cl\textsuperscript{−}] in 0.1 M solutions in which the [HCl] value was changed (samples 18-26) and in solutions having a constant
[H\(^+\)] value of \((5.7\pm0.6) \times 10^{-3}\) M in which [Cl\(^-\)] was varied between 0.14 and 1.5 M (samples 52-54).

Fig. 7 Zr-Zr coordination number as a function of chloride ion concentration ([Zr] = 0.1 M).

[\([H^+]\): ★ = 6.9\times10^{-3} \text{ to } 2.0 \text{ M (samples 18-26)}, \Box = (5.7\pm0.6)\times10^{-3} \text{ M (samples 52-54)}

Fig. 7 demonstrates that maintaining a high pH and increasing only the [Cl\(^-\)] value results in very little change in the Zr-Zr coordination number, thus this parameter does not depend solely on [Cl\(^-\)]. In summary, the Zr-Zr coordination number varies in response to changes in both [H\(^+\)] and the particular acid employed.

The Zr-Zr coordination numbers and the coordination distances as functions of [Zr] over varying [Cl\(^-\)]/[Zr] ranges in the vicinity of 0.7, 1.0-1.5 and 1.8-2.5 are shown in Figs. 8 and 9.
Fig. 8 Zr-Zr coordination number as a function of zirconium concentration at various \([\text{Cl}^-]/[\text{Zr}]\) values. 
\([\text{Cl}^-]/[\text{Zr}]: \times = 0.7 \text{ (samples 1, 10, 18, 29, 30, 37, 38, 43 and 44)}, \circ = 1.0-1.5 \text{ (samples 11, 20, 32, 39 and 45)}, \▲ = 1.8-2.5 \text{ (samples 2, 21, 33, 40 and 46)}

Fig. 9 Zr-Zr coordination distance as a function of zirconium concentration at various \([\text{Cl}^-]/[\text{Zr}]\) values. 
\([\text{Cl}^-]/[\text{Zr}]: \times = 0.7 \text{ (samples 1, 10, 18, 29, 30, 37, 38, 43 and 44)}, \circ = 1.0-1.5 \text{ (samples 11, 20, 32, 39 and 45)}, \▲ = 1.8-2.5 \text{ (samples 2, 21, 33, 40 and 46)}
From Figs. 8 and 9, when \([\text{Cl}^-]/[\text{Zr}]\) is in the range of 1.0 to 1.5 or 1.8 to 2.5, both the Zr-Zr coordination number and distance were significantly changed with variations in [Zr], whereas variations in \([\text{Cl}^-]/[\text{Zr}]\) over the range of 1.0 to 1.5 induced very little change. These data suggest that the structure in solution undergoes little change regardless of the concentration of components so long as \([\text{Cl}^-]/[\text{Zr}]\) is in the vicinity of 0.7.

Fig. 10 presents a plot of the residual ratios of PVA films produced from mixtures to which 0.1 M Zr solutions were added for the purposes of cross-linking and following extraction with hot water, as a function of \([\text{Cl}^-]/[\text{Zr}]\).

Fig. 10 demonstrates the residual ratio increases with decreases in \([\text{Cl}^-]/[\text{Zr}]\). Plain PVA films, to which zirconium was not added, completely disappeared after the hot water wash and thus showed a lack of cross-linking. The solution for which \([\text{Cl}^-]/[\text{Zr}]\) was around 0.7 shows the greatest extent of cross-linking.
Fig. 11 Residual ratios of PVA films after washing with water. The PVA films were treated with crosslinking solutions with various Zr-Zr coordination numbers ([Zr] = 0.1 M).

Fig. 11 presents a plot of the residual ratios of the PVA films as a function of the Zr-Zr coordination number. From Fig. 11, the ratio is obviously decreased at Zr-Zr coordination numbers below 2. This results from the presence of tetrameric and trimeric species, for which the coordination numbers are 2 and 1.3, respectively, which evidently reduces the water resistance of the PVA film. Accordingly, a high degree of polymerization and a chemically stable structure in the solution result from a [Cl⁻]/[Zr] ratio of approximately 0.7, leading to significant cross-linking. These results should assist in the quality control of Zr solutions, since they demonstrate that, at this ratio, the solution performance can be consistently predicted.
3-4 Conclusion

Changes in the polymeric structures of aqueous zirconium chloride solutions over a wide range of chemical compositions were examined by EXAFS analysis. Variations in [H⁺] were determined to have a particularly significant effect on Zr-Zr coordination numbers between 2 and 4 and particular [H⁺] ranges were shown to converge the coordination number on values of either 2 or 4. These results are significant since they demonstrate the possibility of controlling the performance of zirconium chloride solutions by tuning the Zr structure to obtain a high degree of polymerization and good stability of chemical species in solution. In terms of the cross-linking ability of the zirconium solutions, optimal results were obtained with solutions in which the [Cl⁻]/[Zr] ratio was in the vicinity of 0.7.

3-5 Acknowledgments

The synchrotron radiation EXAFS experiments were performed at the BL14B2 beam-line of SPring-8 with the approval of JASRI (Proposal No. 2007B1843 and 2008B2117). We would also like to thank Mr. Hiroyuki Ono of the Nippon Synthetic Chemical Industry Co., Ltd. for assistance during experimental work with PVA films.

References

(3) Pugh, E. U.S. Patent 1,376,161 1921.


(14)


Chapter 4
Nanometer-sized Polynuclear Cluster and Oxide Nanocrystal Formation via Aging Condition-dependent Hydrolysis of Zirconium Oxychloride

Abstract
Aqueous solutions of zirconium oxychloride aged at temperatures between 298 and 333K for 26 days were investigated. Nanoparticles with different size distributions depending on aging temperature and duration were detected by dynamic light-scattering measurements. Extended X-ray absorption fine structure analysis and scanning transmission electron microscopy measurements revealed the nanoparticles formed in the samples to be zirconium polynuclear complexes and zirconium dioxide nanocrystals under mild condition, which was previously unexplored.

4-1 Introduction
Aqueous solutions of zirconium chlorides (including oxychloride) are often used as crosslinking agents for water-soluble macromolecules; e.g., polyvinyl alcohol (PVA) in the paper industry. Very low toxicity is one of the reasons for employing this reagent; for instance, zirconium chloride is used as an antiperspirant. In the ongoing trend to lower the toxicity of industrial materials, expanded use of zirconium chloride as a crosslinker is expected.

On the other hand, it is well known that Zr forms polynuclear complexes whose structures are modulated by polymerization or depolymerization, depending on the chemical formulation in aqueous solution.

It is expected that PVA crosslinking ability could be affected by the structure of the Zr
species, because the affinity for PVA could vary with structural changes of the Zr species. The most effective structure for crosslinking should be resolved in order to make the most efficient use of Zr in various chemical industries. We have been studying the structures of Zr polynuclear complexes in aqueous solution by extended X-ray absorption fine structure (EXAFS) analysis and have previously reported that the structures of aqueous Zr species are affected by coexisting anions and by pH and that its crosslinking ability for PVA depends upon these structures.\textsuperscript{10,11}

In addition, it has been reported that zirconium oxychloride (ZrOCl\textsubscript{2}) dissolved in aqueous solution can be hydrolyzed to ultimately generate zirconium dioxide (ZrO\textsubscript{2}) under reflux conditions.\textsuperscript{8,9,12,13}

Matsui et al. previously suggested the formation mechanism of ZrO\textsubscript{2} in an aqueous solution. In brief, tetranuclear complex [Zr(OH)\textsubscript{2}∙4H\textsubscript{2}O]\textsuperscript{8+} (represented in Fig. 1) is mainly formed by dissolving ZrOCl\textsubscript{2}∙8H\textsubscript{2}O into water.

\begin{equation}
[Zr(OH)\textsubscript{2}∙4H\textsubscript{2}O]\textsuperscript{8+} \rightleftharpoons [Zr(OH)\textsubscript{2+x}∙(4−x)H\textsubscript{2}O]\textsuperscript{(8−4x)+} + 4xH^+ \quad (1)
\end{equation}

Heating of this solution allows increasing the concentration of [Zr(OH)\textsubscript{2+x}∙(4−x)H\textsubscript{2}O]\textsuperscript{(8−4x)+}; when the concentration reaches a critical supersaturation level, crystal
nuclei of hydrous ZrO$_2$ are generated, and primary particles of hydrous ZrO$_2$ are formed by growth of the crystal nucleus. Furthermore, secondary particles of hydrous ZrO$_2$ are formed by hard aggregations among the primary particles. A temperature dependence at $T > 343$ K and generation of nanometer-sized ZrO$_2$ crystals were also reported by Matsui et al.\textsuperscript{13} However, it remains unclear what conditions generate polynuclear complexes of Zr and ZrO$_2$ nanocrystals at lower temperatures, namely, mild condition than the previous reports.\textsuperscript{13}

In this study, EXAFS analysis, dynamic light scattering (DLS), and scanning transmission electron microscopy (STEM) were employed to characterize the chemical species, as well as their structures generated from the hydrolysis of aqueous solutions of zirconium oxychloride in order to evaluate the initial stages of ZrO$_2$ nanocrystal growth.

4-2 Experimental

Zirconium oxychloride octahydrate (ZrOCl$_2$·8H$_2$O, special grade, Mitsuwa Chemicals, Japan) was dissolved in deionized water (prepared using RFU565NA, ADVANTEC, Japan) to obtain a solution in which [Zr] = 2.0 M (mol L$^{-1}$), and the solution was diluted to [Zr] = 0.1 or 0.01 M. The solutions were aged at room temperature (298 K) or in a thermostatted incubator. The pH values of the solutions were measured by a glass electrode (9681-10D, HORIBA, Japan) at 298 K after aging. The chemical properties and experimental conditions of the solutions examined are shown in Table 1.

Zetasizer Nano ZS (Malvern Instruments, U.K.) and HD-2700 (Hitachi High Technologies, Japan) were employed for DLS and STEM measurements, respectively. The specimens for STEM were prepared from the Zr-containing aqueous samples; the sample solutions were quickly frozen using slush nitrogen and sliced into 5-10-nm-thick films.
Zr K-edge X-ray absorption spectra of aqueous solutions of ZrOCl$_2$·8H$_2$O and ZrO$_2$ powders (special grade, Wako Pure Chemical Industries, Japan) were measured using synchrotron radiation at SPring-8 Beamline (BL14B2) via a quick scan of transmission method in the energy region ranging from 17.5 to 19.9 keV. A double crystal monochromator of Si(111) was used for the measurements. EXAFS analyses of the spectra were carried out using REX2000 software (Rigaku, Japan). The phase shifts and backscattering amplitudes required for the analyses were derived from calculations using FEFF6L software.$^{14}$

Table 1. Chemical properties and experimental conditions of samples

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1) Prepared just before the measurements; the solution was not aged.
4-3 Results and Discussion

The EXAFS spectra $k^3 \chi(k)$ of each sample are shown in Fig. 2. Features to discriminate the structures of Zr complexes were not obtained by comparing the shape of spectra.

Fig. 2 EXAFS spectra ($k^3 \chi(k)$). The numbers correspond to the sample No. in Table 1.

The Fourier transforms (FT) of the EXAFS spectra of each sample are shown in Fig. 3. The peaks located near 150 and 320 pm in Fig. 3 are attributed to Zr-O and Zr-Zr coordination, respectively.\textsuperscript{15} The differences in the spectral shape between the samples arise from the conditions, including Zr concentration, aging temperature, and aging time.
Thus, the parameters for Zr-O and Zr-Zr coordination (coordination distance: $r$, coordination number: $N$, and Debye-Waller factor: $\sigma$) obtained from the FT spectra as a function of aging temperature and aging time are shown in Fig. 4 and Fig. 5, respectively. They are summarized in Table 2. The parameters for the samples, including $[\text{Zr}] = 0.01$ and 0.1 M, varied depending on aging time and temperature (Fig. 4 and Fig. 5). The range of parameters for the $[\text{Zr}] = 0.1$ M samples is smaller than that for $[\text{Zr}] = 0.01$ M. These results indicate a very slow progression of hydrolysis for the Zr species, and the degree of hydrolysis progression is smaller at higher concentration. The coordination parameters for $[\text{Zr}] = 2.0$ M (sample 16) are also indicated in Fig. 3. When the sample was aged for 26 days, the parameters remained fundamentally unchanged compared to the unaged sample (sample 9).
Fig. 4 Parameters of Zr-O and Zr-Zr coordination derived from EXAFS analysis as a function of aging temperature. *: [Zr] = 0.1 M, not aged (sample 9), ◇: [Zr] = 0.01 M, aged 26 days (samples 3, 4, 7 and 8), △: [Zr] = 0.1 M, aged 26 days (samples 12-15), ○: [Zr] = 2 M, aged 26 days (sample 16). Broken and dotted broken lines indicate the level of the parameters for pure zirconium oxychloride octahydrate (sample 17) and zirconium dioxide (sample 18), respectively.
Fig. 5 Parameters of Zr-O and Zr-Zr coordinations derived by EXAFS analysis as a function of aging time. ×: [Zr] = 0.01 M, aged at RT (samples 1-3), ◇: [Zr] = 0.01 M, aged at 323 K (samples 5-7), △: [Zr] = 0.1 M, aged at RT (samples 9-12), broken and dotted broken line indicates the level of the parameter for pure zirconium oxychloride octahydrate (sample 17) and zirconium dioxide (sample 18), respectively.
Table 2  Experimental conditions and the parameters for Zr-O coordination and Zr-Zr coordination obtained from EXAFS analyses

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<th>[Cl] / M</th>
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<th>Aging time / days</th>
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Zirconium oxychloride solutions are highly acidic, and as shown in Table 1, the sample pH is lower at higher Zr concentration. Therefore, a high Zr concentration affords a high H⁺ concentration, which prevents hydrolysis of the Zr species. As previously reported, hydrolysis of Zr species generates small ZrO₂ particles.⁴,¹³ DLS measurements were employed to examine the small particle generation in our experimental systems.

The DLS particle size distributions are shown in Fig. 6. Median diameters obtained from Fig. 6 were also analyzed as functions of aging temperature and aging time and were shown in SI, Fig. 7 and Fig. 8, respectively.
Fig. 6  Fourier transforms of EXAFS spectra. The numbers correspond to the sample No. in Table 1.

Fig. 7  Median diameter as a function of aging temperature.
*: [Zr] = 0.1 M, not aged (sample 9), ◇: [Zr] = 0.01 M, aged 26 days (samples 3, 4, 7 and 8),
Δ: [Zr] = 0.1 M, aged 26 days (samples 12 and 14).
Fig. 8  Median diameter as a function of aging time.
×: [Zr] = 0.01 M, aged at RT (sample 3), ◊: [Zr] = 0.01 M, aged at 323 K (samples 5-7), △: [Zr] = 0.1 M, aged at RT (samples 9 and 12).

Because the variations of the parameters in Fig. 4 and Fig. 5 seem to interrelate with the variations of median diameters in Fig. 7 and Fig. 8, respectively, we discussed the structures of Zr species in the samples based on the sizes observed by DLS measurement in Fig. 6.

These sizes are roughly divided into three regions: < 2.0, 0.5-6.0, and > 10 nm. The smallest size distributions (< 2.0 nm) were detected in samples 9 and 16. The results of EXAFS analysis of samples 9 and 16 also exhibit similar coordination parameters (as indicated in Fig. 4 and Table 2). Furthermore, the EXAFS parameters agree roughly with the those for zirconium oxychloride octahydrate (sample 17), which consists of a tetranuclear unit bridged by oxygen atoms (Fig. 1). The formation of the tetranuclear Zr complex in aqueous solution was confirmed via nuclear magnetic resonance and small-angle X-ray scattering under different experimental conditions. Therefore, we conclude the generation of the tetranuclear complex to be the initial stage of Zr hydrolysis. Particle size distributions in the range 0.5-6.0 nm (Fig. 6) were observed for samples 35, 12, and 14. The EXAFS coordination parameters also varied when compared with samples 9 and
16 (Fig. 4 and Table 2). These results indicate that hydrolysis progresses by incrementing aging time and temperature. Matsui and Ohgai also demonstrated Zr hydrolysis under 343-373 K and pointed out the oligomerization of a Zr tetranuclear species.\textsuperscript{13} Sasaki et al. examined similar experimental systems via electrospray ionization mass spectrometry and proposed the presence of octameric, 10-mer, and 12-mer polynuclear species from a hard sphere model analysis.\textsuperscript{7} The size of the models they proposed agrees with the median diameter in this range. Thus, the results in the 0.5-6.0 nm distribution suggest the existence of an oligomerized polynuclear Zr complex derived from the tetramer. Only similar ranges of particle sizes (15 nm) were observed in the STEM image of sample 3 (Fig. 9).

![STEM image of the [Zr] = 0.01 M sample aged at 298 K for 26 days (sample 3).](image)

For samples 12-15, $N_{Zr}$ decreased and $\sigma_{Zr}$ increased with increasing aging temperature. Walther et al. reported similar behavior as being caused by polydispersion of polynuclear Zr complexes in chloride solution by comparison of the results of nanoelectrospray mass spectrometry and EXAFS analysis.\textsuperscript{6} The largest particle size distribution range (> 10 nm) was observed in samples 6-8. The $r_{O,Zr}$ values of these samples obtained from EXAFS analysis came closer to those of zirconium dioxide (sample 18) than the other samples.
Shading of a, b and c indicates zirconium dioxide nanocrystals.

A high contrast image of particles was observed in the STEM of sample 7 (Fig. 10). The particles observed are identified as ZrO$_2$. From the results of the EXAFS analysis, it is suggested that progress of ZrO$_2$ particle formation causes an increase in $\sigma_{Zr}$, because ZrO$_2$ particle formation promotes the coexistence of Zr-(OH)$_2$-Zr (a Zr polynuclear complex) and Zr-O-Zr (ZrO$_2$), which could cause the variance in $r_{Zr}$ to be increased.
4-4 Conclusion

In conclusion, EXAFS, DLS, and STEM analyses were employed to identify the chemical species derived from aqueous solutions of zirconium oxychloride aged for varying times at various temperatures. The final product of the hydrolysis of Zr is ZrO$_2$ nanocrystals with size distributions of 10-80 nm, as determined by DLS. These results reveal that the generation of polynuclear Zr complexes as precursors, and their subsequent oligomerization, are the key processes for the growth of ZrO$_2$ nanocrystals. We found that ZrO$_2$ nanocrystals were generated at lower temperature of 323K than previous reports. This phenomenon is greatly critical for Zr processing in the chemical industries. This information will also help the selective synthesis of polynuclear Zr complexes and ZrO$_2$ nanocrystals.

4-5 Acknowledgment

The synchrotron radiation EXAFS experiments were performed with the approval and support of the Japan Synchrotron Radiation Research Institute (JASRI) (Proposal No. 2010B1836). We would like to thank Prof. Iwao Watanabe for help with the EXAFS analysis.

References

11529-11534.


Chapter 5
Monomeric [Zr(CO₃)₄]⁴⁻ Complex in an Ammonium Zirconium Carbonate Aqueous Solution

Abstract

The speciation of zirconium complexes in ammonium zirconium carbonate (AZC) solutions should be further studied in order to develop higher-performance AZC complexes for use in elaborate industrial materials. Thus, the speciation and structure of various zirconium species in ammonium zirconium carbonate solutions were investigated over a wide range of total carbonate and ammonium concentrations. By employing extended X-ray absorption fine structure analysis (EXAFS), and Raman and ¹³C NMR spectroscopy, it was found that four carbonate ions coordinate bidentately to the zirconium ion. In addition, the exact concentration ranges of carbonate and ammonium in AZC necessary to generate the monomeric zirconium carbonate complex [Zr(CO₃)₄]⁴⁻ were determined.

5-1 Introduction

Zirconium (IV) forms polyoxo-species in aqueous solutions;¹ however, it also generates various mono- or poly-nuclear structures depending on the presence and concentration of other compounds in solution. For instance, Zielen and Connick reported that monomeric Zr⁴⁺ complexes were formed below a threshold zirconium concentration in 1 M and 2 M perchloric acid, and that polymeric species (trimers or tetramers) resulted above that concentration, as observed via UV-Vis absorption spectrophotometry.² Nabivanets utilized electromigration to analyze the charge on aqueous zirconium species (cation / anion / nonion), which was found to vary with the concentration of chloride, nitrate and perchlorate.³ Independent X-ray scattering studies have resolved a tetrameric complex with a
structure analogous to crystalline zirconium oxychloride octahydrate in an aqueous solution. Shinghal, et al. also observed that an octameric species, $\text{Zr}_8(\text{OH})_{20}(\text{H}_2\text{O})_{24}\text{Cl}_{12}$, exists in equilibrium with the tetrameric species, $\text{Zr}_4(\text{OH})_8(\text{H}_2\text{O})_{16}\text{Cl}_6^{2+}$ in highly acidic solutions, with the octameric complex formed via oligomerization of a pair of the tetrameric complexes, depending on the acidity of the aqueous solution. For larger polynuclear complexes, Clearfield has suggested that a sheet-like oligomer is generated via ordered oligomerization of the tetramers resulting from slow, mild hydrolysis in refluxing zirconium chloride solution.

Extended X-ray absorption fine structure (EXAFS) analysis is a superior technique for resolving the average structures of metal complexes without restriction to crystalline or amorphous solid, or even liquid samples. We previously employed EXAFS analysis to resolve the structure of zirconium species dissolved in zirconium chloride solutions, and found that the degree of polymerization (DP) of the zirconium species varied, depending on the solution acidity and the Zr concentration. More recently, Walther, et al. observed a variation in the DP over a range of monomeric to octameric species in zirconium chloride solution via EXAFS analysis coupled with electrospray ionization time-of-flight (ESI-TOF) mass spectrometry. Southon and co-workers also employed EXAFS analysis and found that a sheet-like oligomer was generated via hydrolysis of zirconium nitrate solution. We recently reported that either a polynuclear complex or $\text{ZrO}_2$ nanocrystals were successively generated depending on the aging conditions of zirconium oxychloride solutions, as analyzed by EXAFS and dynamic light scattering analysis.

Zirconium salts are employed in various industrial uses, notably in the cross-linking of polyvinyl alcohol (PVA). It is likely that the structure of the aqueous zirconium species affects the PVA cross-linking performance. From this industrial point of view, a speciation analysis of zirconium in aqueous solution is needed. We previously reported an
EXAFS analysis of zirconium chloride solution, which covered a wider range of [Zr], [H⁺] and [Cl⁻] than previous studies.³,⁵,⁸,¹⁰,¹² The results showed that the DP was dependent upon [Zr], [H⁺] and [Cl⁻], and that an increase in the DP resulted in higher PVA cross-linking performance.¹⁵

Ammonium zirconium carbonate (AZC) is one of the most important industrial salts, used in such varied applications as for metal surface treatment¹⁷ and as a cross-linker for water-soluble macromolecules.¹⁸-²⁰ Several studies of zirconium in the presence of carbonate in aqueous solution have been reported. For example, Karlysheva, et al. predicted the generation of [Zr(OH)₂(CO₃)₂]²⁻ in a mixed solution of zirconium oxychloride and sodium carbonate, at pH > 7 and a molar ratio of ZrOCl₂:Na₂CO₃ = 2-5:1, as analyzed by acid titration and IR spectroscopy.²¹ Malinko, et al. demonstrated the presence of [Zr(OH)₂(CO₃)₂]²⁻, [Zr(OH)(CO₃)₃]³⁻ and [Zr(CO₃)₄]⁴⁻, depending on the concentration of carbonate in a mixed solution of sodium carbonate and zirconium sulfate, in an experiment similar to Karlysheva’s.²² Using potentiometry, dialysis, ¹³C NMR and ¹⁷O NMR, Veyland, et al. revealed a variation in the number of carbonate ions coordinating to zirconium depending on the chemical composition of a mixed solution of K₂CO₃ / KHCO₃ / ZrOCl₂.²³ They also reported that the complex containing the most carbonate is [Zr(CO₃)₄]⁴⁻, and that all of the carbonate ions in the complex are bidentately coordinated to the zirconium ion. Although these studies revealed very important stoichiometric information for zirconium in the presence of carbonate ion, the structures of complexes in solution also containing ammonium ion are less well understood.

In the present study, the speciation and structures of zirconium species in AZC solution are investigated with varying concentrations of total zirconium ([Zr]), carbonate ([carbonate]) and ammonium ([ammonium]) by employing EXAFS analysis, Raman scattering spectroscopy and ¹³C NMR spectroscopy.
5-2 Experimental

Preparation of Samples

Zirconium basic carbonate (Zr(OH)$_4$(CO$_3$)$_b$·nH$_2$O [a ≈ 3.2, b ≈ 0.4, n ≈ 6.9], Daiichi Kigenso Kagaku Kogyo), ammonium hydrogen carbonate (purity NH$_3$: 20-23 wt%, special grade chemicals, Kishida Chemical), and aqueous ammonia (purity NH$_3$: 25 wt%, special grade chemicals, Sigma Aldrich Japan) were mixed in a 1:1.25:0.70 ratio by weight and aged at 353 K for 2 hours, resulting in a transparent solution. This solution was retained at 278 K for 1 week to afford crystals of AZC ((NH$_4$)$_3$ZrOH(CO$_3$)$_3$·2H$_2$O)$^{24}$, and the precipitated crystals were separated from the mother liquor via vacuum filtration. The crystals were confirmed by XRD analysis to be identical to those reported by Clearfield.$^{24}$ The crystals (purity 92 wt%) were dissolved by mixing with ammonium hydrogen carbonate and aqueous ammonia in deionized water (RFU565N, ADVANTEC). In order to compare the structures of the zirconium carbonate species in the presence of ammonium and potassium ion, zirconium oxychloride octahydrate (ZrOCl$_2$·8H$_2$O, special grade, Mitsuwa Chemicals), potassium hydroxide (special grade, Sigma Aldrich Japan) and potassium hydrogen carbonate (special grade, Sigma Aldrich Japan) were dissolved in deionized water to prepare a potassium zirconium carbonate (PZC) solution, for which total zirconium, carbonate and potassium concentrations were 0.08 M, 0.48 M and 0.66 M, respectively. [Zr(CO$_3$)$_4$]$^{4-}$ is generated in this system, as reported by Veyland.$^{23}$ The chemical properties of the sample solutions are summarized in Table 1.
Table 1. Chemical properties of AZC and PZC solutions.

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**EXAFS analysis**

At the beam line of SPring-8, BL14B2, the Zr K-edge X-ray absorption spectra of AZC solutions and the AZC crystal were measured using a quick scan transmission method. Si (111) was used as a double crystal monochromator, and the energy range of the X-rays was set at 17.5-19.9 keV. The optical path length was set at 3 mm for samples 18 and 19, at 15 mm for the others, and at 1 mm for the AZC crystal. From EXAFS analysis using REX 2000 (Rigaku), the Zr-O coordination distances ($r_{Zr-O}$) were derived. The phase shift
and back scattering amplitude parameters corresponding to the Zr-O coordination were calculated using FEFF6L (University of Washington) and REX2000. The theoretical spectra were also calculated using FEFF6L, and used for comparison with the measured spectra.

**Raman Scattering Spectroscopy**

A LabRam HR-800 Raman microscope system (Horiba Jobin Yvon) equipped with an argon ion laser and a cooled CCD detector was used for the Raman studies. A 30 mW, 488 nm laser was applied for excitation, and the scattered light was collected in a backscattering geometry with a 50× objective. Raman spectra were gathered using 5 scans of 20 s exposure time each. Peak fitting and resolving of the spectra were carried out using Origin 9.0 software (OriginLab Corporation).

**13C NMR Spectroscopy**

13C NMR spectra for samples 6, 10 and 14 were recorded at 150 MHz on a JNM-ECA600 spectrometer (JEOL) equipped with a variable temperature controller. The samples were put into the inner layer of double-layered NMR tubes. The outer layer was filled with acetonitrile. The 13C chemical shifts are reported in delta (δ) units, calibrated against the signal of acetonitrile (δ = 118.2) as an external standard. The solutes were maintained at 303 K (±0.1 K) during spectra acquisition. For quantitative NMR analysis, the relaxation delay for 13C (80 s) was set to five times the longitudinal relaxation time (T1) of the samples (16 s).
Evaluation of Cross-linking Performance

100 g of polyvinyl alcohol (PVA, Gohsefimer Z-200, Nippon Synthetic Chemical Industry, DP ≈ 1200) was dissolved in 900 g of deionized water. As a cross-linking agent, 10 mL of the AZC solution was added and mixed to 12.8 g of the PVA solution to obtain the mixed solution of AZC and PVA. This mixed solution of 1.0 g was put into a round-shaped flat-bottomed petri dish with 30 mm in diameter, dried at room temperature (293-298 K) for 1 week, and PVA film that was cross-linked with AZC was obtained.

The PVA film with the petri dish was dried at 343 K for 30 min, and soaked in a water bath kept at 353 K for 1 hour. After the treatment it was dried at 343 K for 90 min. From weighing of the loss of the PVA film, the residual weight ratio of PVA film after soaking in water was obtained. The ratios are considered to be the index of cross-linking performance.
5-3 Results and discussion

EXAFS analysis

Figure 1 shows the Fourier transform spectra of the AZC solutions, AZC crystal, and PZC solution, as well as theoretical spectra corresponding to \([\text{Zr}(\text{CO}_3)_4]^{4-}\) and \([\text{Zr}(\text{CO}_3)_6]^{8-}\) as calculated using FEFF6L. 

![Figure 1: Fourier transform spectra](image)

Structural model:
- \([\text{Zr}(\text{CO}_3)_6]^{8-}\) (Fig. 6)
- \([\text{Zr}(\text{CO}_3)_4]^{4-}\) (Fig. 6)
- PZC solution
- AZC solution
- AZC crystal

Table 1: Peak positions (in pm)

<table>
<thead>
<tr>
<th>Peak</th>
<th>r/pm</th>
</tr>
</thead>
<tbody>
<tr>
<td>1</td>
<td>5</td>
</tr>
<tr>
<td>2</td>
<td>10</td>
</tr>
<tr>
<td>3</td>
<td>15</td>
</tr>
<tr>
<td>4</td>
<td>20</td>
</tr>
<tr>
<td>5</td>
<td>25</td>
</tr>
</tbody>
</table>

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Figure 1. Fourier transform EXAFS spectra of AZC and PZC solutions, AZC crystal and theoretical spectra corresponding to structural models of $[\text{Zr}(\text{CO}_3)_4]^{2-}$ and $[\text{Zr}(\text{CO}_3)_6]^{8-}$.

The first peaks located at 150-200 pm for all of the spectra in Figure 1 are assigned to Zr-O coordination. For example, the Zr-O coordination distance of the AZC crystal was estimated to be 222 pm by fitting of the peak. Clearfield’s structural model of the zirconium environment in the AZC crystal is shown in Figure 2. The value obtained from our analysis roughly agrees with the average Zr-O coordination distance over all of the Zr-O coordinations shown (219 pm).

Figure 2. Structural model surrounding the Zr ion in $(\text{NH}_4)_3\text{ZrOH(CO}_3)_3\cdot2\text{H}_2\text{O}$. This structure was drawn based on the structural dataset reported by Clearfield.

Figure 3 shows the Zr-O coordination distances ($r_{\text{Zr-O}}$) obtained from analysis of Figure 1 as a function of [carbonate]. The values of $r_{\text{Zr-O}}$ increase with increasing this concentration. When [carbonate] $\geq$ 1.0 M, $r_{\text{Zr-O}}$ settles at $\sim$221 pm, independent of [Zr] and [ammonium]. According to the structural model shown in Figure 2, the Zr-O coordination distances for hydroxyl and carbonate ions are 211 pm and 222 pm, respectively. Therefore, the increase in $r_{\text{Zr-O}}$ in Figure 3 indicates an exchange of hydroxyl ion for carbonate.
ion, and the convergence of $r_{Zr-O}$ to 221 pm corresponds to saturation of the coordination number of carbonate ions ($N_c$) on zirconium.

Figure 3. Zr-O coordination distances ($r_{Zr-O}$) in AZC and PZC solutions as a function of [carbonate].
AZC: $[Zr] = 0.1$ M, [ammonium] = 0.3 M (■); $[Zr] = 0.1$ M, [ammonium] = 0.6 M (×); $[Zr] = 0.1$ M, [ammonium] = 1.0 M (○); $[Zr] = 0.1$ M, [ammonium] = 1.6 M (●); $[Zr] = 0.1$ M, [ammonium] = 2.0 M (◊); $[Zr] = 0.1$ M, [ammonium] = 2.6 M (●); $[Zr] = 0.5$ M, [ammonium] = 3.0 M, [Zr] = 0.8 M (●), [ammonium] = 4.8 M (▲). PZC: $[Zr] = 0.08$ M, [potassium] = 0.66 M (●).

Figure 4 shows the $r_{Zr-O}$ obtained from analysis of Figure 1 as a function of pH. The values of $r_{Zr-O}$ decrease with increasing pH at [carbonate] ≥ 0.3 M. The decrease in $r_{Zr-O}$ is conspicuous above pH 9.5, which indicates an increase in the hydroxyl ion coordination number. Veyland reported a rapid decrease in $N_c$ at pH > 9.5 during titration of a PZC solution including $[Zr(CO_3)_4]^{4-}$ with potassium hydroxide solution.23
Figure 4. Zr-O coordination distances ($r_{Zr-O}$) in AZC and PZC solutions as a function of pH. AZC: [Zr] = 0.1 M, [carbonate] = 0.3 M (□); [Zr] = 0.1 M, [carbonate] = 0.6 M (○); [Zr] = 0.1 M, [carbonate] = 1.0 M (■). PZC: [Zr] = 0.08 M, [carbonate] = 0.48 M (×).

The peaks located at 320 pm in all of the spectra in Figure 1 are assigned to Zr-Zr coordination. The Zr-Zr coordination distance in the AZC crystal was estimated to be 350 pm by fitting of the peak. Again, the value obtained from our analysis agrees with the Zr-Zr coordination distance from Figure 2 (350 pm). Figure 5 shows the Fourier transform spectra of the AZC crystal and those calculated using FEFF6L corresponding to single scattering by Zr-Zr coordination and multiple scattering by carbonate ions per the Figure 2 model. The square of the Debye-Waller factor for the calculations was set at 40 pm$^2$. For the multiple scattering calculation, three paths of photo-electron scattering were...
considered, represented by Zr-O*-C-Zr, Zr-C-O*-Zr and Zr-C-O*-C-Zr using the atomic labels from Figure 2.

![Diagram](image)

**Figure 5.** Fourier transform spectra of AZC crystal and those corresponding to Zr-Zr coordination and multiple scattering by coordinated carbonate ions in the model of Figure 2 as calculated using FEFF6L.²⁵ AZC crystal (Solid line), Zr-Zr coordination (□), coordinated carbonate ions (■).

In Figure 5, although the peak tops corresponding to the Zr-Zr coordination and the carbonate ions are near each other, they are resolved at 320 pm and 350 pm, respectively. The Fourier transform spectra of samples 1-5, 8 and 9 have a peak located at ~320 pm. Therefore, it is suspected that the zirconium species in these samples are of oligomer type, having a DP of 2 or more, with Zr-Zr coordination via a double hydroxyl ion bridge—the same as in the Figure 2 model. On the other hand, peaks near 320 pm were either weak or absent in the spectra of samples 6, 7 and 10-20. Therefore, monomeric species lacking
Zr-Zr coordination are dominant in these solutions. In addition, from Figure 3, the $r_{\text{Zr-O}}$ values of samples 6, 7 and 10-20 are about 221 pm, indicating that the $N_c$ is saturated in these samples. Thus, generation of a monomeric species correlates with saturation of $N_c$. This correlation was also reported by Veyland.\textsuperscript{23} From the relationship of [carbonate] or pH with $r_{\text{Zr-O}}$ in Figures 3 and 4, respectively, whether the monomeric species is dominant depends on [carbonate] and [OH\textsuperscript{−}] in AZC solutions. The monomeric species is dominant when $[\text{Zr}] = 0.1-0.8$ M, [carbonate] / [Zr] $\geq 6$ and the pH is below 9.5.

Figure 6 shows structural models of the monomeric species $[\text{Zr(CO}_3\text{)}_4]^{4-}$ and $[\text{Zr(CO}_3\text{)}_6]^{8-}$, with coordinated bidentate carbonate ions the same as in the model of the AZC crystal in Figure 2. The Fourier transform spectra of the models derived from calculation using FEFF6L are shown above in Figure 1. The squares of the Debye-Waller factors required for the calculations were set at 40 pm$^2$ and 60 pm$^2$ for the (CO$_3$)$_4$ and (CO$_3$)$_6$ models, respectively. In Figure 1, the spectral shape of samples 6, 7 and 10-20 agree well with those of the monomeric structural models and the PZC solution composed of $[\text{Zr}] = 0.08$ M, [potassium] = 0.66 M, and [carbonate] = 0.48 M, which contains $[\text{Zr(CO}_3\text{)}_4]^{4-}$, as indicated by Veyland.\textsuperscript{23} Thus, samples 6, 7 and 10-20 have the same structure as that of a monomer species, specifically $[\text{Zr(CO}_3\text{)}_4]^{4-}$.
Figure 6. Structural models of the monomeric species $[\text{Zr(CO}_3\text{)}_4]^{4-}$ and $[\text{Zr(CO}_3\text{)}_6]^{8-}$.

**Raman spectrometry**

Figures 7(A)-(C) depict the Raman spectra of three representative samples containing 0.1 M Zr, but with varying initial concentrations of total carbonate and ammonium (conditions match samples 6, 10 and 14 in Table 1). Peak fitting was carried out to resolve and assign the spectral peaks; a Lorentzian function was employed for this procedure. Figures 7(D)-(F) are the Lorentzian fitting curves of the spectra in 7(A)-(C), respectively. In this region, the peaks observed are assigned to vibrations from carbonate, hydrogen carbonate, carbamate, and zirconium carbonate ions; the peak assignments are summarized in Table 2.
Figure 7. Raman spectra for AZC solutions. (A)-(C): Raman spectra of samples 6, 10 and 14, respectively. (D)-(F): obtained by peak fitting with multiple Lorentzian functions of (A)-(C), respectively. Solid lines in (D)-(F) depict Lorentzian fitting curves for each single peak. Broken lines in (D)-(F) indicate convolutions of the Lorentzian fitting curves in each spectrum.

Table 2. Spectral assignments of Raman shifts.26,27

<table>
<thead>
<tr>
<th>Raman shift / cm$^{-1}$</th>
<th>Chemical species</th>
</tr>
</thead>
<tbody>
<tr>
<td>1017</td>
<td>HCO$_3^-$</td>
</tr>
<tr>
<td>1034</td>
<td>NH$_2$CO$_2^-$</td>
</tr>
<tr>
<td>1051</td>
<td>[Zr(CO$_3$)$_x$]$^{(2x-4)-}$</td>
</tr>
<tr>
<td>1065</td>
<td>CO$_3^{2-}$</td>
</tr>
</tbody>
</table>

An obvious Raman peak at 1051 cm$^{-1}$ that does not change in intensity is observed in all three samples. This signal is assigned to [Zr(CO$_3$)$_x$]$^{(2x-4)-}$ and indicates that the composition of [Zr(CO$_3$)$_x$]$^{(2x-4)-}$ remains constant during carbonate and ammonium ions concentration changes. On the other hand, a large intensity change is observed at 1017 cm$^{-1}$ which is assigned to the hydrogen carbonate ion (HCO$_3^-$), and the peaks for carbamate (NH$_2$CO$_2^-$) and carbonate ions (CO$_3^{2-}$) appear at higher initial concentrations of total carbonate and ammonium in these samples. These results are logical considering the pH, the formation constant of carbamate ion,28 and the acid dissociation constant of carbonic acid.28

In previous studies, tetra- or hexa-coordinated carbonate complexes with high stability were reportedly formed in aqueous carbonate solution.29 In our experimental system, however, Raman peaks for free HCO$_3^-$ were observed, including for a sample with a total carbonate concentration (0.6 M) 6 times higher than the Zr concentration (0.1 M). This indicates that the formation of a hexa-coordinated complex does not occur in our system.
The peak areas for free HCO$_3^-$ in Figures 7(D)-(F) are 3207, 10251 and 20605, respectively. The peak area in (D) increases by roughly 3 and 6 times in (E) and (F), respectively. If the tetra-coordinated species is formed in our experimental system, the remaining HCO$_3^-$ concentrations should be around 0.2, 0.6, and 1.2 M for samples 6, 10, and 14, respectively. Thus, the increment in the Raman intensity for HCO$_3^-$ correlates well with the HCO$_3^-$ concentration, assuming formation of the tetra-coordinated complex. Therefore, the tetra-coordinated complex [Zr(CO$_3$)$_4$]$^{4-}$ is judged to have been formed in this experimental system.

**$^{13}$C NMR Spectroscopy**

The $^{13}$C NMR spectra of samples 6, 10 and 14 are shown in Figure 8. Table 3 shows the chemical shifts, chemical assignments, and relative ratios of the integrated intensities of the $^{13}$C NMR spectra.

![13C NMR spectra of AZC solutions with different total carbonate and ammonium concentrations](image)

Figure 8. $^{13}$C NMR spectra of AZC solutions with different total carbonate and ammonium concentrations. Each sample includes [Zr] = 0.1 M.
Table 3. Chemical shift, assignment, relative intensity and concentration of corresponding carbonate for the $^{13}$C NMR spectra of AZC solutions.

<table>
<thead>
<tr>
<th>No.</th>
<th>Chemical shift / ppm</th>
<th>Assignment</th>
<th>Relative intensity / %</th>
<th>[Corresponding carbonate] / M</th>
</tr>
</thead>
<tbody>
<tr>
<td>6</td>
<td>159.8</td>
<td>free HCO$_3^-$/CO$_3^{2-}$</td>
<td>31</td>
<td>0.19</td>
</tr>
<tr>
<td></td>
<td>166.8</td>
<td>Coordinated carbonate</td>
<td>69</td>
<td>0.41</td>
</tr>
<tr>
<td></td>
<td>159.9</td>
<td>free HCO$_3^-$/CO$_3^{2-}$</td>
<td>51</td>
<td>0.51</td>
</tr>
<tr>
<td>10</td>
<td>165.0</td>
<td>NH$_2$CO$_2^-$</td>
<td>7</td>
<td>0.07</td>
</tr>
<tr>
<td></td>
<td>166.7</td>
<td>Coordinated carbonate</td>
<td>42</td>
<td>0.42</td>
</tr>
<tr>
<td></td>
<td>160.0</td>
<td>free HCO$_3^-$/CO$_3^{2-}$</td>
<td>70</td>
<td>1.12</td>
</tr>
<tr>
<td>14</td>
<td>164.9</td>
<td>NH$_2$CO$_2^-$</td>
<td>5</td>
<td>0.08</td>
</tr>
<tr>
<td></td>
<td>166.3</td>
<td>Coordinated carbonate</td>
<td>25</td>
<td>0.40</td>
</tr>
</tbody>
</table>

In Figure 8, the peaks located at ~160 ppm, 165 ppm and 166-167 ppm are attributed to uncoordinated carbonates (HCO$_3^-$/CO$_3^{2-}$), carbamate (NH$_2$CO$_2^-$) and carbonate coordinated to Zr, respectively. The peaks around 166-167 ppm broaden with increasing [carbonate], which indicates that increasing [carbonate] enhances the exchange rate between coordinated and free carbonate.
For these samples, the concentration of coordinated carbonate determined from the integrated intensities of the peaks near 166-167 ppm was estimated to be about 0.4 M. From this concentration, a molar ratio of coordinated carbonate to zirconium of 4 is obtained. Therefore, the $^{13}$C NMR results also indicate the existence of $[\text{Zr(CO}_3\text{)}_4]^{4-}$ in samples 6, 7 and 10-20.

**Evaluation of Cross-linking Performance**

Figure 9 shows the relationship of [ammonium] and [carbonate] in AZC solution with the residual ratio after water-soaking of PVA film with the addition of AZC solution. When the AZC solution of certain chemical formulation, in which the monomeric species was dominant, was used the residual ratio of PVA film was in the range of 49-57 wt%, which was higher than in other cases. The residual ratio of PVA film without adding AZC solution is zero, all the tested AZC solutions expressed cross-linking performance, and among them the monomeric species showed higher cross-linking reactivity.

![Graph showing the relationship between [carbonate] and residual ratio of PVA film](image)

Figure 9 Residual ratios of PVA film after washing with water as a function of [carbonate] in AZC solutions. The PVA films were treated with AZC solutions with various [ammonium],

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[carbonate] values ([Zr] = 0.1 M). [ammonium]: ◊ = 0.3 M, □ = 0.6 M, Δ = 1.0 M, × = 1.6 M, ○ = 2.0 M

The cross-linking reaction of PVA with AZC is considered to be the reaction between hydrophilic function groups at PVA (hydroxyl group, acetoacetyl group at Gohsefimer Z-200 etc.) and Zr ion via coordinate bond. A reaction model of the cross-linking between the monomeric species [Zr(CO$_3$)$_4$]$^{4-}$ and PVA is shown in Formula (1).

$2\left(\begin{array}{c}
\text{C} - \text{C} \\text{n}
\text{OH}
\end{array}\right) + [\text{Zr(CO}_3\text{)}_4]^{4-} \rightarrow \left(\begin{array}{c}
\text{C} - \text{C} \\text{n}
\text{OH}
\end{array}\right)_{\text{n}} [\text{Zr(CO}_3\text{)}_3]^{2-} + \text{CO}_3^{2-} \cdots \quad (1)$

As shown in Formula (1), formation of the cross-link between PVA and Zr requires detachment of CO$_3^{2-}$ from Zr species. It is considered that coordination number of carbonate ligand per Zr ion is critical factor for the reaction. It is expected that the larger coordination number is, the more progressive cross-linking is. The structural feature of the monomer [Zr(CO$_3$)$_4$]$^{4-}$ which is coordinated by largest number of carbonate ligands may causes high cross-linking performance. Additionally, Song et al. suggested that cross-linking between AZC solution and starch was dominated by diffusion of Zr species in the solution. It is considered that superior cross-linking ability result from greatest diffusion of the monomeric species.

5-4 Conclusion

EXAFS analysis of AZC aqueous solutions containing various concentrations of total zirconium, ammonium and carbonate was undertaken. Changes in Zr-O coordination distance depending on [carbonate], [ammonium] and pH value were observed. In addition,
the Zr-Zr coordination peak disappeared at higher [carbonate] which indicates that a monomeric complex of zirconium exists at higher total carbonate concentrations in AZC solution.

In conditions identical to those for the EXAFS experiments, hydrogen carbonate, carbamate and carbonate ions, as well as a zirconium carbonate complex, were observed by Raman scattering spectrometry and $^{13}$C NMR spectrometry. Quantitative analysis via these two techniques yielded a [coordinated carbonate] / [Zr] ratio of 4 for the monomeric complex. In addition, the shape of the Fourier transform EXAFS spectra of the monomeric species in this study agreed well with calculated spectra corresponding to the structural model $[\text{Zr(CO}_3\text{)}_4]^{4-}$, in which the zirconium ion is coordinated to four bidentate carbonate ions, as well as with that of a PZC solution in which $[\text{Zr(CO}_3\text{)}_4]^{4-}$ is the dominant species. In this study, it was found that $[\text{Zr(CO}_3\text{)}_4]^{4-}$ is generated as the dominant species in AZC aqueous solution when [Zr] = 0.1-0.8 M, [carbonate] / [Zr] ≥ 6 and the pH is below 9.5. In addition, it was clarified that the monomeric species expresses high cross-linking performance toward PVA than polymeric ones.

5-5 Acknowledgment

The synchrotron radiation EXAFS experiments were performed with the approval and support of the Japan Synchrotron Radiation Research Institute (JASRI) (Proposal No. 2007B1920, 2010B1961, 2011B1826 and 2012A1777). We would like to thank Prof. Iwao Watanabe (Ritsumeikan University), Dr. Hiroshi Oji, Dr. Yosuke Taniguchi and Dr. Masafumi Takagaki (JASRI) for help on EXAFS measurements and analyses.

References


Chapter 6

Study of Formation of Zirconium(IV)-Carboxylic Ligand Complexes by UV Absorption Spectrometry and EXAFS Analysis

6-1 Introduction

Zirconium compounds are nowadays widely utilized in solid states as alloys and oxides. For instance, some ceramics or alloys containing zirconium are recognized as candidates for an artificial bone and a dental material due to its biocompatibility.\textsuperscript{1-3} Their low neutron absorption cross-section and high resistance to corrosion allows that they are employed as a cladding material of nuclear fuel in power plants.\textsuperscript{4} Lead zirconate titanate ceramics are high-performance piezoelectric materials, which are widely used in sensors, actuators and other electronic devices.\textsuperscript{4}

On the other hand, chemical species consists of zirconium complexes are essentially chemically inert, for instance they cannot exhibit any strong catalytic properties in aqueous solution very often, except for its polyoxometalate formation by itself or with other metal elements.\textsuperscript{6,7} This chemical inactivity can be associated with the corrosion resistance of the materials including zirconium, and some beneficial utilities, such as a cross-linking
agent for organic backbones to assemble metal-organic frameworks.8,9

Zirconium salts are also employed in industrial uses, especially for cross-linking of polyvinyl alcohol (PVA).10 We considered that the structure of zirconium species in aqueous solution should be affect to cross-linking performance for PVA. In this industrial point of view, the speciation of zirconium in aqueous solution is needed for improving of the utility of zirconium.

Previously, some structural studies of mono- and poly-nuclear Zr complexes in aqueous solutions were achieved by several groups. For instance, Walther et al. demonstrated variation of degree of polymerization of Zr complex, over the range of monomeric to octameric species in zirconium chloride solution by Extended X-ray absorption fine structure (EXAFS) analysis coupled with electrospray ionization time-of-flight mass spectrometry.11 EXAFS analysis is a superior technique to resolve the average structures of metal complexes without the restriction in which samples are crystalline/amorphously solid or even in liquid.12 We also reported that polynuclear complex and ZrO2 nanocrystals, were successively generated depending on aging condition of zirconium oxychloride solutions analyzed by EXAFS and dynamic light scattering analysis.13 Furthermore, we found monomeric complex formation of Zr in ammonium carbonate aqueous system by means of EXAFS and Raman spectrometry.14 It is suggested that monomeric Zr species in an aqueous solution possesses higher cross-linking ability than polymeric Zr by our previous work.15

Stoichiometric study is also important to understand the speciation of zirconium in aqueous solutions. In earlier work, thermodynamic parameters of zirconium were well studied for the systems including simple inorganic ions.16 However, for the system includes organic ligands, the stability parameters such as equilibrium constants have not been well investigated. Organic ligands have generally larger stability constants than in-
Therefore, it is considered that an organic ligand prohibits the generation of polynuclear complex of zirconium by its strong complexation in aqueous systems. Chakravorty and co-workers reported one of valuable experimental results. They studied the ligand exchange between 2-thienyltrifluoroacetone and lactate bound to zirconium by UV absorption spectrophotometry. UV-vis spectrophotometry is very easy to use and powerful tool for equilibrium analysis of simple chemical systems.

In the present study, citric acid, tartaric acid and gluconic acid were selected as candidates of stabilizing agents in which zirconium species are maintained as a monomer in aqueous solution. While these compounds have already been utilized as stabilizing agents, its structure and details of chemical reactions were still unknown. We investigated ligand-exchange reactions between these carboxylic acid ligands and carbonate coordinated onto zirconium in an aqueous solution by means of EXAFS spectrometry and UV absorption spectrophotometry.

6-2 Experimental

Preparation of Samples

D-gluconic acid (Sigma-Aldrich Japan), potassium dihydrogen citrate, citric acid anhydride and ammonium L-tartrate (Kishida chemical Co., Japan) were purchased and used. Acidic agents were neutralized by equivalent aqueous ammonia (purity NH\textsubscript{3}: 25 mass%, special grade chemicals, Sigma Aldrich Japan) before addition to ammonium zirconium carbonate (AZC) solution. Zirconium basic carbonate \( \text{Zr(OH)}_a\text{(CO}_3)_b\cdot n\text{H}_2\text{O} \) \( [a \approx 3.2, b \approx 0.4, n \approx 6.9] \), Daiichi Kigenso Kagaku Kogyo Co.), ammonium hydrogen carbonate (purity NH\textsubscript{3}: 20-23 mass%, special grade chemicals, Kishida Chemical Co.), and aqueous ammonia were mixed, and aged at 353 K for 2 hours to obtain a transparent solution. This solution was retained at 278 K for 1 week to obtain the crystal of AZC.
((NH₄)₃ZrOH(CO₃)₂·2H₂O),¹⁰ and precipitated crystal was separated from the mother liquor. The obtained crystal was confirmed to be identical with AZC crystal in the literature through the X-ray diffraction analysis.²¹ The final aqueous solution was prepared from this crystal. Deionized water prepared by RFU565N water purification system (ADVANTEC, Japan) was used in all of experiments in this study.

**Synchrotron radiation EXAFS analysis**

Zr K-edge X-ray absorption spectra of aqueous solutions of the samples were measured using synchrotron radiation at the SPring-8 Beamline (BL14B2), via a quick scan of transmission method in the energy region ranging from 17.5 keV to 19.9 keV. A double crystal monochromator of Si(111) was used for the measurements. Optical path length was set at 15 mm for the liquid samples. EXAFS analyses of the spectra were carried out using REX2000 software (Rigaku, Japan). The phase shifts and backscattering amplitudes required for the analyses were derived from calculations using FEFF6L software.²²

**UV absorption spectrophotometry**

A conventional UV/vis spectrophotometer (V-550; JASCO Co., Japan) was used to measure absorption spectra of the prepared samples. Optical cells with the optical paths of 0.5, 1.0 and 10 mm were used depending on light absorption strengths of the samples, respectively. Experiments were carried out in a room in which the temperature was maintained at 298 ± 2 K.

**6-3 Results and discussion**

**EXAFS analysis**

Fig. 1 shows Fourier transform spectra of EXAFS region for the samples. All of sample solutions were containing [Zr] = 0.1 M, [NH₄⁺] = 0.6-0.9 M and [CO₃²⁻] = 0.6 M as final concentration, respectively, besides the carboxylic acid ligands, and pH values were
maintained in the range of 8.5-8.6. We already have confirmed that zirconium forms mononuclear complex \([\text{Zr} (\text{CO}_3)_4]^{4-}\) at the same experimental condition in the absence of the carboxylic acid ligands in our previous research by EXAFS and Raman spectrometry.\(^{14}\) In the absence of the carboxylic acid ligands, the peaks located at around 220 pm and 390 pm are assigned to Zr-O coordination and multiple scattering by carbonates, which are coordinated onto Zr atom.
Fig. 1 Fourier transform spectra of EXAFS region for AZC solutions in the presence and absence of (a): gluconic acid, (b): citric acid and (c): tartaric acid, respectively. The numbers in these Figs. indicate the concentration of carboxylic acids. All of sample solution was containing \([\text{Zr}]=0.1\ \text{M}, \ [\text{NH}_4^+] = 0.6\ \text{M} \text{ and } [\text{CO}_3^{2-}] = 0.6\ \text{M} \text{ as final concentration, respectively.}

The largest spectral changes against the carboxylic acid ligands were observed for gluconic acid (Fig. 1 (a)), obviously new peak was found in shorter coordination range, and decreasing of the peak intensity due to a multiple scattering by carbonates were observed by increasing of the gluconic acid concentration. This peak is located at \(< 300\ \text{pm, which is shorter than Zr-Zr coordination observed in polynuclear complex of zirconium.}^{13}\)

Therefore, we judged this peak is attributable to a multiple scattering by gluconic acid exchanged with carbonate on Zr atom, and these ligands are exchanged with remaining zirconium complex is mononuclear complex. The reaction can be described as follows:

\[
[Zr(CO_3)_4]^{4-} + L^- \leftrightarrow [ZrL(CO_3)_3]^{3-} + CO_3^{2-}
\] (1)

where \(L^-\) indicates the carboxylic ligands.

Fig. 2 shows Zr-O coordination distance as a function of the carboxylic acid concentrations. These Zr-O coordination distances were analyzed from the datasets of Fourier transform spectra indicated in Fig. 1. For citric acid, the change of the distance depending on its concentration was smaller than other two carboxylic acids. For tartaric acid and gluconic acid, Zr-O coordination distance is obviously decreased with the increment of these concentrations. Especially for gluconic acid, the coordination distance reaches
plateau at its concentrations are larger than 0.020 M. It is suggested that these results represents gluconic acid is the strongest ligand in these three carboxylic acids employed in this study.

Fig. 2 Zr-O coordination distance analyzed from the datasets in Fig. 1, as a function of the carboxylic acid concentrations. Lines are guides with the eye.

**UV absorption spectrophotometric analysis**

UV absorption spectra of the samples including gluconic acid in the presence and absence of zirconium are displayed in Fig. 3 and 4, respectively. Since all of compounds
employed in this study have strong optical absorption at the range of 190-250 nm, the optical cells with 0.5 and 1.0 mm was used for this region. Although absorbance of spectra in the absence of zirconium is increasing with increment of gluconic acid concentration as shown in Fig. 4, large absorption change depending of gluconic acid concentration was observed as in Fig. 3. This absorption change should be associated with metal complexation of gluconic acid with zirconium, and attributable to the change of electronic state of whole complex and ligand.23
Fig. 3 UV absorption spectra for AZC solutions in the presence and absence of gluconic acid. The numbers in the Fig. indicate the concentration of gluconic acid. All of sample solution was containing \([\text{Zr}] = 0.1 \text{ M}, [\text{NH}_4^+] = 0.6-0.7 \text{ M} \) and \([\text{CO}_3^{2-}] = 0.6 \text{ M} \) as final concentration, respectively. The spectra (a) and (b) were measured by using the optical cell with optical path of 0.5 mm and 10 mm, respectively.
Fig. 4 UV absorption spectra for gluconic acid solutions. The numbers in the Fig. indicate the concentration of gluconic acid. All of sample solution was containing $[\text{NH}_4^+] = 0.6-0.7$ M and $[\text{CO}_3^{2-}] = 0.6$ M as final concentration, respectively. The spectra (a) and (b) were measured by using the optical cell with optical path of 1.0 mm and 10 mm, respectively.

This strong absorption change depending of gluconic acid concentration was utilized for equilibrium analysis of the ligand exchange reaction indicated as Eq.(1). Equilibrium constant $K$ of the reaction of Eq.(1) can be expressed as:

$$K = \frac{[[\text{ZrL(CO}_3^3]^{3-}] [\text{CO}_3^{2-}]}{[[\text{Zr(CO}_3^4]^{4-}][\text{L}^-]} \quad (2)$$

In the presence of the carboxylic acid ligand $\text{L}^-$, the concentrations $[[\text{Zr(CO}_3^4]^{4-}$, $[\text{CO}_3^{2-}]$, and $[\text{L}^-]$ are adopted by following equations.

$$[[\text{Zr(CO}_3^4]^{4-}] = C_{\text{Zr}} - [[\text{ZrL(CO}_3^3]^{3-}] \quad (3)$$

$$[\text{L}^-] = C_{\text{L}} - [[\text{ZrL(CO}_3^3]^{3-}] \quad (4)$$

$$[\text{CO}_3^{2-}] = C_{\text{CO}_3} + [[\text{ZrL(CO}_3^3]^{3-}] \quad (5)$$

Where $C_{\text{Zr}}$, $C_{\text{L}}$, and $C_{\text{CO}_3}$ are total concentration of zirconium, a carboxylic acid ligand, and carbonate ion, respectively. From Eqs. (2)-(5), following equation as a function of $[[\text{ZrL(CO}_3^3]^{3-}]$ can be obtained as:

$$(K - 1)[[\text{ZrL(CO}_3^3]^{3-}]^2 - \{K(C_{\text{Zr}} + C_{\text{L}}) + C_{\text{CO}_3}[[\text{ZrL(CO}_3^3]^{3-}] + KC_{\text{Zr}}C_{\text{L}} = 0$$
The solution for Eq(6) can be expressed by following equation:

$$[[ZrL(CO_3)_3]^{3-}] = \frac{K(C_{Zr}+C_L)+C_{CO_3}±\sqrt{(K(C_{Zr}+C_L)+C_{CO_3})^2-4(K-1)KC_{Zr}C_L}}{2(K-1)}$$

Since $[ZrL(CO_3)_3]^{3-} = 0$ when $C_L = 0$, then the solution for (6) is finally obtained as

$$[[ZrL(CO_3)_3]^{3-}] = \frac{K(C_{Zr}+C_L)+C_{CO_3}±\sqrt{(K(C_{Zr}+C_L)+C_{CO_3})^2-4(K-1)KC_{Zr}C_L}}{2(K-1)}$$

To simplify the analysis, the spectral analysis was examined at the wavelengths in which no light absorption of carbonate and ammonium ions. Then the ligand exchange equilibriums were analyzed by using Lambert-beers law and combination of Eqs.(3), (4) and (8). For gluconic acid system, the light absorption at 260nm and molar absorptivity coefficient of gluconic acid at 260 nm : 0.667 cm$^{-1}$M$^{-1}$ was used.

Absorbance at 260 nm of Zirconium complex $[ZrL(CO_3)_3]^{3-}$, as a function of gluconic acid concentration is shown in Fig. 5, and solid line was drawn by non-linear least-square curve fitting with excellent correlation coefficient of R$^2 = 1$.This result indicates the ligand exchange reaction assumed in Eq.1 is adequate relationship.

Finally, the results of this experiment are summarized in Table 1. As predicted by EXAFS analysis, both of equilibrium constants of ligand exchange with carbonate for citric acid and tartaric acid are significantly smaller than that for gluconic acid. The value of equilibrium constant is same order with the one between 2-tenoyltrifluoroacetone.
(TFA) and lactate, which is also summarized in Table 1. Comparing the structure between gluconic acid and TFA, gluconic acid is obviously hydrophilic than TFA. This hydrophilicity and strong binding ability can be main force as stabilizing agent of zirconium in aqueous systems.

Table 1 Summarized equilibrium constants for ligand exchange reaction

<table>
<thead>
<tr>
<th>Ligand (L)</th>
<th>Reaction</th>
<th>equilibrium constants</th>
</tr>
</thead>
<tbody>
<tr>
<td>D-gluconic acid</td>
<td>$[\text{Zr(CO}_3\text{)}_4]^{4-} + L^-$ → $[\text{ZrL(CO}_3\text{)}_3]^{3-} + \text{CO}_3^{2-}$</td>
<td>$K = 7.17 \times 10^4 \text{ M}^{-1}$</td>
</tr>
<tr>
<td>citric acid</td>
<td>$[\text{Zr(CO}_3\text{)}_4]^{4-} + L^-$ → $[\text{ZrL(CO}_3\text{)}_3]^{3-} + \text{CO}_3^{2-}$</td>
<td>$K = 5.43 \text{ M}^{-1}$</td>
</tr>
<tr>
<td>L-tartaric acid</td>
<td>$[\text{Zr(CO}_3\text{)}_4]^{4-} + L^-$ → $[\text{ZrL(CO}_3\text{)}_3]^{3-} + \text{CO}_3^{2-}$</td>
<td>$K = 5.19 \text{ M}^{-1}$</td>
</tr>
</tbody>
</table>
2-thenoyltrifluoroacetone

\[ Zr + L^+ZrL \quad \log K = 4 \]

6-4 Conclusion

Mono-, di-, and tri-carboxylic acid, namely, gluconic acid, tartaric acid and citric acid were employed to examine its binding ability to zirconium carbonate complex. By adding the carboxylic acid ligand to the system includes mononuclear complex \([\text{Zr(CO}_3\text{)}_4]^{4-}\), ligand exchange reaction were observed. The structural evidence for ligand exchange was obtained by EXAFS analysis. Furthermore, UV absorption spectrophotometry revealed the equilibrium constants of these carboxylic ligands. We found and quantitated that significantly strong binding ability of gluconic acid to zirconium. Namely, it is quantitatively found that gluconic acid is a desirable stabilizer of zirconium due to its strong affinity for zirconium. In future, our results can be served as guideline for development of new stabilizer of zirconium and zirconium-related materials.

6-5 Acknowledgment
The synchrotron radiation EXAFS experiment was performed at the BL14B2 of SPring-8 with the approval of the Japan Synchrotron Radiation Research Institute (JASRI) (Proposal No. 2010B1961, 2011B1826 and 2012A1777). We would like to thank Prof. Iwao Watanabe, Dr. Hiroshi Oji, Mr. Yosuke Taniguchi and Dr. Masafumi Takagaki for help on EXAFS measurements and analyses.

References


(10) Farnworth, E.; Jones, S. L.; McAlpine, I. The production, properties, and uses of


(19) for example, commercially available as "Ammonium zirconium(IV) carbonate solution in H2O, contains 1-2 mass% tartaric acid as stabilizer" from Sigma-Aldrich; CAS No. 12616-24-9, in.


Chapter 7
Structure of Zr(IV) in Polyvinyl Alcohol Film Cross-linked by Ammonium Zirconium Carbonate Solution Containing Chelate Agent

7-1 Introduction

In Chapter 5, it is indicated that monomeric species, \([\text{Zr}(\text{CO}_3)_4]^4^-\), in AZC solutions is superior to polymeric species in cross-linking ability against polyvinyl alcohol. Furthermore, by addition of gluconic acid (Glu) and triethanolamine (TEA) to the AZC solution, in which \([\text{Zr}(\text{CO}_3)_4]^4^-\) is dominant species, cross-linking ability of the solutions was improved. On the other hand, the previous study\(^1\) indicated that gluconic acid reacted \([\text{Zr}(\text{CO}_3)_4]^4^-\), so that \([\text{Zr}(\text{CO}_3)_3(\text{Glu})]^3^-\) was generated.

We assume that gluconic acid and triethanolamine added to AZC solution affect the structure of zirconium species, which relates closely to cross-linking performance, in PVA film cross-linked by the AZC solution. Confirming the assumption, structure of zirconium in PVA films cross-linked by AZC solutions to which gluconic acid and triethanolamine were added were investigated by Zr-K edge extended X-ray absorption fine structure (EXAFS) analysis.

7-2 Experimental

AZC crystal was prepared the same as the previous study.\(^2,3\) Through dissolving this crystal (purity 92 wt%) by mixing with gluconic acid (1st agent, Sigma Aldrich Japan) neutralized by equivalent ammonia, triethanolamine (special grade agent, Sigma Aldrich Japan) and deionized water (made by RFU565N, ADVANTEC), multiple AZC solutions with the following composition were prepared: \([\text{Zr}] = 0.1 \text{ M}, [\text{NH}_4^+] = 0.6-0.7 \text{ M}, \text{and} \)
\([\text{CO}_3^{2-}] = 0.6 \text{ M}, [\text{Glu or TEA}] = 0-0.1 \text{ M}.\)

PVA films cross-linked the AZC solutions were prepared and evaluated by water resistance the same as Chapter 5. As for conditions of pre-drying in the PVA film preparation, temperature, humidity and duration were set in 293 K, 80% and 3 days, respectively.

Zr-K edge EXAFS analyses of the PVA films and AZC crystal were performed using BL14B2, SPring-8 the same as Chapter 5. PVA films were piled up until becoming the thickness of 1-2 mm to measure EXAFS spectra.

**7-3 Results and discussion**

Fig. 1 shows the residual ratio of PVA film as a function of concentration of chelate agent in AZC solutions.

![Graph showing residual ratio of PVA film](image)

**Akita University**

Fig. 1 Residual ratios of PVA film after washing with water as a function of [chelate agent]. The PVA films were treated with AZC solutions with various [chelate agent] values ([Zr] = 0.1 M, [NH\(_4^+\)] = 0.6-0.7 M, and [CO\(_3^{2-}\)] = 0.6 M). ×: gluconic acid, □: triethanolamine
The residual ratio increased with increase of concentration of chelate agent. Cross-linking ability of the AZC solution was improved by addition of chelate agent to it. Fig. 2 and 3 show Fourier transform spectra of PVA film cross-linked by AZC solutions containing various concentration of gluconic acid and triethanolamine, respectively. Additionally, the spectrum of AZC crystal was also shown in Fig. 2 and 3. The previous study indicated that the peaks located near 320 pm and 350 pm were attributed to Zr-Zr coordination and Zr-carbonate ion coordination, respectively. From Fig. 2 and 3, structures surrounding zirconium in PVA films cross-linked by AZC solutions were changed, depending on concentration of chelate in the solutions. In Fig. 2 and 3, the peaks located near 320 pm were grown with decrease of concentration of chelate agent in AZC solution. Therefore, formation of Zr-Zr coordination was prevented by addition of chelate agent.

Song et al. indicated that the preference of reaction of AZC to AZC inducing formation of Zr-Zr coordination and AZC to starch is comparable in cross-linking reaction, since the activation energy of cross-linking between AZC and starch closed to that of AZC and AZC. To summarize, addition of chelate agent to AZC solution prevent Zr-Zr coordination from forming, namely self-cross-linking reaction, when PVA film cross-linked by the AZC solution was formed. This indirectly promotes cross-linking reaction between AZC and PVA that competes against self-cross-linking reaction.
Fig. 2  Fourier transform spectra of PVA films cross-linked by AZC solutions containing various concentration of gluconic acid; □: 0.0 M, △: 0.02 M, ○: 0.04 M, ×: 0.08 M, Solid line: AZC crystal ((NH₄)₃ZrOH(CO₃)₃·2H₂O)

Fig. 3  Fourier transform spectra of PVA films cross-linked by AZC solutions containing various concentration of triethanolamine; □: 0.0 M, △: 0.02 M, ○: 0.04 M, ×: 0.08 M, Solid line: AZC crystal ((NH₄)₃ZrOH(CO₃)₃·2H₂O)
7-4 Conclusion

By addition of gluconic acid and triethanolamine to AZC solution, in which the monomeric species \([\text{Zr(CO}_3\text{)}_4]\)\(^{4-}\) was dominant species, cross-linking ability of the AZC solution was improved. The cross-linking performance was promoted with increasing of concentration of the chelate agents in the solution. It is considered that the chelate agents are inhibitor of formation of Zr-Zr coordination that competes with cross-linking reaction between PVA and AZC. The effect mechanism of gluconic acid and triethanolamine in AZC solution to cross-linking ability were clarified.

7-5 Acknowledgment

The synchrotron radiation EXAFS experiments were performed with the approval and support of the Japan Synchrotron Radiation Research Institute (JASRI) (Proposal No. 2010B1961, 2011B1826 and 2012A1777). We would like to thank Prof. Iwao Watanabe for help with the EXAFS analysis.

References


Chapter 8
Concluding Remarks

Based on an assumption that the structure of zirconium species in zirconium salt solutions is a critical factor of applied performance, for instance cross-linking ability for polyvinyl-alcohol, structural analyses of zirconium salt solutions over a wide range of chemical compositions were performed in this study.

In the study of zirconium chloride solutions, principal conditions for formation certain structure of zirconium species, for instance tri-, tetra-, poly-nuclear complexes and zirconium oxide nanocrystal, were revealed. In addition, it was confirmed that the variation of structure correlated with change of cross-linking performance for polyvinyl-alcohol and the structure and chemical composition which have superior cross-linking ability were clarified. In the study of ammonium zirconium carbonate solutions, concentration of zirconium, ammonium and carbonate in the solutions to form the monomeric zirconium complex \([\text{Zr(CO}_3\text{)}_4]^\text{4-}\) were determined. It was revealed that the monomer was superior to polymeric species in cross-linking ability for PVA.

Through these studies, it was substantiated that applied performance of zirconium salt aqueous solution results from the structure of zirconium species in the solution.
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Papers relevant to the present study


