Introduction

Zirconium compounds are nowadays widely utilized in solid state materials as alloys and oxides. For instance, some ceramics or alloys containing zirconium are recognized as candidates for artificial bone and dental materials due to their biocompatibility.1–3 Their low neutron absorption cross-section and high resistance to corrosion has led to their use as a cladding material for nuclear fuel in power plants.4 Lead zirconate titanate ceramics are high-performance piezoelectric materials, which are widely used in sensors, actuators and other electronic devices.4

On the other hand, chemical species consists of zirconium complexes are essentially chemically inert. For instance, they rarely exhibit any striking catalytic properties in aqueous solution, but they do exhibit polyoxometalate formation on their own or with other metallic elements.5 The chemical inactivity can be associated with the corrosion resistance zirconium-containing materials, and provides other beneficial uses, such as a cross-linking agent for organic backbones to assemble metal-organic frameworks.6,7

Zirconium salts are also employed in industrial uses, especially for cross-linking of polyvinyl alcohol (PVA).8,9 We expect that the structures of zirconium species in aqueous solution will affect their cross-linking performance for PVA. In this industrial point of view, more information on the speciation of zirconium in aqueous solution is needed for improving its utility.

Some structural studies of mono- and poly-nuclear Zr complexes in aqueous solutions have been reported by several groups. For instance, Walther et al. demonstrated variations in the degree of polymerization of Zr complexes, 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 that the samples are crystalline, being applicable to amorphous solids or even in liquids.12 We also reported that polynuclear complexes and ZrO2 nanocrystals were successively generated, depending on the aging conditions, in zirconium oxychloride solutions, as revealed by EXAFS and dynamic light scattering analysis.13 Furthermore, we found monomeric complex formation of Zr in the ammonium carbonate aqueous system by means of EXAFS and Raman spectrometry.14 Our previous work has also suggested that monomeric Zr species in an aqueous solution possesses a higher cross-linking ability than polymeric Zr.15

Stoichiometric studies are also important to understand the speciation of zirconium in aqueous solutions. In earlier work, the thermodynamic parameters of zirconium were well studied.
for systems including simple inorganic ions. However, for systems containing organic ligands, the stability parameters such as equilibrium constants have not been well investigated. Organic ligands have generally larger stability constants than inorganic ones for metal complexation. Therefore, it is likely that an organic ligand will suppress the generation of polynuclear zirconium complexes due to its strong complexation in aqueous systems. Chakravarty and co-workers reported a set of valuable experimental results. They studied the ligand exchange between 2-thienyltrifluoroacetate and lactate bound to zirconium by UV absorption spectrophotometry. This technique is very easy to use and is a powerful tool for equilibrium analysis of simple chemical systems.

In the present study, gluconic acid, l-tartaric acid and citric acid, which are mono-, di- and tri-carboxylic acids, respectively, were selected as candidates for stabilizing agents that will act to maintain monomeric zirconium species in aqueous solution. While these compounds have already been utilized as stabilizing agents, the structures of their complexes and the details of their chemical reactions were still unknown. We therefore have investigated ligand-exchange reactions between these carboxylic acid ligands and carbonate coordinated to zirconium in an aqueous solution by means of EXAFS spectroscopy and UV absorption spectrophotometry.

**Experimental**

**Preparation of samples**

D-Gluconic acid (Sigma Aldrich Japan), citric acid anhydrate and ammonium l-tartarate (Kishida Chemical Co., Japan) were purchased and used. Zirconium basic carbonate (Zr(OH)4(CO3)3·2H2O [a ≈ 3.2, b = 0.4, n ≈ 6.9], Daiichi Kigenso Kagaku Kogyo Co., Japan), ammonium hydrogen carbonate (purity NH3: 20 – 23 wt%, special grade chemicals, Kishida Chemical Co., Japan), and aqueous ammonia (purity NH3: 29 wt%, special grade chemicals, Sigma Aldrich Japan) were mixed and aged at 353 K for 2 h to obtain a transparent solution. This solution was left at 278 K for 1 week to obtain crystals of ammonium zirconium carbonate (AZC—(NH4)3ZrO2(CO3)2·2H2O), and the precipitated crystals were separated from the mother liquor. The crystals obtained were confirmed to be identical with AZC crystals described in the literature through X-ray diffraction analysis. A final aqueous solution was prepared from these crystals. Deionized water prepared by an RFU565N water purification system (ADVANTEC, Japan) was used in all of the experiments conducted 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 in the energy region ranging from 17.5 to 19.9 keV. A double crystal monochromator of Si(111) was used for the measurements. The 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.

**Raman spectrometry**

A Raman spectrometer (NRS-4200, JASCO Co., Japan) was used with a diode laser of 785 nm and the macro measurement unit (RMC-457-115, JASCO Co., Japan). The sample solutions in a quartz cell with optical paths of 10 mm were exposed for 60 s. Raman spectra were obtained by integration of 10 times of the measurements. The measurement room temperature was kept at 298 ± 2 K.

**UV absorption spectrophotometry**

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

**Results and Discussion**

**EXAFS analysis**

Figure 1 shows Fourier transform spectra of the Zr EXAFS region for the samples. All of the sample solutions contained \([\text{Zr}] = 0.1 \text{ M}, \ [\text{NH}_4]^+ = 0.6 \text{ M} \) and \([\text{CO}_3^{2-}] = 0.6 \text{ M}\) as final concentrations 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 a mononuclear complex \([\text{Zr}^{[\text{CO}_3]}_3]^{3+}\) under the same experimental condition in the absence of the carboxylic acid ligands in our previous research by EXAFS and Raman spectrometry. In the absence of the carboxylic acid ligands, the peaks located at around 170 and 350 pm are assigned to Zr-O coordination and multiple scattering by carbonates, which are coordinated to the Zr atom. The largest spectral changes produced by carboxylic acid ligands were observed for increasing concentrations of gluconic acid (Fig. 1(a)), where an obvious new peak was found in the short coordination range, and a decrease of the peak intensity due to multiple scattering by carbonates was observed. This new peak is located at <300 pm, which is shorter than the Zr-Zr distance usually seen in the polynuclear complex of zirconium. Therefore, we judged that this peak is attributable to multiple scattering by gluconic acid exchanged for carbonate on the Zr atom, and that after these ligands are exchanged, the resulting zirconium complex is still mononuclear. The reaction can be described as follows:

\[
[\text{Zr}^{[\text{CO}_3]}_3]^{4-} + L^+ \rightleftharpoons [\text{ZrL}^{[\text{CO}_3]}_3]^{2+n} + \text{CO}_3^{2-}
\]

where \(L^+\) indicates a carboxylic ligand. Figure 2 shows change of geometric structure of zirconium tetra-carbonate complex following the exchange reaction with gluconic acid and relationship between the reaction and Fourier transform spectra of EXAFS.

**Raman spectrometry**

Figure 3 shows Raman spectra for the samples to which carboxylic acid ligands were added and the controlled sample in the absence of the ligands. All samples exhibited strong absorption at around 1050 cm\(^{-1}\). On the samples containing gluconic acid, the magnitude of the peak significantly decreased with increasing gluconic acid concentration. This indicates that gluconic acid is more apt to substitute \(\text{CO}_3^{2-}\) ligand than the others. The results matched the conclusion led by the present EXAFS analyses.

**UV absorption spectrophotometric analysis**

UV absorption spectra of the samples including gluconic acid in the presence and absence of zirconium are displayed in Figs. 4 and 5, respectively. Since all of the compounds employed in this study have strong optical absorption in the
The optical cells with pathlengths of 0.5 and 1.0 mm were used for this region. Although the spectra absorbance in the absence of zirconium rises with an increase in the gluconic acid concentration, as shown in Fig. 5, a much larger absorption change dependent on the gluconic acid concentration was observed in Fig. 4 when Zr is present. This absorption is presumably associated with metal complexation of gluconic acid with zirconium, and is attributable to a change of the electronic state of the whole complex and ligand. This strong absorption change that depends on the gluconic acid concentration was utilized for an equilibrium analysis of the ligand exchange reaction indicated as Eq. (1). The equilibrium constant $K$ of the reaction expressed by Eq. (1) can be expressed as:

$$K = \frac{[\text{ZrL}]}{[\text{Zr}][\text{L}]}.$$

In the presence of the carboxylic acid ligand L, the concentrations $[\text{Zr}][\text{CO}_3]$, $[\text{CO}_3]^-$, and $[\text{L}]$ are given by the following equations:

$$[\text{Zr}][\text{CO}_3] = C_{\text{Zr}} - [\text{ZrL}]$$

$$[\text{L}] = C_{\text{L}} - [\text{ZrL}]$$

$$[\text{CO}_3]^- = C_{\text{CO}_3} + [\text{ZrL}]$$
where \( C_{Zr} \), \( C_L \), and \( C_{CO_3} \) are the total concentration of zirconium, a carboxylic acid ligand, and the carbonate ion, respectively. From Eqs. (2) - (5), the following equation as a function of \([ZrL(CO_3)_{3}(3+n)^-]\) can be obtained as:

\[
(K - 1)[[ZrL(CO_3)_{3}]^{2(n-1)}] - 
\frac{K(C_Zr + C_L) + C_{CO_3}}{[ZrL(CO_3)_{3}][K_ZrL_CCO_3]} + K C_Zr C_L = 0. \tag{6}
\]

The solution for Eq. (6) can be expressed by the following equation:

\[
[[ZrL(CO_3)_{3}]^{2(n-1)}] = 
\frac{K(C_Zr + C_L) + C_{CO_3} \pm \sqrt{(K(C_Zr + C_L) + C_{CO_3})^2 - 4(K - 1)K C_Zr C_L}}{2(K - 1)} \tag{7}
\]

Since \([ZrL(CO_3)_{3}]^+ = 0\) when \( C_L = 0 \), then the solution for Eq. (6) is finally obtained as

\[
[[ZrL(CO_3)_{3}]^{2(n-1)}] = 
\frac{K(C_Zr + C_L) + C_{CO_3} - \sqrt{(K(C_Zr + C_L) + C_{CO_3})^2 - 4(K - 1)K C_Zr C_L}}{2(K - 1)} \tag{8}
\]

According to the Beer-Lambert law, the total UV absorption at an arbitrary wavelength can be expressed as

\[
A = (\varepsilon_{Zr(CO_3)_4})[[Zr(CO_3)_4]^+] + \varepsilon_{CO_3} [CO_3^2^-] + 
\varepsilon_L [L^-] + \varepsilon_{ZrL(CO_3)_{3}^-} [[ZrL(CO_3)_{3}^{3+n^-}]] l \tag{9}
\]

where \( A \), \( \varepsilon_{Zr(CO_3)_4} \), \( \varepsilon_{CO_3} \), \( \varepsilon_L \), \( \varepsilon_{ZrL(CO_3)_{3}^-} \), and \( l \) indicate absorbance, molar absorption coefficients (M\(^{-1}\) cm\(^{-1}\)) of \([Zr(CO_3)_4]^+\), \([CO_3^2^-] \), \([L^-] \), \([ZrL(CO_3)_{3}^{3+n^-}] \) (M) and the optical path length (cm), respectively.

The ligand exchange equilibriums were also analyzed using the Beer-Lambert law (9). For the gluconic acid system, the analysis was conducted at a wavelength of 260 nm, at which no light absorptions of \([Zr(CO_3)_4]^+\) and \([CO_3^2^-] \) occurs, namely, \( \varepsilon_{Zr(CO_3)_4} = \varepsilon_{CO_3} = 0 \). The molar absorptivity coefficient of gluconic acid at 260 nm: 0.667 M\(^{-1}\) cm\(^{-1}\) was determined from the experimental datasets of Fig. 5 and was used in this analysis. In addition, the lack of light absorption by the ammonium ion in
the wavelength range of UV absorption experiments used in this study was confirmed.

The absorbance at 260 nm of the zirconium complex [Zr(gluconic acid)(CO₃)₃]⁴⁻, as a function of gluconic acid concentration is shown in Fig. 6, together with a solid line corresponding to a non-linear least-square curve fit that has an excellent correlation coefficient of \( R = 1 \). Values of the equilibrium constant \( K = 7.17 \times 10^4 \) M⁻¹ and \( \varepsilon_{ZrL(CO_3)} = 7.51 \) M⁻¹ cm⁻¹ were also obtained by this analysis. This fact that this result has such a high correlation coefficient indicates that the ligand exchange reaction assumed in Eq. (1) is adequate.

For the citric acid and L-tartaric acid systems, the absorbance at 230 nm was used due to the weaker light absorption at the longer wavelength (250 - 400 nm) range than in the gluconic acid system. The absorption spectra for AZC solutions in the presence and absence of these carboxylic acids are indicated in Supporting Information. Values of \( \varepsilon_{Zr(CO_3)} \), \( \varepsilon_{CO_3} \), \( \varepsilon_L \) for citric acid and L-tartaric acid at 230 nm were separately determined as 1.06, 43.8, 24.7, and 0.202 M⁻¹ cm⁻¹, respectively, before this analysis.

Finally, the results of these experiments are summarized in Table 1. As predicted by the EXAFS analysis, both of the 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 of the same order as that between 2-tenoyltrifluoroacetone (TFA) and lactate, which is also summarized in Table 1. Comparing the structures of gluconic acid and TFA, gluconic acid is obviously more hydrophilic than TFA. This hydrophilicity and strong binding ability are probably major forces that can promote the use of gluconic acid as a stabilizing agent of zirconium in aqueous systems.

**Advantage of gluconic acid as a stabilizing agent for AZC solution**

We revealed that AZC solutions containing a certain concentration of gluconic acid were superior to ones including other ligands for cross-linking agent of polyvinyl alcohol (PVA), and the structure of zirconium species in the AZC solutions were monomeric by EXAFS analysis in previous research. PVA films to which the AZC solutions were added exhibited excellent insolubility in water. The advantage results from high stability of the monomeric structure of the zirconium carbonate gluconate complex, which prevents oligomerization by hydrolysis. The monomeric structure remains until cross-linking reaction with hydrophilic functional groups of PVA molecules. This is supported by the fact that gluconic acid is the strongest ligand for zirconium tetra-carbonate complex demonstrated in this study.

**Conclusions**

Examples of mono-, di-, and tri-carboxylic acids, namely, gluconic acid, L-tartaric acid and citric acid, were employed to examine their binding abilities to a zirconium carbonate complex. By adding the carboxylic acid ligand to a system that contains the mononuclear complex [Zr(CO₃)₄]⁴⁻, a ligand exchange reaction was observed. The structural evidence for ligand exchange was obtained by EXAFS analysis and Raman spectrometry. Futhermore, UV absorption spectrophotometry allowed the calculation of the equilibrium constants of these carboxylic ligands. We found and quantified a significantly increased stability of the monomeric structure of the zirconium carbonate gluconate complex, which prevents oligomerization by hydrolysis.

![Fig. 6 Absorbance at 260 nm of the zirconium tri-carbonate gluconate complex, as a function of gluconic acid concentration. Each sample contained [zirconium] = 0.1 M, [ammonium ion] = 0.6 M and [carbonate ion] = 0.6 M as final concentrations. The solid line was obtained by a non-linear least-square regression with a correlation coefficient \( R = 1.00 \).](image)

| Ligand (L) | Reaction | Equilibrium constant |
|-----------|----------|----------------------|
| D-Gluconic acid | \([Zr(CO_3)_4]^{4-} + L^- \rightleftharpoons [ZrL(CO_3)_3]^{5-} + CO_3^{2-}\) | \( K = 7.17 \times 10^4 \) M⁻¹ |
| Citric acid | \([Zr(CO_3)_4]^{4-} + L_3^- \rightleftharpoons [ZrL_2(CO_3)_2]^{6-} + CO_3^{2-}\) | \( K = 5.43 \) M⁻¹ |
| L-Tartaric acid | \([Zr(CO_3)_4]^{4-} + L_2^- \rightleftharpoons [ZrL(CO_3)_3]^{5-} + CO_3^{2-}\) | \( K = 5.19 \) M⁻¹ |
| 2-Thenoyltrifluoroacetone | \( Zr + L \rightleftharpoons ZrL \) | \( \log K = 4^{18} \) |

Table 1  Summarized equilibrium constants for ligand exchange reaction
strong binding ability of gluconic acid to zirconium. Our results show that gluconic acid is likely to be a good stabilizer of zirconium due to its strong affinity for that metal. In future, we hope that our results can serve as guidelines for the development of new stabilizers of zirconium and zirconium-related materials.

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Supporting Information

UV absorption spectra of citric acid solution, l-tartaric acid solution, and AZC solutions in the presence and absence of the carboxylic acids. Absorbance at 230 nm of zirconium complex as a function of concentration of the carboxylic acids. This material is available free of charge on the Web at http://www.jsac.or.jp/analsci/.

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