Thermodynamic interpretation of zirconium solubility in the presence of hydroxyacetic, 3-hydroxypropionic, and 2,3-dihydroxypropanoic acids

Taishi Kobayashi[a,*] , Wang Peng[a], Takayuki Sasaki[a]

[a]*Department of Nuclear Engineering, Kyoto University, Kyotodaigaku-katsura, Nishikyo-ku, Kyoto 615-8540, Japan*

The solubility of zirconium hydroxide in the presence of hydroxyacetic (glycolic, O20), 3-hydroxypropionic (O21), and 2,3-dihydroxypropanoic (glyceric, O201) acids was investigated as a function of $pH_c = -\log [H^+] = 7-13$ and total hydroxycarboxylic acid concentrations, $[L]_{tot} = 10^{-4}-10^{-1}$ mol/dm^3. The Zr solubility dependences on pH_c and $[L]_{tot}$ indicated that ternary $Zr(OH)_4(L)_2^{2-}$ complexes were the dominant soluble species under the experimental conditions. The formation constants of the $Zr(OH)_4(L)_2^{2-}$ complexes were determined by least square fitting analysis of the solubility data and compared to the values for zirconium-poly(hydroxy)carboxylate analogs to elucidate the complexation mechanism of Zr-hydroxycarboxylates.

1. Introduction

Tetravalent zirconium, Zr(IV), is known to undergo extensive hydrolysis in aqueous solution. Various mononuclear and polynuclear hydrolytic species have been identified directly or indirectly in acid solutions [1-5]. However, strong hydrolysis reactions lead to the formation of a sparingly soluble amorphous hydroxide solid phase, $Zr(OH)_4(am)$, in neutral to alkaline pH range. Zr(IV) solubility in neutral to alkaline solutions is controlled by $Zr(OH)_4(am)$ and limited to values of 10^{-8} mol/dm^3 (M) or lower in the absence of complexing ligands [6,7]. In the presence of suitable inorganic or organic ligands, Zr(IV) solubility is increased by the formation of soluble complexes [8-10]. Enhanced Zr(IV) solubility is an issue in the environmental context of safe radioactive waste disposal, because the long half-life fission product ^{93}Zr ($T_{1/2}$=1.53×10^6 y) in radioactive waste forms Zr(IV) and can migrate with groundwater under the disposal conditions.

Zirconium(IV) solubility in groundwater is generally limited by its sparingly soluble $Zr(OH)_4(am)$, and a very few inorganic or organic ligands can compete with the strong hydrolysis reactions that occur in neutral to alkaline solutions. For example, oxalic acid $((COOH)_2$, C20) forms stable Zr(IV) complexes via its two carboxylate groups in acidic to weakly acidic solutions [11-13]. However, according to thermodynamic calculations [13], the hydrolysis reaction competes effectively with C20 complexation which causes only a minor change in Zr(IV) solubility in neutral to alkaline solutions. We recently investigated the degree of Zr(IV) solubility in the presence of gluconic $(HOCH_2(CHOH)_4COOH$, GLU) and α-isosaccharinic $(CH_2OHCHOHCH_2COH-(CH_2OH)COOH$, ISA) acids [14]. These poly(hydroxy)carboxylic acids are present at disposal sites since GLU is used as a cement additive and ISA is a degradation product of cellulose found in low- and intermediate-level radioactive wastes [15-17]. They were found to form stable complexes with Zr(IV) in neutral to alkaline solutions with high complexation constants, which suggests that the hydroxyl as well as the carboxyl groups of GLU and ISA bind Zr(IV) [14].

In this work, we investigated the solubility of Zr(IV) in the presence of three simple hydroxycarboxylic acids (hydroxyacetic (glycolic, O20), 3-hydroxypropionic (O21), and 2,3-dihydroxypropanoic acid (glyceric, O201)) to clarify the role of the hydroxy groups in Zr complexation. The Zr(IV) solubility dependence on hydrogen ion concentrations (pH_c) and hydroxycarboxylic acid concentrations ($[L]_{tot}$) was examined to identify the dominant soluble species and to determine their formation constants. The constants obtained were discussed and compared with the values for Zr-poly(hydroxy)carboxylate complexes.

2. Experimental methods and materials

2.1. Chemicals and analytical methods. The chemicals used in this study were of reagent grade. Hydroxyacetic (glycolic, O20) acid was purchased from FUJIFILM Wako Pure Chemical Corp. 3-Hydroxypropionic (O21) and 2,3-dihydroxypropanoic (glyceric, O201) acids were obtained from Tokyo Chemical Industry Co., Ltd. A stock suspension of $Zr(OH)_4(am)$ was prepared from $ZrCl_4$ (FUJIFILM Wako) as described in our previous study [14]. A PIPES buffer (Dojindo) was used to adjust pH_c in the neutral pH region. Deionized purified water (Milli-Q, Millipore) was used in the preparation of all solutions.

All reagent preparations and sample handling procedures were performed in an Ar-filled glove box with O_2 concentrations below 10 ppm at 25 °C. A combination glass electrode (9615-10D, Horiba Ltd.) was used to measure pH_c. The reference Ag/AgCl electrode was filled with 3.6 M NaCl and 0.4 M $NaClO_4$ to prevent precipitation of $KClO_4$ at the junction of the electrode and sample solution. The electrode was calibrated against standard HCl and NaOH solutions adjusted to 0.5 M ionic strength (I) with $NaClO_4$ to correct experimentally measured pH_{exp} values to pH_c.

2.2. Solubility experiments. Sample solutions were prepared by an undersaturation method [10,14]. An aliquot of $Zr(OH)_4(am)$ stock suspension was added to sample solutions at selected pH_c and $[L]_{tot}$ values within the pH_c range of 7 to 13 and $[L]_{tot}$ range of 10^{-4} to 10^{-1} M. Total dissolution of $Zr(OH)_4(am)$ equated to a maximum Zr concentration of 0.01 M. The structures of the hydroxycarboxylic acids used in this study and of GLU and ISA are shown in Figure 1, together with their reported dissociation constants for the carboxylic

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*Corresponding author. Email: kobayashi@nucleng.kyoto-u.ac.jp, FAX: 075-383-3919
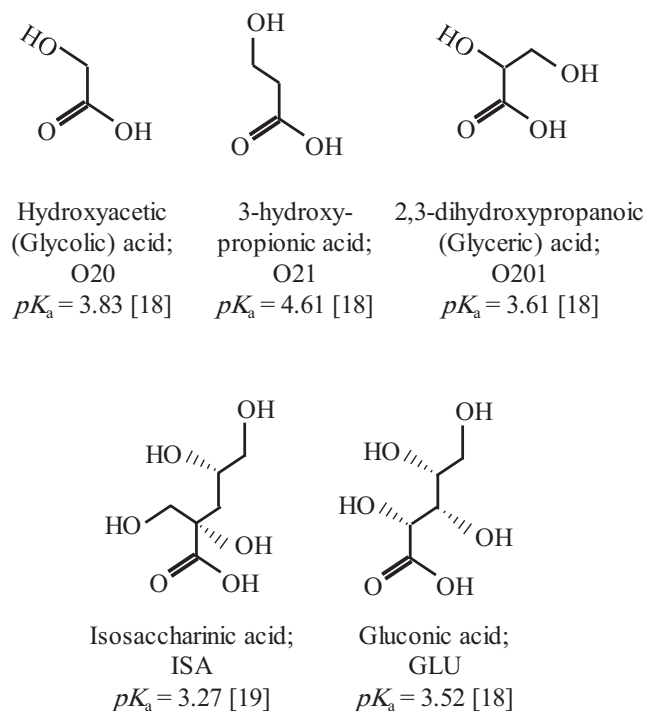
Hydroxyacetic
(Glycolic) acid;
O20
$pK_a = 3.83$ [18]

3-hydroxy-
propionic acid;
O21
$pK_a = 4.61$ [18]

2,3-dihydroxypropanoic
(Glyceric) acid;
O201
$pK_a = 3.61$ [18]

Isosaccharinic acid;
ISA
$pK_a = 3.27$ [19]

Gluconic acid;
GLU
$pK_a = 3.52$ [18]

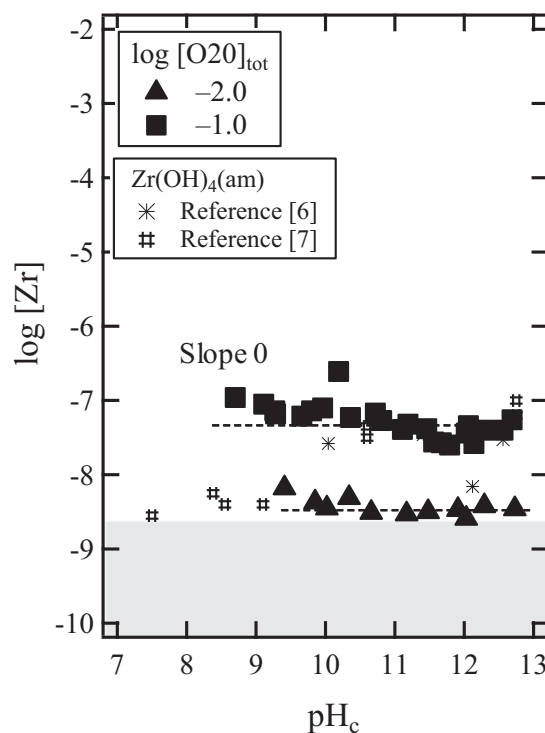**Figure 1.** Hydroxycarboxylic acids in this study.

Figure 2. Zr(IV) solubility in the presence of 0.01 and 0.1 M O20 after aging for 20–323 d. The ICP-MS detection limit is indicated by the gray shading.
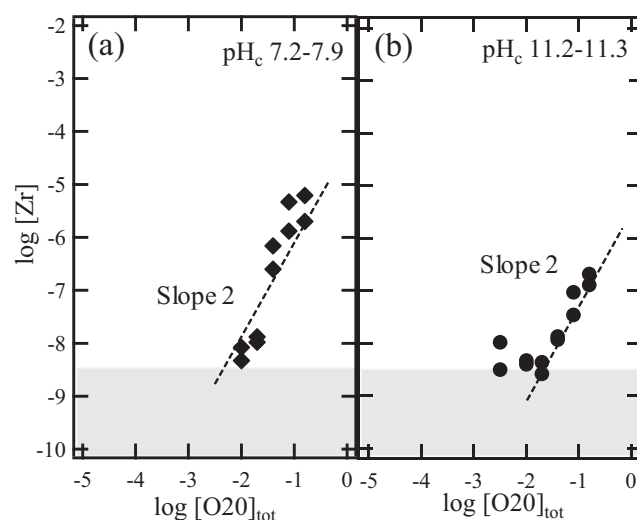

Figure 3. Zr(IV) solubility at two levels of pH_c as a function of total O20 concentration after aging for 84–323 d: (a) pH_c = 7.2–7.9 and (b) pH_c = 11.2–11.3. The ICP-MS detection limit is indicated by the gray shading.

group [18,19]. The ionic strength of sample solutions was adjusted to $I = 0.5$ M by adding an appropriate amount of $NaClO_4$. Sample solutions in polypropylene tubes were kept in the Ar-filled glove box and in some cases manually shaken for a few minutes. After given aging periods, the pH_c of the sample solutions was measured and a 0.5-mL aliquot of the supernatant was passed through an ultrafiltration membrane (Microcon, nominal molecular weight limit (NMWL) = 3 kDa, pore size ~2 nm, Millipore). The filtrate was acidified with 0.1 M nitric acid prior to the concentration measurements by inductively coupled plasma mass spectrometry (ICP-MS) (ElanDRC II, PerkinElmer). The detection limit of Zr(IV) solubility was approximately $10^{-8.5}$ M. Solubility measurements of Zr were repeated several times to confirm the attainment of a steady state. The standard error of ICP-MS measurements was ±10%, which corresponded to an uncertainty of ±0.1 log units for the Zr(IV) concentration.

3. Results and discussion

3.1. Zr(IV) solubility in the presence of hydroxycarboxylic acids.
Figure 2 shows the Zr(IV) solubility in the presence of 0.01 and 0.1 M glycolic acid (O20) as a function of pH_c. Zirconium solubility in the absence of O20 [6,7] is plotted in the same figure for comparison. The solubility after aging for 20 to 323 d exhibited similar values, which indicated that the solution mixture reached a steady state within several weeks. The Zr(IV) solubility in the presence of 0.01 M O20 was close to that in the absence of O20, although concentrations were almost at the detection limit of ICP-MS. However, Zr(IV) solubility in the presence of 0.1 M O20 equaled 10^{-7} M throughout the whole pH_c range, and the solubility was about one order of magnitude higher than that in the absence of O20. Zr(IV)-O20 complexes were considered to be the predominant Zr(IV) species in 0.1 M O20 solution. Assuming that the solid phase retained its $Zr(OH)_4(am)$ stoichiometry, the zero slope of the log [Zr] versus pH_c plot indicated that the soluble Zr(IV)-O20 complex contained four OH groups in its chemical formula.

Figure 3 shows Zr(IV) solubility in the presence of O20 as a function of $[O20]_{tot}$ at effectively constant pH_c levels of 7.2–7.9

and 11.2–11.3. At both pH_c levels, Zr solubility increased monotonically with a slope of two, indicating that two O20 ligands were present in the Zr(IV)-O20 complex. Therefore, we assumed that $Zr(OH)_4(O20)_2^{2-}$ was the major species in the solution.

The formation of glycolate (O20) complexes with trivalent and tetravalent metal ions has been reported in the literature, but mainly in acidic solutions. Binary O20 complexes including polynuclear species have been proposed under conditions of higher metal ion and O20 concentrations [20,21]. The concentration of free Zr(IV) is strictly limited by $Zr(OH)_4(am)$ at neutral to alkaline pH. The difference in O20 behavior between acidic and neutral to alkaline solutions may arise from this condition. We noted in our previous study that ternary $Zr(OH)_4(L)_2^{2-}$ complexes are found in the presence of
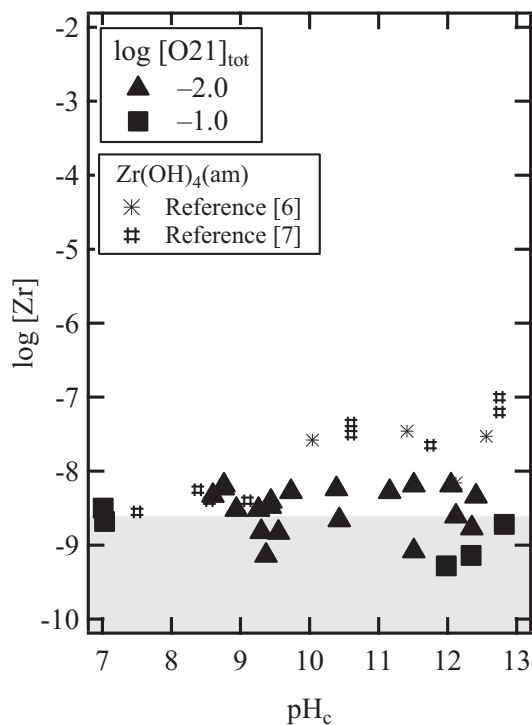
Figure 4. Zr(IV) solubility in the presence of 0.01 and 0.1 M O21 after aging for 33–50 d. The detection limit of ICP-MS is indicated by the gray shading.
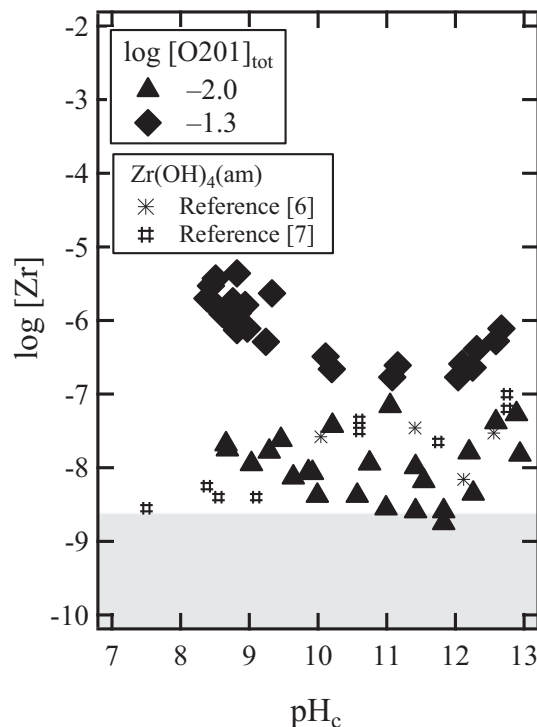

Figure 5. Zr(IV) solubility in the presence of 0.01 and 0.05 M O201 after aging for 63–176 d. The ICP-MS detection limit is indicated by the gray field.

GLU and ISA at neutral and alkaline pH [14].

Figure 4 shows the solubility of Zr(IV) in the presence of 0.01 and 0.1 M 3-hydroxypropionic acid (O21) as a function of pH_c. Solubility was lower than 10^{-8} M in both 0.01 and 0.1 M O21, which was close to the value in the absence of O21 and close to the ICP-MS detection limit. This result suggested that complexation by O21 was not strong enough to solubilize Zr(IV) under the present experimental conditions. Zirconium(IV) solubility also was examined as a function of $[O21]_{tot}$, but no significant increase above the detection limit was observed up to 0.1 M O21. A decrease in complexation with increasing alkyl chain length is also observed for Zr–dicarboxylates, wherein complexation by oxalate $((COOH)_2$, C20) is stronger than that of malonate $(CH_2(COOH)_2$, C21) [9]. Similar to dicarboxylic acids, Zr(IV) chelation featuring 5-membered rings with O20 might be more stable than that with 6-membered rings with O21.

Zirconium(IV) solubility in the presence of 0.01 and 0.05 M glyceric acid (O201) is plotted as a function of pH_c in Figure 5. At 0.01 M O201, the solubility was slightly higher than that in the absence of O201. In 0.05 M O201, the solubility was approximately 10^{-6} M at pH_c 8 and $10^{-6.5}$ M at $pH_c > 10$. Provided that the solid phase retained its $Zr(OH)_4(am)$ stoichiometry, the slope of -1 found at pH_c 8–10 indicated that the soluble Zr(IV)-O201 complex contained three OH groups in its chemical formula. On the other hand, the slope of log [Zr] against pH_c was almost zero at pH_c 10–12, similar to the case of O20, indicating that four OH groups bound to Zr(IV) to form the Zr(IV)-O201 complex in this pH region. At $pH_c > 12$, the Zr(IV) was observed to increase with increasing pH_c at, suggesting that one additional OH$^-$ was involved in the Zr(IV)-O201 complex in this pH region. This might be due to further coordination of an OH$^-$ to the Zr(IV)-O201 complex or to deprotonation of the hydroxyl group of O201 as discussed for GLU and ISA in our previous study [14].

Figure 6 displays the Zr(IV) solubility as a function of $[O201]_{tot}$ at pH_c =6.0–6.9 and pH_c = 9.2–10.6. Solubility increased with increasing $[O201]_{tot}$ with a slope of two, which indicated that the dominant Zr(IV)-O201 complex contained
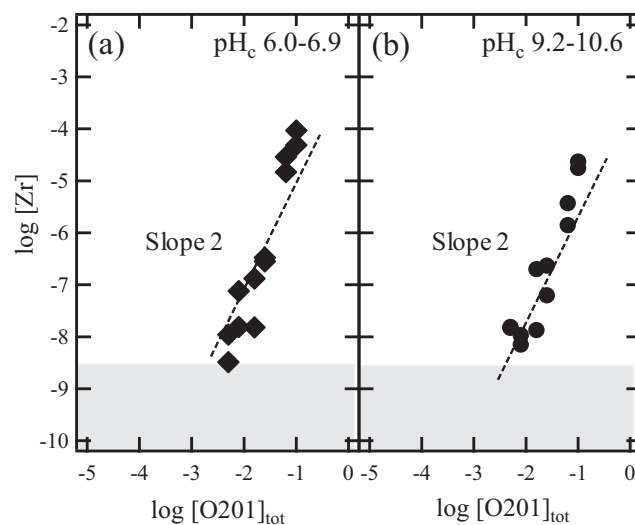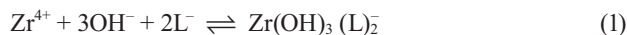

Figure 6. Zr(IV) solubility at (a) pH_c = 6.0–6.9 and (b) pH_c = 9.2–10.6 as a function of total O201 concentration after aging for 63–176 d. The ICP-MS detection limit is indicated by the gray shading.

two O201 ligands. Thus, we established that the ternary complexes, $Zr(OH)_3(O201)_2^-$ and $Zr(OH)_4(O201)_2^{2-}$, formed under the experimental conditions. Although an additional Zr(IV)-O201 complex with five OH groups might exist in the high alkaline pH region at $pH_c > 12$ as discussed above, this species was not taken into consideration in the analysis due to the lack of data for the Zr(IV) solubility dependence on $[O201]_{tot}$.

3.2. Thermodynamic model for Zr(IV) hydroxycarboxylic acid complex formation. Assuming the solid phase to be $Zr(OH)_4(am)$, the dependence of Zr(IV) solubility on pH_c and $[L]_{tot}$ suggested the formation of ternary Zr(IV)-OH-L complexes (L = O20 or O201) as described below.

$$Zr^{4+} + 3OH^- + 2L^- \rightleftharpoons Zr(OH)_3(L)_2^- \tag{1}$$

$$
\begin{aligned}
\log\beta_{132} = {} & \log[Zr(OH)_3(L)_2^-] - \log[Zr^{4+}] \\
& - 3\log[OH^-] - 2\log[L^-]
\end{aligned} \tag{2}
$$

$$Zr^{4+} + 4OH^- + 2L^- \rightleftharpoons Zr(OH)_4(L)_2^{2-} \tag{3}$$

$$
\begin{aligned}
\log\beta_{142} = {} & \log[Zr(OH)_4(L)_2^{2-}] - \log[Zr^{4+}] \\
& - 4\log[OH^-] - 2\log[L^-]
\end{aligned} \tag{4}
$$

In addition to Zr(IV)-OH-hydroxycarboxylate complexes, free Zr^{4+} was assumed to hydrolyze to $Zr(OH)_m^{(4-m)}$, so that the total concentration of soluble Zr(IV), $[Zr(IV)]_{tot}$, is expressed by the following sum:

$$
\begin{aligned}
[Zr(IV)]_{tot} &= [Zr^{4+}] + \sum_m [Zr(OH)_m^{(4-m)}] + \sum_{n=3,4} [Zr(OH)_n(L)_2^{(4-n-2)}] \\
&= \frac{K_{sp}}{[OH^-]^4}\left\{1 + \sum_m \beta_{1m0}[OH^-]^m + \sum_{n=3,4}\beta_{1n2}[OH^-]^n[L^-]^2\right\},
\end{aligned} \tag{5}
$$

where K_{sp}, β_{1m0}, and β_{1n2} are the solubility product, hydrolysis constant, and formation constant, respectively, of the Zr(IV)-hydroxycarboxylate system. Because the O20 and O201 carboxylate groups are deprotonated at the experimental pH_c range according to their dissociation constants [18,19], and $[L]_{tot}$ is much higher than $[Zr(IV)]_{tot}$, the concentrations of free O20 or O201 were assumed to have equal $[L]_{tot}$. As in our previous study [14], K_{sp}, and β_{1m0} were taken from the literature [4,6], and corrections for ionic strength were applied using the specific ion interaction theory (SIT) [8]. Values of β_{132}° and β_{142}° at $I = 0$ determined by least square fitting analysis of the solubility data are summarized in Table 1, which includes results for ISA and GLU [14].

Our $\log\beta_{142}^\circ$ value for O20 was higher than the hydrolysis constant $\log\beta_{160}^\circ = 48.0$ [4] and 50.95 [22] reported for $Zr(OH)_6^{2-}$, where six monodentate OH^- ligands bound to Zr. This possibly suggested that the deprotonated α-hydroxyl and carboxylate groups of O20 ($O20_{-H}$) combined to bind in a bidentate manner as described below.

$$
\begin{aligned}
Zr(OH)_4(O20)_2^{2-} &\rightleftharpoons Zr(OH)_3(O20)(O20_{-H})^{2-} + H_2O \\
&\rightleftharpoons Zr(OH)_2(O20_{-H})_2^{2-} + 2H_2O
\end{aligned} \tag{6}
$$
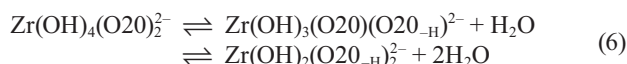
However, the difference between the formations of these species did not appear in the solubility experiment and analysis as a function of pH_c and $[L]_{tot}$. In the present study, the expression $Zr(OH)_4(O20)_2^{2-}$ was used for simplicity. The β_{142}° value for O201 was one order of magnitude higher than that for O20. Because steric hindrance makes it difficult for the α- and β-hydroxyl groups of O201 to bind simultaneously to a single Zr atom, the larger β_{142}° value for O201 may point to the formation of polynuclear species with the identical [Zr(OH)₄

$(O201)_2^{2-}]_n$ stoichiometry, as suggested for U(VI) [23]. The log β_{142}° values for O20 and O201 in Table 1 are a few orders of magnitude smaller than those for GLU and ISA. Because GLU and ISA have four (α-, β-, γ-, and δ-) hydroxyl groups on their alkyl chains (Figure 1), the additional two γ- and δ-hydroxyl groups likely play a role in the formation of more stable Zr-OH-GLU and Zr-OH-ISA complexes.

4. Conclusion

Zirconium(IV) solubility in the presence of the O20, O21, and O201 hydroxycarboxylic acids was investigated at $pH_c = 7–13$ and $[L]_{tot} = 10^{-4}–10^{-1}$ M. The dependence of Zr(IV) solubility on pH_c and $[L]_{tot}$ suggested that $Zr(OH)_3(L)_2^-$ and $Zr(OH)_4(L)_2^{2-}$ were the principal species under the experimental conditions. Formation constants determined by least square fitting analysis of solubility data were compared with the formation constants of zirconium-poly(hydroxy) carboxylates to understand the mechanism of Zr(IV)-hydroxycarboxylate complex formation. These results may also help to identify some organic ligands which can compete against the strong hydrolysis reactions of polyvalent radionuclides to enhance their solubilities under disposal conditions.

References

(1) C. Ekberg, G. Kallvenius, Y. Albinsson, P. Brown, J. Solution Chem. 33, 47 (2004).

(2) C. Hagfeldt, V. Kessler, I. Persson, J. Chem. Soc. Dalton Trans. Inorg. Chem. 14, 2142 (2004).

(3) C. Walther, J. Roche, M. Füss, S. Büchner, S. Koltsov, T. Bergmann, Anal Bioanal Chem. 388, 409 (2007).

(4) T. Sasaki, T. Kobayashi, I. Takagi, H. Moriyama, J. Nucl. Sci. Technol. 45, 735 (2008).

(5) T. Sasaki, O. Nakaoka, R. Arakawa, T. Kobayashi, I. Takagi, H. Moriyama, J. Nucl. Sci. Technol. 47, 1211 (2010).

(6) T. Sasaki, T. Kobayashi, I. Takagi, H. Moriyama, Radiochim. Acta 94, 489 (2006).

(7) M. Altmaier, V. Neck, Th. Fanghänel, Radiochim. Acta 96, 541 (2008).

(8) W. Hummel, G. Anderegg, L. Rao, I. Puigdomènech, O. Tochiyama, Chemical Thermodynamics of Compounds and Complexes of U, Np, Pu, Am, Tc, Se, Ni and Zr with Selected Organic Ligands. Elsevier, North-Holland, Amsterdam (2005).

(9) T. Kobayashi, T. Sasaki, I. Takagi, H. Moriyama, J. Nucl. Sci. Technol. 48, 993 (2011).

(10) T. Kobayashi and T. Sasaki, J. Solution Chem. 46, 1741 (2017).

(11) A. Grinberg and V. Astapovich, Russ. J. Inorg. Chem. 6, 164 (1961).

(12) R. Caletka, M. Kyrs, J. Rais, J. Inorg. Nucl. Chem. 26,

TABLE 1: Formation constants of Zr(IV)-OH-hydroxycarboxylate complexes ($I = 0$)

Reactions	Values		Reference
$Zr^{4+} + 4OH^- + 2O20^- \rightleftharpoons Zr(OH)_4(O20)_2^{2-}$	$\log\beta^\circ_{142}$	51.8±0.1	Present study
$Zr^{4+} + 3OH^- + 2O201^- \rightleftharpoons Zr(OH)_3(O201)_2^-$	$\log\beta^\circ_{132}$	48.2±0.2	Present study
$Zr^{4+} + 4OH^- + 2O201^- \rightleftharpoons Zr(OH)_4(O201)_2^{2-}$	$\log\beta^\circ_{142}$	52.7±0.1	Present study
$Zr^{4+} + 4OH^- + 2GLU^- \rightleftharpoons Zr(OH)_4(GLU)_2^{2-}$	$\log\beta^\circ_{142}$	54.1	[14]
$Zr^{4+} + 5OH^- + 2GLU^- \rightleftharpoons Zr(OH)_5(GLU)_2^{3-}$	$\log\beta^\circ_{152}$	56.5	[14]
$Zr^{4+} + 4OH^- + 2ISA^- \rightleftharpoons Zr(OH)_4(ISA)_2^{2-}$	$\log\beta^\circ_{142}$	54.2	[14]
$Zr^{4+} + 5OH^- + 2ISA^- \rightleftharpoons Zr(OH)_5(ISA)_2^{3-}$	$\log\beta^\circ_{152}$	55.6	[14]

1443 (1964).

(13) T. Kobayashi, T. Sasaki, I. Takagi, H. Moriyama, J. Nucl. Sci. Technol. 46, 142 (2009).

(14) T. Kobayashi, T. Teshima, T. Sasaki, A. Kitamura, J. Nucl. Sci. Technol. 54, 233 (2017).

(15) B.F. Greenfield, A.D. Moreton, M.W. Spindler, S.J. Williams, D.R. Woodwark, Mater. Res. Soc. Symp. Proc. 257, 299 (1992).

(16) J. Tits, E. Wieland, M. H. Bradbury, P. Eckert, A. Schaible, Paul Scherrer Institut, PSI Report No. 02-03, Switzerland (2002).

(17) X. Gaona, V. Montoya, E. Colas, M. Grive, L. Duro, J. Contaminant Hydrology 102, 217, (2008).

(18) R. M. Smith *NIST Critically Selected Stability Constants of Metal Complexes Database Version 5.0*, National Institute of Standards & Technology, U.S. Secretary of Commerce, Gaithersburg, USA (1998).

(19) D. Rai, M. Yui, D. A. Moore, L. Rao, J. Solution Chem. 38, 1573 (2009).

(20) T. Stumpf, Th. Fanghänel, I. Grenthe, J. Chem. Soc., Dalton Trans. 3799 (2002).

(21) T. Toraishi, I. Farkas, Z. Szabo, I. Grenthe, J. Chem. Soc., Dalton Trans. 24, 3805 (2002).

(22) D. Rai, A. Kitamura, M. Altmaier, K. M., Rosso, T. Sasaki, T. Kobayashi, J. Solution Chem. 47, 855 (2018).

(23) H. Brinkmann, M. Patzschke, P. Kaden, M. Raiwa, A. Rossberg, R. Kloditz, K. Heim, H. Moll, T. Stumpf, Dalton Trans. 48, 13440 (2019).