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

Taishi Kobayashi*a, Wang Pengb, Takayuki Sasakia

aDepartment of Nuclear Engineering, Kyoto University, Kyotodaigaku-katsura, Nishikyo-ku, Kyoto 615-8540, Japan

Received January 14, 2020; Accepted March 18, 2020; Published online April 14, 2020

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 pHc = −log [H+] = 7−13 and total hydroxycarboxylic acid concentrations, [L]tot = 10−4−10−1 M. The Zr solubility dependences on pHc and [L]tot indicated that ternary Zr(OH)4(L)2 complexes were the dominant soluble species under the experimental conditions. The formation constants of the Zr(OH)4(L)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/dm³ (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 93Zr (T1/2=1.53×106 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, C2O) 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 C2O 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 (HOCH2(CHOH)4COOH, GLU) and α-isosaccharinic (CH2OHCHOHCH2OH-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 (pHc) 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 ZrCl4 (FUJIFILM Wako) as described in our previous study [14]. A PIPES buffer (Dojindo) was used to adjust pHc 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 O2 concentrations below 10 ppm at 25 °C. A combination glass electrode (9615-10D, Horiba Ltd.) was used to measure pHc. The Ag/AgCl electrode was filled with 3.6 M NaCl and 0.4 M NaClO3 to prevent precipitation of KClO3 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 NaClO4 to correct experimentally measured pHexp values to pHc.

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 pHc and [L]tot values within the pHc range of 7 to 13 and [L]tot range of 10−4 to 10−1 M. Total dissolution of Zr(OH)4(am) was determined to a maximum Zr concentration of 0.01 M. The structures of the hydroxyacetic acids used in this study and of GLU and ISA are shown in Figure 1, together with their reported dissociation constants for the carboxylic...
Kobayashi J. Nucl. Radiochem. Sci., Vol. 20, 2020

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 O$_2$O as a function of pH$_c$. Zirconium solubility in the absence of O$_2$O [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 O$_2$O was close to that in the absence of O$_2$O, although concentrations were almost at the detection limit of ICP-MS. However, Zr(IV) solubility in the presence of 0.1 M O$_2$O 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 O$_2$O. Zr(IV)-O$_2$O complexes were considered to be the predominant Zr(IV) species in 0.1 M O$_2$O 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)-O$_2$O complex contained four OH groups in its chemical formula.

Figure 3 shows Zr(IV) solubility in the presence of O$_2$O as a function of [O$_2$O]$_{tot}$ 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 O$_2$O ligands were present in the Zr(IV)-O$_2$O complex. Therefore, we assumed that Zr(OH)$_4$(O$_2$O)$_2^{2-}$ was the major species in the solution.

The formation of glycolate (O$_2$O) complexes with trivalent and tetravalent metal ions has been reported in the literature, but mainly in acidic solutions. Binary O$_2$O complexes including polynuclear species have been proposed under conditions of higher metal ion and O$_2$O 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 O$_2$O 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...
Thermodynamic interpretation of zirconium solubility in the presence of 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 pHc. 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 (CH2(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 pHc 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 pHc 8 and $10^{-6.5}$ M at pHc > 10. Provided that the solid phase retained its Zr(OH)4(am) stoichiometry, the slope of $-1$ found at pHc 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 pHc was almost zero at pHc 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 pHc > 12, the Zr(IV) was observed to increase with increasing pHc 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 pHc $= 6.0–6.9$ and 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.

3.2. Thermodynamic model for Zr(IV) hydroxyacarboxylic acid complex formation. Assuming the solid phase to be Zr(OH)4(amide), the dependence of Zr(IV) solubility on pHc and [L]tot suggested the formation of ternary Zr(IV)-OH-L complexes (L = O20 or O201) as described below.
\[ \text{Zr}^{4+} + 3\text{OH}^- + 2\text{L}^- \rightleftharpoons \text{Zr(OH)}_3^+\text{(L)}_2^2^- \] (1)

\[ \text{log} \beta_1^{132} = \text{log} \left[ \text{Zr(OH)}_3^+(\text{L})_2^2^- \right] - \text{log} \left[ \text{Zr}^{4+} \right] - 3 \text{log}[\text{OH}^-] - 2\text{log}[\text{L}^-] \] (2)

\[ \text{Zr}^{4+} + 4\text{OH}^- + 2\text{L}^- \rightleftharpoons \text{Zr(OH)}_4^+\text{(L)}_2^2^- \] (3)

\[ \text{log} \beta_1^{142} = \text{log} \left[ \text{Zr(OH)}_4^+(\text{L})_2^2^- \right] - \text{log} \left[ \text{Zr}^{4+} \right] - 4 \text{log}[\text{OH}^-] - 2\text{log}[\text{L}^-] \] (4)

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

\[ [\text{Zr(IV)}]_{\text{tot}} = [\text{Zr}^{4+}] + \sum_{n=1}^{m} [\text{Zr(OH)}^{4n-m}_m] + \sum_{n=1}^{m} [\text{Zr(OH)}_n^m(\text{L})^{4-n-2}_2] \] (5)

where \( K_{\text{sp}, \text{Zr(IV)}} \) and \( \beta_{132} \) are the solubility product, hydrolysis constant, and formation constant, respectively, of the Zr(IV)-hydroxycarboxylate system. Because the O20 and O201 hydroxycarboxylic acids was investigated at \( \text{pH}_c = 7-13 \) and \([\text{L}]_{\text{tot}} = 10^{-4}-10^{-1} \text{M} \), the dependence of Zr(IV) solubility against the strong hydrolysis reactions of polyvalent radionuclides 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. Koltsosv, 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, Radincho. Acta 94, 489 (2006).
7. M. Altmaier, V. Neck, Th. Fanghanel, Radiochim. Acta 96, 541 (2008).
8. W. Hummel, G. Anderleg, L. Rao, I. Puigdomènech, O. Tochiyama, Chemical Thermodynamics of Compounds and Complexes of U, Np, Pu, Am, Th, 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,
Thermodynamic interpretation of zirconium solubility in the presence of

(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. Woodwarke, 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. Fanghanel, 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. Altmairer, 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).