

**Solubility of zirconium and thorium
in aqueous solutions containing organic acids**

2010

Taishi Kobayashi

Contents

CHAPTER 1	GENERAL INTRODUCTION.....	1
1.1	INTRODUCTION.....	1
1.1.1	<i>The influence of organic acids on migration behavior of radionuclide</i>	<i>1</i>
1.1.2	<i>Hydrolytic behavior of tetravalent metal ion</i>	<i>3</i>
1.2	CURRENT KNOWLEDGE IN LITERATURE	4
1.2.1	<i>Hydrolysis of zirconium(IV)</i>	<i>4</i>
1.2.2	<i>Hydrolysis of thorium(IV)</i>	<i>6</i>
1.2.3	<i>Interactions of zirconium(IV) and thorium(IV) with organic acids</i>	<i>8</i>
1.3	CONCLUSION	9
	REFERENCES	10
CHAPTER 2	SOLUBILITY OF HYDROXIDE AND OXIDE	29
2.1	INTRODUCTION.....	29
2.2	EXPERIMENTAL	30
2.2.1	<i>Sample preparation</i>	<i>30</i>
2.2.2	<i>Solubility measurement</i>	<i>31</i>
2.3	RESULTS AND DISCUSSION.....	32
2.3.1	<i>Solubility of Amorphous Zirconium Hydroxide by Oversaturation Method</i>	<i>32</i>
	Solubility in the acidic, neutral and alkaline pH _c range	32
	Size distributions of colloidal species.....	33
	Solubility product of Zr(OH) ₄ (am)	35
2.3.2	<i>Solubility of Amorphous Thorium Hydroxide by Oversaturation Method</i>	<i>36</i>
	Solubility in the acidic, neutral and alkaline pH _c range	36
	Size distributions of colloidal species and solubility product of Th(OH) ₄ (am)	36
2.3.3	<i>Solubility of Crystalline Zirconium Oxide and Dehydrated Hydroxide by Undersaturation Method</i>	<i>37</i>
	Solubility in the acidic, neutral and alkaline pH _c range	37
	Solubility product of ZrO ₂ (cr)	39
	Influence of the formation of colloidal species on solubility	39
2.4	CONCLUSION	40
	REFERENCES	41
CHAPTER 3	HYDROLYSIS CONSTANT OF ZIRCONIUM AND THORIUM ...	60
3.1	INTRODUCTION.....	60
3.2	HARD SPHERE MODEL FOR POLYNUCLEAR SPECIES	61
3.2.1	<i>The structure and formation reaction of polynuclear hydrolysis species</i>	<i>61</i>

3.2.2	<i>Model parameters and analytical procedure</i>	62
	Dielectric constant	62
	Effective charges of ions	63
	Hydrolysis constants	63
	Analytical procedure	64
3.3	DISCUSSION	65
3.3.1	<i>Obtained parameters and hydrolysis constants</i>	65
3.3.2	<i>Contributions of polynuclear species to the solubility</i>	66
3.4	CONCLUSION	66
	REFERENCES	67
CHAPTER 4	SOLUBILITY IN THE PRESENCE OF ORGANIC ACID	79
4.1	INTRODUCTION	79
4.2	EXPERIMENTAL	80
4.2.1	<i>Sample preparation</i>	80
4.2.2	<i>Solubility measurement</i>	80
4.2.3	<i>Solid phase analysis</i>	81
4.3	RESULTS AND DISCUSSION	82
4.3.1	<i>Zirconium solubility in ternary aqueous system of Zr(IV)-OH-carboxylate</i>	82
	Solubility in the presence of oxalic and malonic acids	82
	Solid phase in the presence of oxalic and malonic acids	83
4.3.2	<i>Solubility products in Zr(IV)-OH-carboxylate system</i>	85
	Formation constants and solubility products in Zr-OH-oxalate system	85
	Formation constants and solubility products in Zr-OH-malonate system	87
4.3.3	<i>Thorium solubility in ternary aqueous system of Th(IV)-OH-carboxylates</i>	88
	Solubility in the presence of oxalic and malonic acids	88
	Solid phase in the presence of oxalic and malonic acids	89
4.3.4	<i>Solubility products in Th(IV)-OH-carboxylate system</i>	90
	Formation constants and solubility products in Th-OH-oxalate/malonate system	90
4.4	CONCLUSION	91
	REFERENCES	92
CHAPTER 5	GENERAL CONCLUSION	116
	ACKNOWLEDGEMENT	119
	LIST OF PUBLICATIONS	120

Chapter 1 General Introduction

1.1 Introduction

1.1.1 The influence of organic acids on migration behavior of radionuclide

Radioactive waste disposal is a critical problem involved in the development of sustainable use of nuclear energy. Furthermore, disposal of the waste is also essential for the implementation of the nuclear fuel cycle, which is necessary from the standpoint of global warming issues, as well as energy security issues. Waste with relatively high levels of radioactivity, such as High Level Waste (HLW) and transuranium (TRU) waste requires careful attention in order to properly manage the disposal process. In accordance with the Atomic Energy Commission in Japan, these wastes are to be laid and disposed in a stable geological formation at a depth of more than 300 meters, so as not to pose a threat to humans or the environment. The establishment of a reliable safety assessment for geological disposal based on an understanding of radionuclide migration behavior underground is therefore required. Geological disposal of the radioactive waste requires that the waste is vitrified and covered with a stainless container and buffer materials. Thus, the radionuclide in the waste would have to penetrate various barrier systems in order to migrate into the natural environment. Slow groundwater flow and sorption to natural rocks around the disposal site also slows the radionuclide transport before reaching the biosphere. Among the many processes, radionuclide migration by groundwater flow is one of the primary processes and the most feasible. However, the chemical behavior of radionuclides in groundwater needs to be clarified in order to better understand radionuclide migration.

In groundwater, there are various inorganic and organic ligands. Anionic species interact with radionuclides to form stable complexes and compounds and subsequently influence the migration behavior. Among a wide variety of anionic ligands, some organic acids with multidentate chelating ligands can coordinate with metal ions strongly, and would thus play an important role in their behavior. In order to achieve a reliable assessment, the quantitative prediction of the reactions must be considered to estimate the quantity of radionuclide that can be transported in the aqueous phase.

Therefore, it is essential to characterize soluble species, the solid phase, and to know the relative stabilities of both. Thermodynamic data such as equilibrium constants are required for modeling the behavior of radionuclides in groundwater.

Among the various organic acids, oxalic acid can coordinate a metal ion with a bidentate configuration, and is known to have high coordination strength. The high coordination strength and simple structure of oxalic acid make it a good candidate for a model system for organic acids and organic matters. Additionally, oxalic acid is the major product of radiolytic degradation of ion exchange resins used in decontamination procedures. Thus, oxalic acid is one of the most important organic acids for understanding the behavior of actinide elements and fission products at the disposal site [1].

The interaction between oxalic acid and the tetravalent metal ion may shed some light on the strong coordination ability of oxalic acid. Tetravalent metal ions are present as M^{4+} ions in aqueous solution and have a very strong tendency to hydrolyze [2-6]. This indicates that the complexation of oxalic acid with a tetravalent ion is competitive with the hydrolysis reaction. Soluble species and solid phase precipitates will be produced as a result of competitive reactions. However, there very little are known about the dominant soluble species and solid phase composition, especially in the near neutral pH region, where the hydrolysis reaction is thought to be competitive with the complexation reaction.

Thorium, plutonium and neptunium in HLW are known to exhibit high levels of radioactivity for a long period of time and are present as tetravalent ions under reductive conditions deep underground (Fig. 1) [7]. Thus, an understanding of the migration behavior of tetravalent actinides is essential for safety assessment. Recently, it has been reported that the tetravalent colloidal species may play an important role in the acceleration of radionuclide migration [8]. In order to reveal the characteristic reactions of such colloidal species, the fundamental hydrolysis reaction and interactions with typical organic acids need to be clarified. The migration behavior of the tetravalent actinides is predominantly controlled by their solubility in groundwater; therefore, thermodynamic data such as the stability constant of soluble complexes and the solubility product of solid phases are required.

In the present study, malonic acid, which has a similar structure to oxalic acid and weaker coordination strength (due to steric effects) [9,10], is investigated in order to reveal a relationship between the coordination strength and the formation of the complexes and the solid phases. Zirconium(IV) and thorium(IV) are studied as typical and stable tetravalent ions in aqueous solution.

1.1.2 Hydrolytic behavior of tetravalent metal ion

Before discussing the competition between complexation and hydrolysis reactions, the hydrolysis reactions of zirconium and thorium are discussed in the present study. As described above, tetravalent metal ions in aqueous solution are quite easily hydrolyzed. The hydrolysis reactions of zirconium and thorium are accompanied by the formation of not only mononuclear species, but also polynuclear and colloidal species. These processes are very complicated [11-21] and the mechanisms remain controversial. Various different polynuclear species have been proposed in the analysis of experimental data, and their hydrolysis constants have been obtained. However, in most cases, the polynuclear species were confirmed by indirect methods such as potentiometry, solvent extraction and solubility analysis. Moreover, the determination of hydrolysis constants requires some assumptions about the dominant species. These assumptions differ in the literature. In a recent study, polynuclear species in solution have been directly observed using electrospray ionization mass spectrometry (ESI-MS) [22,23]. Some types of polynuclear species were confirmed to be present in solution; however the hydrolysis constants of polynuclear species still remain controversial. Colloidal species obtained by hydrolysis have been reported in the literature [24-31]. A recent laser induced breakdown detection (LIBD) measurement detected colloidal species of zirconium(IV) and thorium(IV) in an oversaturated solution [28-31], but there is very little quantitative information.

The apparent solubility is a summation of the concentrations of mononuclear, polynuclear and colloidal species in solution, which are in equilibrium with the solid phase. Therefore, the solubility-limiting solid phase is another important factor involved with understanding solubility. The concentration of free tetravalent ion ($[M^{4+}]$) in a solution is controlled by the solubility-limiting solid phase. In the case of amorphous

hydroxide, the state of the solid phase such as crystallinity can be easily influenced by the experimental conditions [32]. The scatter of the data and thermodynamic constants may be also caused by the differences among the solid phases. Therefore, attention to the solubility-limiting solid phase is required.

1.2 Current knowledge in literature

1.2.1 Hydrolysis of zirconium(IV)

The outer electron configuration of zirconium is $4s^2 4p^6 4d^2 5s^2$ and zirconium exists in a stable tetravalent state, releasing four electrons from the $4d$ and $5s$ orbital in aqueous solution. The long lived isotope ^{93}Zr (1.53×10^6 y) is included in HLW abundantly as a fission product, therefore, it is an important element for safety assessment of the disposal.

Hydrolysis constant

Similar to other tetravalent metals, zirconium has been thought to form not only mononuclear hydrolysis species, but also polynuclear and colloidal species in aqueous solution [11-15,33-35]. The hydrolysis constants reported in the literature are summarized in Table 1.1 [5,11-15,31,36-40]. The reported values of the first hydrolysis constant ($\beta_{1,1}$) are in relatively good agreement with each other, although they have been obtained by various experimental methods including; potentiometric measurements, solubility measurements and solvent extraction. In contrast, the values for the highly hydrolyzed species differ from each other and the values of $\beta_{1,4}$ vary by more than 10 orders of magnitude. The constant of formation of the highly hydrolyzed species was determined under high pH conditions and in such pH regions that zirconium can easily form polynuclear and colloidal species. The scatter of the reported values is thought to be due to the contribution of polynuclear and colloidal species.

As shown in Table 1.1, a number of different polynuclear species have been proposed, and among these species, the existence of $\text{Zr}_3(\text{OH})_4^{8+}$ and $\text{Zr}_4(\text{OH})_8^{8+}$ have been noted in a number of literature reports. Recently, several kinds of zirconium polynuclear species including $\text{Zr}_3(\text{OH})_4^{8+}$ and $\text{Zr}_4(\text{OH})_8^{8+}$ were directly detected using ESI-MS [22]. The relative abundances of mononuclear and polynuclear species present

simultaneously in solution were measured, and their hydrolysis constants were estimated (Table 1.1). Although these values were not expected to have sufficient accuracy, it was indicated that a realistic description of zirconium hydrolysis required a much larger number of complexes [22].

Contribution of colloidal species

In an oversaturated zirconium solution, colloidal species over 5 nm were detected by LIBD measurement [31]. The size of the species increased with an increase of pH in the solution, indicating the growth of the colloidal species. In this work, the size of colloidal species was observed to vary from a few nanometers to a few hundred nanometers. Small colloidal species may pass through filters, which would be used to separate the liquid phase in a solubility experiment. It is necessary to reveal the contribution of colloidal species to the apparent solubility for a reliable evaluation of the solubility.

Solubility-limiting solid phase and solubility product

The reported solubility products and solubility data are shown in Table 1.2 and Fig. 1.2, respectively [2,5,14,15,31,36,37,41]. There is a large discrepancy in the reported values, which may be because of the differences in both experimental and analytical conditions.

Cho et al. reported that a solution prepared by the oversaturation method may contain colloidal species [31]. High solubility data were reported by Bilinski et al. [37]; however, in this work no filtration was carried out, which suggests the presence of colloidal species. The apparent solubility is also influenced by the state of the solid phase. Kovalenko and Bagdsarov [36] and Veyland et al. [14] prepared sample solutions from $\text{Zr}(\text{OH})_4(\text{am})$ precipitate using an undersaturation method. In their experiments, the precipitate was neither dried nor treated at high temperature. This solid phase is thought to be different from $\text{Zr}(\text{OH})_4(\text{s})$ (Aldrich), which consisted of dried powder and was used in the solubility experiment by Ekberg et al. [15]. Thus, in the case of hydroxide, the differences in experimental conditions and treatments of the solid phases may contribute to the scattered solubility product values. The differing hydrolysis constants used in the analysis of the solubility data may also play a role in

these differences.

Zirconium hydroxide has been reported to be dehydrated and crystallized to form zirconium oxide at high temperatures [42], indicating that zirconium oxide is thermodynamically stable. In the safety assessment, especially a long-term assessment, solubility under a stable condition must be estimated, however, there have been very few reports on the solubility product of crystalline zirconium oxide ($\text{ZrO}_2(\text{cr})$) [41].

1.2.2 Hydrolysis of thorium(IV)

The outer electron configuration of thorium is $6s^2 6p^6 6d^2 7s^2$ and thorium exists in the stable tetravalent state in aqueous solution. The isotopes ^{229}Th (7.34×10^3 y) and ^{230}Th (7.54×10^4 y), which are the daughter radionuclide of uranium, are regarded as important nuclides in the safety assessment of geological disposal.

Hydrolysis constant

Similar to zirconium, thorium is known to form mononuclear and polynuclear species in an aqueous solution [16-21]. A large number of studies have been conducted in order to evaluate the hydrolysis behavior of thorium [16-21,23,43-45], and various hydrolysis species have been found to form and recently reviewed [46] (Table 1.3). For example, Grenthe et al. investigated the stability constants of Th(IV) hydrolysis species using an electromotive force titration technique at a concentration of $10^{-3} \text{ mol} \cdot \text{dm}^{-3}$ (M). In order to determine the hydrolysis constants from the titration curve, both mononuclear and polynuclear complexes such as $\text{Th}_4(\text{OH})_8^{8+}$ were considered [18]. Ekberg et al. applied both potentiometry and solvent extraction techniques. At acidic pHs, the presence of the mononuclear ThOH^{3+} and $\text{Th}(\text{OH})_2^{2+}$ and polynuclear $\text{Th}_4(\text{OH})_8^{8+}$ and $\text{Th}_6(\text{OH})_{15}^{9+}$ species was assumed, on the other hand, the additional mononuclear species $\text{Th}(\text{OH})_3^+$ and $\text{Th}(\text{OH})_4(\text{aq})$ were considered in solvent extraction at near-neutral pH conditions [21]. Some of the values may be inconsistent hypotheses concerning the existence of mononuclear and polynuclear species in solutions.

In order to obtain reliable hydrolysis constants for mononuclear species, the Th concentration in an experiment must be lowered to assure no effect from polynuclear and colloidal species. In our previous work, a solvent extraction technique was adopted with a trace amount of thorium in order to avoid the formation of polynuclear and

colloidal species [10].

Contribution of colloidal species

Th colloidal species was observed by LIBD measurement and the effect on the solubility was investigated [28-30]. Altmaier et al. measured and discussed the contribution of the colloidal species in diluted and concentrated NaCl and MgCl₂ solution [27]. The colloidal species had a long-time stability of more than 400 days and called “eigencolloid”. Ionic strength and chloride concentration were observed to have no effect on the stability of these eigencolloid. This hydrophilic oxyhydroxide eigencolloid was considered to be a large aqueous species and had high solubility in the neutral pH region ($[Th] \approx 10^{-6}$ M). Furthermore, if centrifugation for phase separation was not sufficient, the apparent solubility may include the contribution of the colloid.

Solubility-limiting solid phase and solubility product

The reported solubility products and solubility data are shown in Table 1.4 and Fig. 1.3, respectively [2,19,28,29,32,45-50]. A large number of studies have been performed and the reported solubility product values are scattered. In the case of thorium, although the dominant soluble species in a solution is still controversial, the difference in the solid phase is a more likely reason for the scattering. Moon, Felmy and Rai et al. prepared sample solutions from amorphous hydroxide using an undersaturation method and used similar filters in size to separate the liquid phases before measurement of the solubility [19,47-49]. This solubility data showed similar values to those shown in Fig. 1.3. On the other hand, Östhols and Neck et al. dried the amorphous precipitate before preparing sample solutions by the undersaturation method [29,32]. The solubility was obviously lower than those reported by Moon, Felmy and Rai et al., indicating that the solid phases are possibly different. It is interesting that the solubility of dried Th(OH)₄(am) using the undersaturation method and Th concentrations at the onset of colloid formation showed similar values [29].

Bundschuh and Neck proposed the existence of another kind of solid phase, microcrystalline (ThO₂ · xH₂O(mcr)) [28, 50]. This solid phase was formed by titrating NaOH very slowly into an oversaturated solution. Recently, the differences of the solubility products in these solid phases have been discussed in terms of particle size

effects [46]. The variation of the apparent solubility was considered to be a result of surface hydration and particle size variation. Dehydration by condensation of smaller particles leads to larger and less hydrated particles with smaller molar surface and hence to a bulk solid phase of lower Gibbs energy and solubility. Aging effect observed for fresh amorphous precipitates were discussed in terms of the increasing particle size and the solubility products for $\text{ThO}_2(\text{am, hyd, fresh})$ and $\text{ThO}_2(\text{am, hyd, aged})$ were selected in the literature [46].

The solubility of crystalline thorium oxide ($\text{ThO}_2(\text{cr})$) was measured in the literature, however; experiments using well-crystallized $\text{ThO}_2(\text{cr})$ are expected to be inconsistent due to the very slow dissolution kinetics [49,50]. After additional heating of $\text{ThO}_2(\text{cr})$ at 750°C for 8 hours, Neck et al. measured the solubility and found that the equilibrium was not achieved, even after 318 days [50]. On the other hand, Rai et al. prepared $\text{ThO}_2(\text{cr})$ firing Th oxalate salt at 750°C for 2 hours, and confirmed the possible presence of a finite amount of less crystalline material (estimated from their experiments to be about one percent) [49]. However, the solubility after heating at 90°C to remove the less crystalline material was still higher than that reported by Neck et al. There may be still a difference between the two solid phases.

The solubility products of tetravalent actinides including thorium have been compared and discussed in terms of ionic radius [51]. In tetravalent actinides, the ionic radius decreases from Th to Pu due to actinide contraction, and the force of electrostatic interactions is expected to increase along with an increase in the surface density of charge. The solubility products of hydroxide and oxide are thought to decrease in proportion to inverse of the square of the ionic radius (Fig. 1.4) [19,32,45,47-50,52-58]. This relationship may help to determine reliable solubility products for thorium hydroxide and oxide.

1.2.3 Interactions of zirconium(IV) and thorium(IV) with organic acids

The thermodynamic constants of Zr and Th with oxalic and a number of other carboxylic acids are summarized in Table 1.5 [10,59-67]. In general, it was observed that precipitates formed on adding oxalic acid or oxalate salts to solutions of zirconium and thorium, and that the precipitates dissolved and very stable soluble complexes were

formed when excess acids were added [1]. However, there have been very few reports of thermodynamic constants such as the solubility product and complex formation constants. There have been a few reported values of Zr, Th along with other carboxylic acids including malonic acid.

In our previous work, a solvent extraction technique was developed using a trace amount of Th in order to avoid the formation of polynuclear and colloidal species, and the complex formation constants of Th with some carboxylic acids were determined [10]. A systematic trend of the constants was discussed based on the alkyl chain length of the acids. In the case of Eu(III), similar trends were also observed and applied to the prediction of formation constant with humic acid. [9,68].

In order to understand and predict the solubility in the presence of organic acids, the solubility-limiting solid phase is another important factor. As described above, Zr and Th insoluble salts have been observed with carboxylic acids even under the competitive reaction of hydrolysis. Characterization of both dominant soluble species and the solid phase is required.

1.3 Conclusion

The aim of this thesis is to reveal the interactions of oxalic acid with Zr(IV) and Th(IV) during its competition with the hydrolysis reaction. By investigating the solubility, soluble species and the solid phase in a wide range of pH and the oxalic acid concentrations, the interactions between Zr(IV), Th(IV) ions and oxalic acid are discussed. Malonic acid revealed a relationship between the coordination strength and the formation of complexes and compounds. In order to achieve a quantitative understanding of the solubility, which is a result of the formation of soluble species and solid phases, the following should be taken into account.

1. Contribution of polynuclear species
2. Contribution of colloidal species
3. Solubility-limiting solid phase

The solubility of hydroxide and oxide in the absence of organic acid are discussed in the first half of this thesis in an effort to elucidate the contributions of polynuclear species and colloidal species on the apparent solubility.

Chapter 2 will address the solubility of zirconium hydroxide, oxide and thorium hydroxide. The solubility is measured over a wide range of pH and ionic strengths after filtration through various pore size filters. The contributions of the colloidal species on the apparent solubility and the solubility of mononuclear species were calculated based on the size distribution of the soluble species. The solubility products of hydroxide and oxide were determined from the “mononuclear” solubility.

The mononuclear and polynuclear hydrolysis constants are considered in Chapter 3, from a systematic point of view. The Hard Sphere Model is improved in order to calculate the polynuclear hydrolysis constants based on the electrostatic interactions between metal ions, hydroxyl ions and water molecules. The contribution of polynuclear species on the apparent solubility is discussed.

Based on the obtained knowledge and thermodynamic data in the previous chapters, the solubility of thorium and zirconium in the presence of oxalic and malonic acids are discussed in Chapter 4. Dominant soluble species and solubility-limiting solid phases, and the reactions of tetravalent metal ions with the acids are investigated and discussed with respect to competing hydrolysis reactions. Attention is especially given to the characterization of the solid phase.

References

1. Hummel, W., Anderegg, G., Rao, L., Puigdomènech, I., Tochiyama, O.: *Chemical Thermodynamics of Compounds and complexes of U, Np, Pu, Am, Tc, Se, Ni and Zr with selected organic ligands*, In: *Chemical Thermodynamics* (Eds.: F. J. Mompean et al.) Vol. 9, Elsevier, North-Holland, Amsterdam (2005).
2. Baes, C. F., Mesmer, R. E.: *The Hydrolysis of Cations*. John Wiley & Sons, New York (1976).
3. Grenthe, I., Fuger, J., Konings, R. J. M., Lemire, R. J., Müller, A. B., Nguyen-Trung, C., Wanner, H.: *Chemical Thermodynamics of Uranium*, In:

- Chemical Thermodynamics* (Eds.: F. J. Mompean et al.) Vol. 1. Elsevier, North-Holland, Amsterdam (1992).
4. Guillaumont, R., Fanghänel, Th., Fuger, J., Grenthe, I., Neck, V., Palmer, D., Rand, M.: *Update on the Chemical Thermodynamics of Uranium, Neptunium, Plutonium, Americium and Technetium*, In: *Chemical Thermodynamics* (Eds.: F. J. Mompean et al.) Vol. 5. Elsevier, North-Holland, Amsterdam (2003).
 5. Brown, P., Curti, E., Grambow, B., Ekberg, C.: *Chemical Thermodynamics of Zirconium*, In: *Chemical Thermodynamics* (Eds.: F. J. Mompean et al.) Vol. 8. Elsevier, North-Holland, Amsterdam (2005).
 6. Silva, R. J., Nitsche, H.: Actinide Environmental Chemistry. *Radiochim. Acta* **70/71**, 377 (1995).
 7. *H12: Project to Establish the Scientific and Technical Basis for HLW Disposal in Japan, Supporting Report 2*, Japan Nuclear Cycle Development Institute (2000).
 8. Kersting, A. B., Efurud, D. W., Finnegan, D. L., Rokop, D. K., Thompson, J. L.: Migration of plutonium in groundwater at the Nevada Test Site. *Nature*, **397**, 56 (1999).
 9. Sasaki, T., Kubo, S., Kobayashi, T., Takagi, I., Moriyama, H.: Measurement and Analysis of Formation Constants of Europium with Carboxylates. *J. Nucl. Sci. Technol.*, **42**, 724 (2005).
 10. Sasaki, T., Takaoka, Y., Kobayashi, T., Fujii, T., Takagi, I., Moriyama, H.: Hydrolysis constants and complexation of Th(IV) with carboxylates. *Radiochim. Acta*, **96**, 79 (2008).
 11. Zielen, A. J., Connick, R. E.: The hydrolytic polymerization of zirconium in perchloric acid solutions. *J. Amer. Chem. Soc.* **78**, 5785 (1956).
 12. Muha, G. M., Vaughan, P. A.: Structure of the complex ion in aqueous solutions of zirconyl and hafnyl oxyhalides. *J. Chem. Phys.* **33** 194 (1960).
 13. Tribalat, S., Schriver, L.: Zirconium(IV) thiocyanate complex. Its use as an indicator of thiocyanate or free zirconium. *C. R. Séances Acad. Sci., Ser. C*, **274**, 849 (1972).
 14. Veyland, A., Dupont, L., Pierrad C., Rimbault, J., Aplincourt, M.: Thermodynamic stability of zirconium(IV) complexes with hydroxy ions. *Eur. J. Inorg. Chem.* 1765

- (1998).
15. Ekberg, C., Kallvenius, G., Albinsson, Y., Brown, P.: Studies on the hydrolytic behavior of zirconium(IV). *J. Solution Chem.* **33**, 47 (2004).
 16. Baes, C. F., Meyer, N. J., Roberts, C. E.: Hydrolysis of thorium(IV) at 0 and 95°C. *J. Inorg. Chem.* **4**, 518 (1965).
 17. Brown, P. L., Ellis, J., Sylva, R. N.: The hydrolysis of metal-ions. Part 5. Thorium(IV). *J. Chem. Soc. Dalton Trans.* 31 (1983).
 18. Grenthe, I., Lagerman, B.: Studies on metal carbonate equilibria .23. Complex—formation in the Th(IV)-H₂O-CO₂(g) system. *Acta Chem. Scand.* **45**, 231(1991).
 19. Moon, H.: Equilibrium Ultrafiltration of Hydrolyzed Thorium(IV) Solutions. *Bull. Korean Chem. Soc.* **10**, 270 (1989).
 20. Engkvist, I., Albinsson, Y.: Hydrolysis Studies of Thorium Using Solvent Extraction Technique. *Radiochim. Acta* **58/59**, 109 (1992).
 21. Ekberg, C., Albinsson, Y., Comarmond, M. J., Brown, P. L.: Studies on the complexation behavior of thorium(IV). 1. Hydrolysis equilibria. *J. Sol. Chem.*, **29**, 63 (2000).
 22. Walther, C., Roche, J., Füss, M., Büchner, S., Koltsov, S., Bergmann, T.: Investigation of polynuclear Zr(IV) hydroxide complexes by nanoelectrospray mass-spectrometry combined with XAFS. *Anal Bioanal Chem.* **388**, 409 (2007).
 23. Walther, C., Fuss, M., Böchner, S.: Formation and hydrolysis of polynuclear Th(IV) complexes - a nano-electrospray mass spectrometry study. *Radiochim. Acta* **96**, 411 (2008).
 24. Neilson, G. F.: Small-Angle X-ray Scattering Analysis of Particle Size Distributions of Colloidal ThO₂ Sol. *J. Appl. Cryst.*, **6**, 386 (1973).
 25. Yamaguchi, S., Takahashi, Y., Shiba, K.: Preparation of ThO₂ Sols Having Colloid-Size Distributions Suitable for Gelation into Microspheres. *J. Nucl. Sci. Technol.*, **27**, 528 (1984).
 26. Rothe, J., Denecke, M. A., Neck, V., Müller, R., Kim, J. I.: XAFS Investigation of the Structure of Aqueous Thorium(IV) Species, Colloids, and Solid Thorium(IV) Oxide/Hydroxide. *Inorg. Chem.*, **41**, 249 (2002).
 27. Altmaier, M., Neck, V., Fanghänel, Th.: Solubility and colloid formation of Th(IV)

- in concentrated NaCl and MgCl₂ solution. *Radiochim. Acta* **92**, 537 (2004).
28. Bundschuh, T., Knopp, R., Müller, R., Kim, J. I., Neck, V., Fanghänel, Th.: Application of LIBD to the determination of the solubility product of thorium(IV)-colloids. *Radiochim. Acta* **88**, 625 (2000).
 29. Neck, V., Bouby, M., Altmaier, M., Rothe, J., Denecke, M. A., Kim, J. I.: Solubility of amorphous Th(IV) hydroxide - application of LIBD to determine the solubility product and EXAFS for aqueous speciation. *Radiochim. Acta* **90**, 485 (2002).
 30. Bitea, C., Müller, R., Neck, V., Walther, C., Kim, J. I.: Study of the generation and stability of thorium(IV) colloids by LIBD combined with ultrafiltration. *Colloids and Surfaces A: Physicochem. Eng. Aspects* **217**, 63 (2003).
 31. Cho, H., Walther, C., Roche, J., Neck, V., Denecke, M. A., Dardenne, K., Fanghänel, Th.: Combined LIBD and XAFS investigation of the formation and structure of Zr(IV) colloids. *Anal. Bioanal. Chem.* **383**, 28 (2005)
 32. Östhols, E., Bruno, J., Grenthe, I.: On the influence of carbonate on mineral dissolution: III. The solubility of microcrystalline ThO₂ in CO₂-H₂O media. *Geochim. Cosmochim. Acta* **58**, 613 (1994).
 33. Clearfield, A.: Structural aspects of zirconium chemistry. *Rev. Pure Appl. Chem.*, **14**, 91 (1964).
 34. Fryer, J. R., Hutchison, J. L., Paterson, R.: An electron microscopic study of the hydrolysis products of zirconyl chloride. *J. Colloid Interface Sci.*, **34**, 238 (1970).
 35. Southon, P. D., Bartlett, J. R., Woolfrey, J. L., Ben-Nissan, B.: Formation and Characterization of an Aqueous Zirconium Hydroxide Colloid. *Chem. Mater.*, **14**, 4313 (2002).
 36. Kovalenko, P. N., Bagdsarov, K. N.: The solubility of zirconium hydroxide. *Russ. J. Inorg. Chem.*, **6**, 272 (1961).
 37. Bilinski, H., Branica, M., Sillen, L. G.: Preparation and hydrolysis of metallic ions. II. Studies on the solubility of zirconium hydroxide in dilute solutions and 1M NaClO₄. *Acta Chem. Scand.* **20**, 853 (1966).
 38. Solovkin, A. S., Ivantsov, A. I.: Hydrolysis constants of the Zr⁴⁺ ion in perchlorate media. *Russ. J. Inorg. Chem.* **11**, 1013 (1966).
 39. Nazarenko, V. A., Mandzhgaladze, O. V.: Determination of the formation constants

- of hydroxo-complexes of zirconium by the method of competing reactions. Russ. J. Inorg. Chem. **14**, 639.(1969).
40. Norén, B.: The hydrolysis of Zr^{4+} and Hf^{4+} , Acta Chem. Scand. **27**, 1369 (1973).
 41. Pouchon, M. A., Curti, E., Degueldre, C., Tobler, L.: The influence of carbonate complexes on the solubility of zirconia: new experimental data. Progress in Nuclear Energy, **38**, 443 (2001).
 42. Keramidas, V., White, W.: Raman scattering study of the crystallization and phase transformations of ZrO_2 . J. Am. Ceram. Soc., **57**, 22 (1974).
 43. Nakashima, T., Zimmer, E.: Hydrolysis of $Th(NO_3)_4$ and its Extractability by TBP. Radiochim. Acta **37**, 165 (1984).
 44. Moulin, C., Amekraz, B., Hubert, S., Moulin, V.: Study of thorium hydrolysis species by electrospray-ionization mass spectrometry. Anal. Chim. Acta **441**, 269 (2001).
 45. Neck, V., Kim, J. I.: Solubility and hydrolysis of tetravalent actinides. Radiochim. Acta **89**, 1 (2001).
 46. Rand, R., Fuger, J., Grenthe, I., Neck, V., Rai, D.: *Chemical Thermodynamics of Thorium*, In: *Chemical Thermodynamics* (Eds.: F. J. Mompean et al.) Vol. 11, Elsevier, North-Holland, Amsterdam (2009).
 47. Felmy, A. R., Rai, D., Mason, M. J.: The Solubility of Hydrous Thorium(IV) Oxide in Chloride Media: Development of an Aqueous Ion-Interaction Model. Radiochim. Acta **55**, 177 (1991).
 48. Rai, D., Felmy, A. R., Sterner, S. M., Moore, D. A., Mason, M. J.: The Solubility of Th(IV) and U(IV) Hydrous Oxides in Concentrated NaCl and $MgCl_2$ Solutions. Radiochim. Acta **79**, 239 (1997).
 49. Rai, D., Moore, D., Oakes, C., Yui, M.: Thermodynamic model for the solubility of thorium dioxide in the $Na^+-Cl^--OH^--H_2O$ system at 23°C and 90°C. Radiochim. Acta **88**, 297 (2000).
 50. Neck, V., Altmaier, M., Müller, R., Bauer, A., Fanghänel, Th., Kim, J. I.: Solubility of crystalline thorium dioxide. Radiochim. Acta **91**, 253 (2003).
 51. Rai, D., Swanson, J. L., Ryan, J. L.: Measured and extrapolated values of solubility products of tetravalent actinide hydrous oxides. Abstracts of Papers of the

- American Chemical Society **192**, 106 (1986).
52. Rai, D., Felmy, A. R., Ryan, J. L.: Uranium(IV) Hydrolysis Constants and Solubility Product of $\text{UO}_2 \cdot x\text{H}_2\text{O}(\text{am})$. *Inorg. Chem.*, **29**, 260 (1990).
 53. Yajima, T., Kawamura, Y., Ueta, S.: Uranium(IV) Solubility and Hydrolysis Constants under Reduced conditions. *Mat. Res. Soc. Symp. Proc.* **353**, 1137 (1995).
 54. Rai, D.: Solubility Product of Pu(IV) Hydrous Oxide and Equilibrium Constants of Pu(IV)/Pu(V), Pu(IV)/Pu(VI), Pu(V)/Pu(VI) Couples. *Radiochim. Acta* **35**, 97 (1984).
 55. Kim, J. I., Kanellakopulos, B.: Solubility Products of Plutonium(IV) Oxide and Hydroxide. *Radiochim. Acta* **48**, 145 (1989).
 56. Capdevila, H., Vitorge, P.: Solubility Product of $\text{Pu}(\text{OH})_4(\text{am})$. *Radiochim. Acta* **82**, 11 (1998).
 57. Knopp, R., Neck, V., Kim, J. I.: Solubility, Hydrolysis and Colloid Forms of Plutonium(IV). *Radiochim. Acta* **86**, 101 (1999).
 58. Fujiwara, K., Yamana, H., Fujii, T., Moriyama, H.: Solubility product of Pu(IV) hydrous oxide. *Radiochim. Acta*, **91**, 81 (2003).
 59. Babko, A. K., Dubovenko, L. I.: Zirconium oxalate complexes. *Izv. Vyssh. Uchebn. Zaved., Khim. Khim. Tekhnol.*, **3**, 226 (1960).
 60. Shvedov, V., Maslov, E.: Determination of the composition and stability constants of complex compounds by electromigration. I. Determination of the composition and stability constants of oxalate complexes of zirconium. *Sov. Radiochem.* **4**, 376 (1962).
 61. Caletka, R., Kyrs, M., Rais, J.: Sorption of Zirconium by Silica Gel from Nitrate Medium in the presence of Oxalic Acid, EDTA and Arsenazo I. *J. Inorg. Nucl. Chem.*, **26**, 1443 (1964).
 62. Zaitsev, L. M., Bochkarev, G. S.: Solubility Product of Zirconium Oxide Oxalate. *Russ. J. Inorg. Chem.* **9**, 1147 (1964).
 63. Bagawde, S. V., Ramakrishna, V. V., Patil, S. K.: Oxalate complexing of tetravalent actinides. *J. Inorg. Nucl. Chem.* **38**, 1669 (1976).
 64. Erten, H. N., Mohammed, A. K., Choppin, G. R.: Variation of stability constants of thorium and uranium oxalate complexes with ionic strength. *Radiochim Acta* **66/67**,

123 (1994).

65. Bernardo, P. Di., Dinapoli, V., Cassol, A., Magon, L.: Thermodynamic properties of actinide complexes. 4. Thorium(IV)-malonate system and uranyl(VI)-malonate system. *J. Inorg. Nucl. Chem.* **39**, 1659 (1977).
66. Tomat, G., Magon, L., Portanova, R., Cassol, A.: Complexes of Thorium(IV). *Z.Anorg.Allq.Chem.***393**.184 (1972).
67. Pazukhin, E., Smirnova, E., Pazurkhina, Y., Kiselev, P.: Optimization of Conditions for Precipitation of Thorium Oxalate. 4. State of Thorium in Oxalate Solutions. *Soviet Radiochim.* **30**, 308 (1988)
68. Sasaki, T., Kobayashi, T., Takagi, I., Moriyama, H.: Discrete Fragment Model for Complex Formation of Europium(III) with Humic Acid. *J. Nucl. Sci. Technol.*, **45**, 718 (2008).
69. Neck, V., Kim, J. I.: An electrostatic approach for the prediction of actinide complexation constants with inorganic ligands-application to carbonate complexes. *Radiochim. Acta*, **88**, 815 (2000).
70. Moriyama, H., Sasaki, T., Kobayashi, T., Takagi, I.: Systematics of Hydrolysis Constants of Tetravalent Actinide Ions. *J. Nucl. Sci. Technol.*, **42**, 626 (2005).

Table 1.1 Reported values of zirconium hydrolysis constants ($I = 0$).

	log $\beta^{\circ}_{1,1}$ log $\beta^{\circ}_{1,2}$ log $\beta^{\circ}_{1,3}$ log $\beta^{\circ}_{1,4}$ log $\beta^{\circ}_{1,5}$ log $\beta^{\circ}_{1,6}$							Experimental Condition			Ionic strength
								Method	Total [Zr]	Media	
Bilinski [37]	-	25.23	37.67	47.5	-	-	-	Solubility	1×10^{-3} M	HClO ₄ / NaClO ₄	1.0, dilute
Solovkin [38]	14.62±0.07 ^{a)}	29.05±0.08 ^{a)}	42.81±0.14 ^{a)}	56.77 ^{a)}	-	-	-	Solvent Extraction	-	(Li, H)ClO ₄ / (Na, H)ClO ₄	1.0
Nazarenko [39]	14.04	27.76	41.33	54.52	-	-	-	Spectrophotometry	1×10^{-5} M	NaClO ₄ / KNO ₃	0.1 - 1.0
Norén [40]	13.45±0.07 ^{a)}	-	-	-	-	-	-	Potentiometry	$< 5 \times 10^{-4}$ M	HClO ₄ / NaClO ₄	4.0
Baes [2]	14.3±0.05	26.3	36.9	46.3±1.0	54	-	-	^{b)}	^{b)}	^{b)}	^{b)}
Veyland [14]	-	-	41.48±0.01	51.48±0.07	-	-	-	Potentiometry	8×10^{-3} M	KNO ₃	0.01 - 0.3
Ekberg [15]	14.29±0.06	27.7±0.2	40.1±0.3	52.1±0.3	-	-	-	Potentiometry, Solvent Extraction	0.004 - 0.03 M, 1×10^{-7} M	HClO ₄ / NaClO ₄	1.0
Cho [31]	14.3 ^{c)}	27.6 ^{c)}	38.1 ^{c)}	45.4 ^{c)}	-	-	-	-	-	-	-
Walther [22]	14.1	27.8	37.1	45.8	-	-	-	ESI-MS	$1.5, 10 \times 10^{-3}$ M	HCl	0.001 - 1.0
NEA-TDB [5]	14.32±0.22	28.98±1.06	-	53.81±1.70	-	55.0±0.7	-	^{b)}	^{b)}	^{b)}	^{b)}

Table 1.1 (continued)

	Experimental Condition						
	$\log \beta_{2,6}^{\circ}$	$\log \beta_{2,7}^{\circ}$	$\log \beta_{3,4}^{\circ}$	$\log \beta_{3,5}^{\circ}$	$\log \beta_{3,9}^{\circ}$	Method	Ionic strength
Zeilen [11]	-	-	61.39±0.08	-	-	Solvent Extraction	0.1 M - 1×10^{-5} M (Li, H)ClO ₄ 1.0, 2.0
Tribalat [13]	-	-	62.19±0.28 ^{a)}	-	-	Spectrophotometry	3.6×10^{-4} M HClO ₄ 3.5
Baes [2]	-	-	55.4±0.1	73.7±0.1	-	See above.	
Veyland [14]	-	95.78±0.05	-	-	-	See above.	
Ekberg [15]	85.90±0.13 ^{d)}	-	55.9±0.5 ^{d)}	-	-	See above.	
Walther [22]	-	-	55.4	-	-	See above.	
NEA-TDB [5]	-	-	56.4±0.3	-	138.19±0.08	See above.	
	Experimental Condition						
	$\log \beta_{4,8}^{\circ}$	$\log \beta_{4,10}^{\circ}$	$\log \beta_{4,15}^{\circ}$	$\log \beta_{4,16}^{\circ}$		Method	Ionic strength
Zeilen [11]	120.24±0.07	-	-	-		See above.	
Baes [2]	118.0±0.1	-	-	-		See above.	
Ekberg [15]	115.2±0.2 ^{d)}	-	-	-		See above.	
Walther [22]	121.5	149	-	-		See above.	
NEA-TDB [5]	118.52±0.65	-	222.58±0.24	232.39±0.8		See above.	
	Experimental Condition						
	$\log \beta_{5,11}^{\circ}$	$\log \beta_{5,12}^{\circ}$	$\log \beta_{5,16}^{\circ}$	$\log \beta_{8,19}^{\circ}$	$\log \beta_{8,22}^{\circ}$	$\log \beta_{8,27}^{\circ}$	Ionic strength
Walther [22]	165.4	180	230	281.3	324.5	385.75	See above.

a) Corrected to $I = 0$ by NEA-TDB [5].

b) The literature reviewed reported values and selected data.

c) Estimated from a model by Neck et al. [69].

d) Corrected to $I = 0$ by SIT.

Table 1.2 Reported values of solubility product of zirconium hydroxide and oxide and experimental conditions.

	$\log K_{sp}^{\circ}$		Sample preparation				Aging Time	Solid-liquid separation	Zr Measurement
	Zr(OH) ₄ (am)	ZrO ₂ (cr)	Solid phase	Media	Total [Zr] ^{a)}	Ionic strength			
Kovalenko [36]	-53.9	-	Zr(OH) ₄ (am)_not dried undersat ^{b)}	HNO ₃	not mentioned	dilute solution	24 h	not mentioned	photocolorimetric
Bilinski [37]	-51.6	-	Zr(OH) ₄ (am) oversat ^{c)}	HClO ₄ / NaClO ₄	1×10 ⁻³ M	1, dilute	1 day	not mentioned	tyndalometric
Baes [2]	-57.9±1.0	-	- ^{d)}	- ^{d)}	- ^{d)}	- ^{d)}	- ^{d)}	- ^{d)}	- ^{d)}
Veyland [14]	-55.26±0.08	-	Zr(OH) ₄ (am)_not dried undersat ^{b)}	KNO ₃	not mentioned	0.2, 0.5, 1.0, 2.0	-15 days	centrifugation and 0.45 µm	not mentioned
Pouchon [41]	-	-63.0 ^{e)}	ZrO ₂ (cr)	Pure water	0.03 M	dilute solution	1-250 days	dialysis	ICP-MS
Ekberg [15]	-56.7±0.29	-	Zr(OH) ₄ (s)_dried powder, undersat ^{b)}	HClO ₄ / NaClO ₄	0.1 M	1	3 days -2 months	centrifugation 14,000 G	ICP-MS /OES
Cho [31]	-53.1±0.5	-	Zr(OH) ₄ (am) oversat ^{c)}	HCl / NaCl	5×10 ⁻³ M	0.5	in-situ	colloids > 5 nm	CT-LJBD, ICP-MS
NEA-TDB [5]	-59.24±0.10	-63.0±1.6	- ^{d)}	- ^{d)}	- ^{d)}	- ^{d)}	- ^{d)}	- ^{d)}	- ^{d)}

a) Zr concentration when the solid phase is completely dissolved.

b) Undersaturation method.

c) Oversaturation method.

d) The literature reviewed reported values and selected data.

e) Calculated by NEA-TDB [5] using their experimental data.

Table 1.3 (continued)

	Experimental Condition					Ionic strength			
	$\log \beta^{o,2,2}$	$\log \beta^{o,2,3}$	$\log \beta^{o,2,4}$	$\log \beta^{o,4,8}$	$\log \beta^{o,4,12}$		Method	Total [Th]	Media
Baes [16]	22.12	-	-	91.29	-		See above.		
Brown [17]	-	-	-	-	141.11		See above.		
Grenthe [18]	21.42±0.17	35.19±0.05	-	90.8±0.2	142.77±0.05		See above.		
Moon [19]	29.47±0.04 ^{a)}	33.62±0.11 ^{a)}	62.15±0.04 ^{a)}	-	-		See above.		
Ekberg [21]	-	-	-	91.2±0.1	-		See above.		
Neck [45]	22.3	-	-	91.6	141.3		See above.		
NEA-TDB [46]	22.1±0.5	35.2±0.2	-	91.6±0.4	141.4±0.2		See above.		

	Experimental Condition					Ionic strength			
	$\log \beta^{o,5,14}$	$\log \beta^{o,5,17}$	$\log \beta^{o,6,14}$	$\log \beta^{o,6,15}$	$\log \beta^{o,6,16}$		Method	Total [Th]	Media
Baes [16]	-	-	-	173.16	-		See above.		
Brown [17]	-	-	-	175.25	-		See above.		
Grenthe [18]	-	-	158.62±0.05	-	185.9±0.4		See above.		
Ekberg [21]	-	-	-	170.4±0.2	-		See above.		
Neck [45]	-	-	-	176	-		See above.		
Walther [23]	166.3	197	-	-	-	ESI-MS	$6 \times 10^{-6} - 1 \times 10^{-1}$ M	HCl	< 0.1
NEA-TDB [46]	-	-	159.2±1.2	173.2±1.5	-		See above.		

a) Corrected to $I = 0$ by SIT.

b) The literature reviewed reported values and selected data.

c) Calculated from Hard Sphere Model [70].

Table 1.4 Reported values of solubility product of thorium hydroxide and oxide and experimental conditions.

	$\log K_{sp}^{\circ}$		Sample preparation				Aging Time	Solid-liquid separation	Th Measurement
	Th(OH) ₄ (am), ThO ₂ (am)	ThO ₂ (cr)	Solid phase	Media	Total [Th] ^{a)}	Ionic strength			
Baes [2]	-49.7	-	^{b)}	^{b)}	^{b)}	^{b)}	^{b)}	^{b)}	^{b)}
Moon [19]	-50.76±0.08	-	Th(OH) ₄ (am) undersat ^{c)}	NaClO ₄	0.01	0.5	-2 months	5k Da filter	neutron activation analysis
Östhols [32]	-48.69±0.30	-	ThO ₂ (s) ₂ dried undersat ^{c)}	NaClO ₄	0.04	0.5	1-6 months	0.01-0.22 µm	spectrophotometric
Felmy [47]	-45.5	-	Th(OH) ₄ (am) undersat ^{c)}	NaCl, NaClO ₄	0.009	0.6, 1.2, 3.0	7-98 days	2.5k Da filter	ICP-MS
Rai [48,49]	-44.9±0.5	-	Th(OH) ₄ (am) undersat ^{c)}	NaCl	< 0.01	0.1	5-22 days	30k Da filter	ICP-MS
Bundschuh [28]	-	> -56.9	ThO ₂ (cr) ^{d)} undersat	NaCl	< 0.01	0.1	-687 days	30k Da filter	ICP-MS
	-	-52.8±0.3	ThO ₂ :x H ₂ O(mcr) ^{e)} oversat ^{f)}	NaCl	8.9×10 ⁻⁵ - 2.8×10 ⁻² M	0.5	in-situ	colloids > 5 nm	CT-LIBD, ICP-MS
Neck [45]	-47.0±0.8	-	^{b)}	^{b)}	^{b)}	^{b)}	^{b)}	^{b)}	^{b)}
Neck [29]	-47.8±0.3	-	Th(OH) ₄ (am) oversat ^{f)}	NaCl	1.0×10 ⁻⁵ - 1.2×10 ⁻² M	0.5	in-situ	colloids > 5 nm	CT-LIBD
	-	-	ThO ₂ (s) ₂ dried undersat ^{c)}	NaCl	0.01	0.5	5-204 days	10k Da filter or centrifugation	ICP-MS, spectro- photometric

Table 1.4 (continued)

	$\log K^{\circ}_{sp}$		Sample preparation				Aging Time	Solid-liquid separation	Th Measurement
	Th(OH) ₄ (am), ThO ₂ (am)	ThO ₂ (cr)	Solid phase	Media	Total [Th] ^{a)}	Ionic strength			
Neck [50]	-	-52.9±0.5	ThO ₂ ·xH ₂ O(mer) ^{e)}	NaCl	3.2×10 ⁻⁵	0.5	in-situ	colloids > 5 nm	CT-LIBD, ICP-MS, spectrophotometric
	-	-53.2±0.4	oversat ^{f)}		-7.6×10 ⁻³ M		36-160 days	10k Da filter or centrifugation	
	-	-54.3±1.3 ^{g)}	ThO ₂ (cr) ^{h)} undersat ^{e)}	NaCl	0.01	0.1, 0.5	79-318 days	10k Da filter or centrifugation	spectrophotometric, ICP-MS
NEA-TDB [46]	-46.7±0.9 ⁱ⁾ -47.5±0.9 ^{j)}		^{b)} _	^{b)} _	^{b)} _	^{b)} _	^{b)} _	^{b)} _	^{b)} _

a) Th concentration when the solid phase is completely dissolved.

b) Reviewed the reported values and selected data.

c) Undersaturation method.

d) Produced by firing the Th oxalate salt in air for 2 hours at 750 °C.

e) Careful titration at the onset of colloid formation.

f) Oversaturation method.

g) Obtained from thermodynamic calculation.

h) Additionally heated for 8 hours at 750 °C.

i) Value for ThO₂(am, hyd, fresh).

j) Value for ThO₂(am, hyd, aged).

Table 1.5 Reported values of zirconium and thorium complex formation constants with some organic acids ($I = 0$).

Species			Babko [59]	Shevedov [60]	Caletka [61]	Zaitsev [62]
C20	Zr(C20) ₂ (s)	$\log K_{\text{sp,L},2}^{\circ}$				
Oxalic acid	Zr(OH) ₂ (C20)(s)	$\log K_{\text{sp,L},21}^{\circ}$				-37.3 ^{a)}
	Zr(C20) ²⁺	$\log \beta_{\text{L}1}^{\circ}$	11.65 ^{a)}	11.13 ^{a)}	12.92 ^{a)}	
	Zr(C20) ₂ (aq)	$\log \beta_{\text{L}2}^{\circ}$	20.05 ^{a)}	20.31 ^{a)}	23.19 ^{a)}	
	Zr(C20) ₃ ²⁻	$\log \beta_{\text{L}3}^{\circ}$	23.2 ^{a)}	26.97 ^{a)}		
	Zr(C20) ₄ ⁴⁻	$\log \beta_{\text{L}4}^{\circ}$	21.31 ^{a)}	33.04 ^{a)}		

Species			Sasaki [10]	Bagawde Erten [63,64]	Bernardo [65]	Tomat [66]	Pazukhin [67]
C20	Th(C20) ₂ (s)	$\log K_{\text{sp,L},2}^{\circ}$	-				-22.4 ^{a)}
Oxalic acid	Th(OH) ₂ (C20)(s)	$\log K_{\text{sp,L},21}^{\circ}$	-				
	Th(C20) ²⁺	$\log \beta_{\text{L}1}^{\circ}$	9.60±0.14	9.79			
	Th(C20) ₂ (aq)	$\log \beta_{\text{L}2}^{\circ}$	16.0±0.6	17.1			
	Th(C20) ₃ ²⁻	$\log \beta_{\text{L}3}^{\circ}$	22.2±0.1	22.4			
C21	Th(C21) ²⁺	$\log \beta_{\text{L}1}^{\circ}$	9.18±0.26		9.4	9.35	
Malonic acid	Th(C21) ₂ (aq)	$\log \beta_{\text{L}2}^{\circ}$	15.7±0.1		15.8	15.7	
	Th(C21) ₃ ²⁻	$\log \beta_{\text{L}3}^{\circ}$	19.7±0.8		18.7		
C22	Th(C22) ²⁺	$\log \beta_{\text{L}1}^{\circ}$	8.09±0.16			8.16	
Succinic acid	Th(C22) ₂ (aq)	$\log \beta_{\text{L}2}^{\circ}$	12.4±0.5				
	Th(C22) ₃ ²⁻	$\log \beta_{\text{L}3}^{\circ}$	15.8±0.3				
C23	Th(C23) ²⁺	$\log \beta_{\text{L}1}^{\circ}$	7.78±0.17				
Glutaric acid	Th(C23) ₂ (aq)	$\log \beta_{\text{L}2}^{\circ}$	11.9±0.4				
	Th(C23) ₃ ²⁻	$\log \beta_{\text{L}3}^{\circ}$	14.9±0.5				
C24	Th(C24) ²⁺	$\log \beta_{\text{L}1}^{\circ}$	7.69±0.15				
Adipic acid	Th(C24) ₂ (aq)	$\log \beta_{\text{L}2}^{\circ}$	11.0±0.1				
	Th(C24) ₃ ²⁻	$\log \beta_{\text{L}3}^{\circ}$					

a) Corrected to $I = 0$ by SIT.

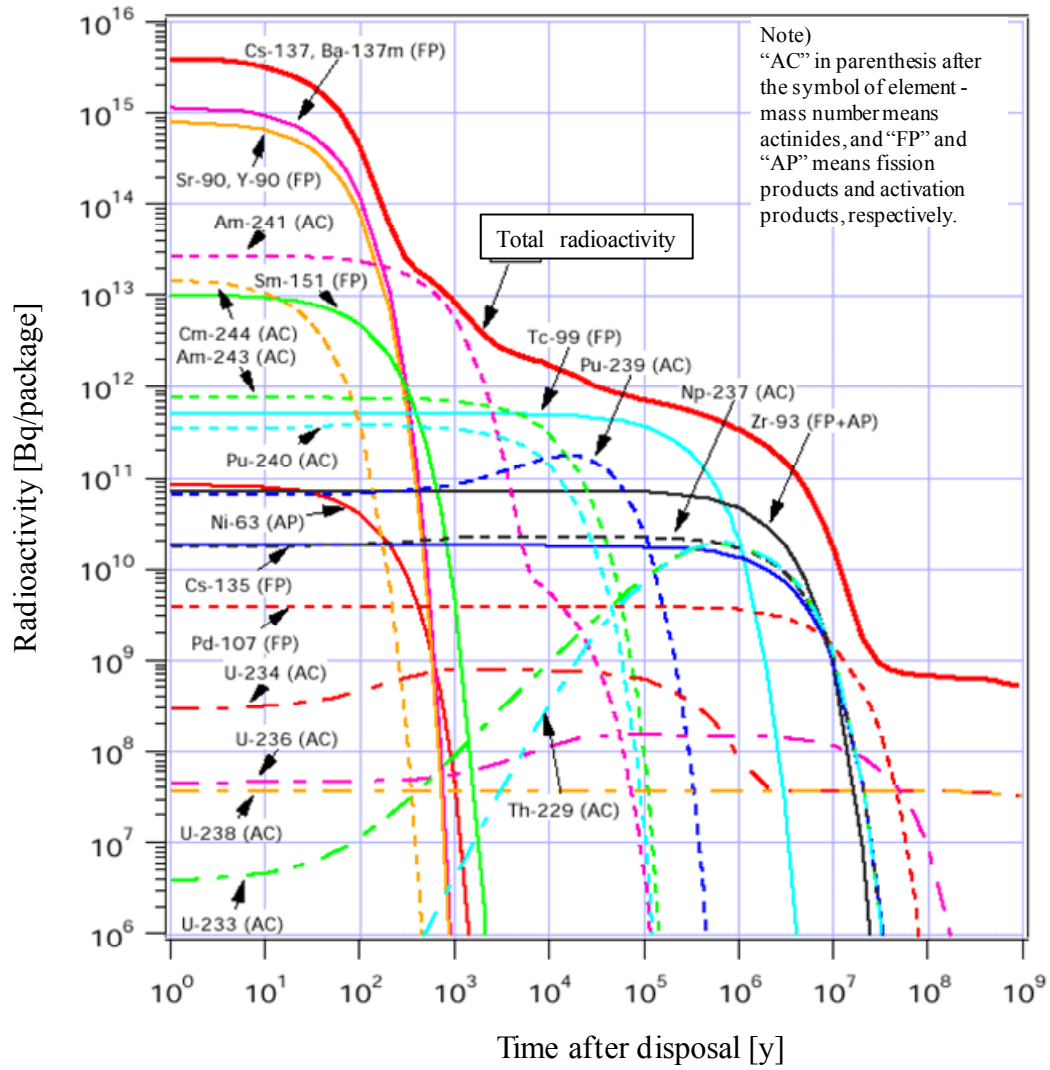


Fig. 1.1 Variations in radioactivity of vitrified waste with time after emplacement.
 (Assuming 54 years after discharge of spent nuclear fuel from the reactor)

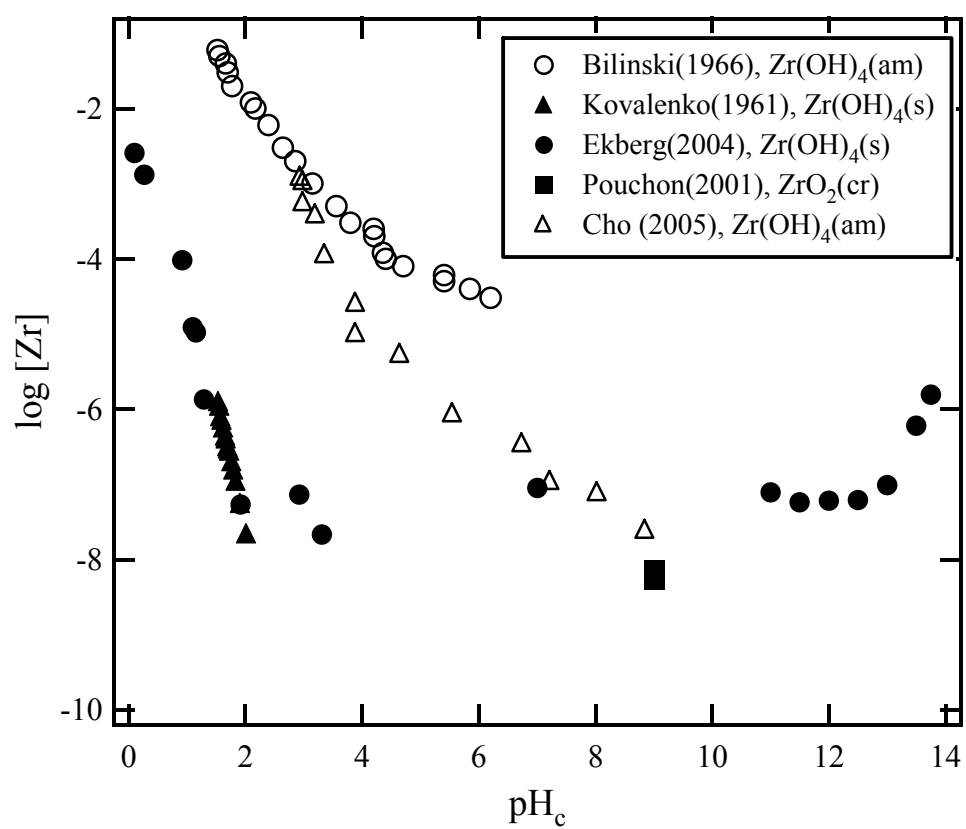


Fig. 1.2 Reported solubility of zirconium(IV) hydroxides and oxides as a function of pH_c .

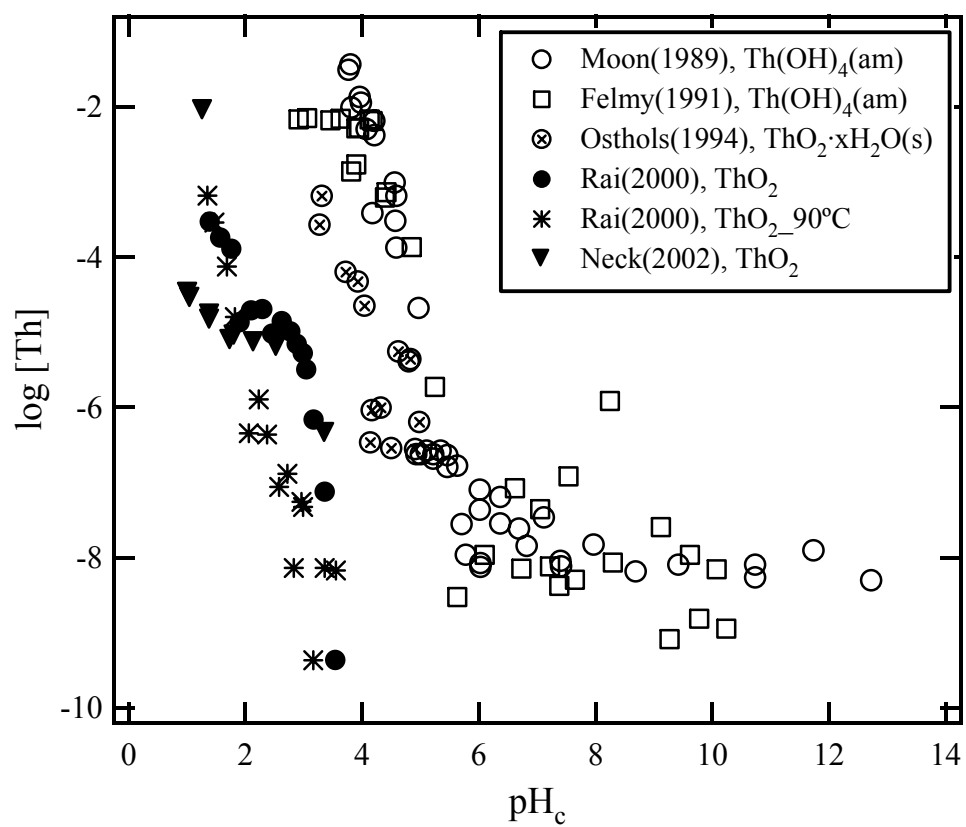


Fig. 1.3 Reported solubility of thorium(IV) hydroxides and oxides as a function of pH_c .

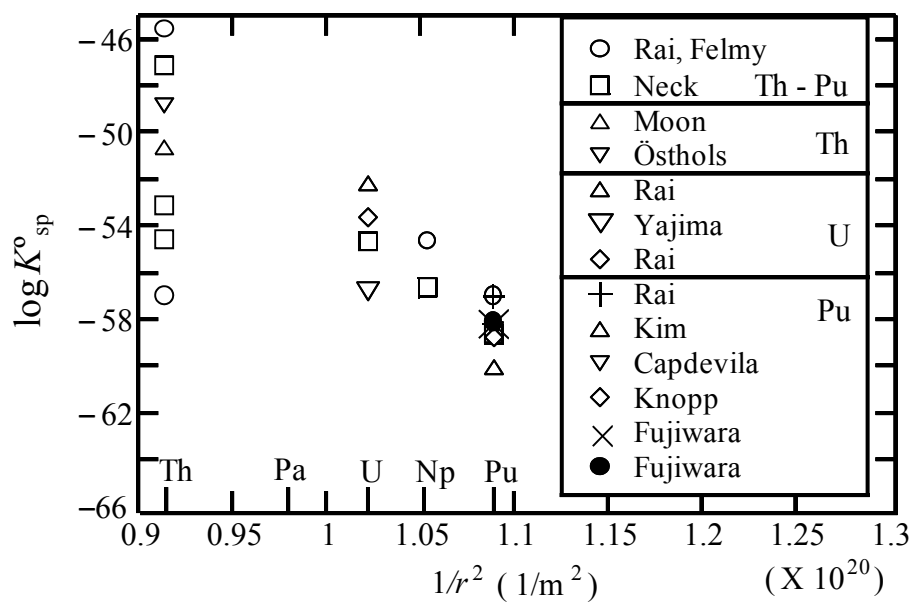


Fig. 1.4 Solubility product of tetravalent hydroxide and oxide.

Chapter 2 Solubility of Hydroxide and Oxide

2.1 Introduction

The present chapter deals with the solubility and solubility products of Zr(IV) hydroxide and oxide and Th(IV) hydroxide [1-3]. As described in Chapter 1, the knowledge of the solubility behavior of these solid phases is of highest priority for the safety assessment of nuclear waste disposal. In groundwater, Zr and Th solubility is generally controlled by hydroxide and oxide as a solubility-limiting solid phase and the reactions can be described as



$$K_{sp} = [M^{4+}][OH^{-}]^4. \quad (2.3)$$

The solubility product (K_{sp}) value is determined by the concentrations of M^{4+} and OH^{-} ions which are equilibrated with the solid phase. However, the tetravalent metal ion forms not only mononuclear but also polynuclear hydrolysis species in the aqueous solution [4-8]. Moreover, recent LIBD study showed the existence of colloidal species [9,10]. The “apparent” solubility is, thus, a sum of these species in the solution.

The experimental difficulty in determining the solubility products is related to the contribution of these species to the apparent solubility. For example, if a wide-pore-sized filter was used to separate the liquid phase from the solid phase, some part of the polynuclear and colloidal species might pass through the filter and the “apparent” solubility would include their contributions. The colloidal species is thought to be varied in a wide range size from a few nm to μm , so the amount of the colloidal species in the apparent solubility may depend on the filter pore size. The size distribution of the colloidal species can be easily affected by experimental conditions such as solution pH and aging time and these differences may be one of the reasons for the scatter in the reported solubility data and solubility products.

Another problem arises from the analytical procedure to obtain the solubility product. Various kinds of hypotheses concerning the dominant species and reported

hydrolysis constants are needed to determine the solubility product from the solubility data. However, the lack of hydrolysis constants especially about the polynuclear species remains, and even there is still a controversy on the dominant polynuclear species.

In the present study, an ultrafiltration method was adopted for the separation of the liquid and solid phases and the solubility of $\text{Zr(OH)}_4(\text{am})$, $\text{Th(OH)}_4(\text{am})$ and $\text{ZrO}_2(\text{cr})$ were measured in wide range of hydrogen ion concentration (pH_c). The dependence of the filter pore size on the apparent solubility was measured to investigate the size distribution of the soluble species. In this chapter, the contribution of colloidal species was mainly discussed. A simple polymer model was used to explain and analyze the size distribution of colloidal species. The concentration of “mononuclear species” was estimated from the analysis of the size distribution and the solubility products of hydroxide and oxide were determined using only mononuclear hydrolysis constants.

2.2 Experimental

2.2.1 Sample preparation

Amorphous Zr(IV) hydroxide by an oversaturation method : A stock solution of zirconium was prepared from perchlorate salt which was obtained from ZrCl_4 (Aldrich, <99.9%) by perchloric acid fuming in a Teflon beaker covered with a watch glass. The initial Zr concentration was 0.01 mol/dm^3 (M) at pH_c 1, and the ionic strength (I) was kept constant at 0.1, 0.5 and 1.0 M by adding an appropriate amount of NaClO_4 stock solution. The starting pH_c value of the sample solution was adjusted with NaOH/HClO_4 of the same ionic strength while stirring continuously with a magnetic stirrer.

Powdery Zr(IV) hydroxide and Crystalline Zr(IV) oxide by an undersaturation method : The reagents Zr(OH)_4 (Aldrich, 97%) and ZrO_2 (WAKO Pure Chem. 99%) were used as purchased with no additional purification. The reagent of Zr(OH)_4 and ZrO_2 were added to 10 ml of $\text{HClO}_4/\text{NaOH}$ solution at a definite pH_c in a polypropylene tube, and its total amount was controlled to be 0.01-1.0 M when all of added reagents were dissolved. Ionic strength was kept constant at 0.1, 0.5 and 1.0 by NaClO_4 .

Amorphous Th(IV) hydroxide by an oversaturation method : The reagent of Th(IV) nitrate ($\text{Th(NO}_3)_4 \cdot 4\text{H}_2\text{O}$ (Nakalai Chemicals Ltd.)) was dissolved in 0.1 M perchlorate acid and 3% aqueous NH_3 was quickly added to neutralize and precipitate thorium hydroxide. The precipitate was washed with deionized distilled water several times and finally dissolved

in a concentrated solution of perchlorate acid. The solution was then filtered with a 0.25 μm filter to remove any residue, resulting in a stock solution of thorium perchlorate ($[\text{Th}] = 0.25 \text{ M}$). The stock solution was diluted to prepare an initial thorium concentration of 0.01 M. The ionic strength was kept at 0.2, 0.6, 1.0 and 2.0 by adding appropriate amounts of NaClO_4 , and the pH_c was controlled by adding dropwise portions of $\text{NaOH}/\text{HClO}_4$ to the initial solution while stirring continuously with a magnetic stirrer.

The pH_c was measured using a combination glass electrode, and its reference electrode was filled with 3.6 M $\text{NaCl} + 0.4 \text{ M NaClO}_4$ to avoid precipitation of KClO_4 at the junction of the electrode and the solution. The sample preparation and its aging for a given period were in the CO_2 -free Ar atmosphere glove box at $25.0 \pm 2.0 \text{ }^\circ\text{C}$. All other chemicals used were of analytical grade.

2.2.2 Solubility measurement

The sample solutions were divided in quantities of 10 mL in polypropylene tubes and allowed to stand for a given aging period, and sometimes agitated by hand. After a given period, the pH_c values of the sample solutions were measured. The supernatants were filtered through Microcon (Millipore) centrifugal filters with a nominal molecular weight limit (NMWL) of 3k Da and approximately 2 nm pore sizes. In order to investigate the dependence of the apparent solubility on the filter pore size, some supernatants were also filtered through 10k, 30k, 50k and 100k Da NMWL membranes, corresponding to approximately 3, 4.2, 5.2 and 7 nm pore sizes, respectively. Aliquots of the filtrate were acidified with 0.1 M nitric acid to determine the Zr and Th concentration by inductively coupled plasma-mass spectroscopy (ICP-MS; HP4500, Hewlett Packard) with a detection limit of approximately 10^{-8} M .

The matrix effect of sodium perchlorate and nitric acid on the determination of zirconium concentration was investigated. An example of the effect on the intensity of zirconium is shown in Fig. 2.1a. It was found that the ionization efficiency of zirconium decreases with increasing ionic strength and acidity. A memory effect was observed in the use of the Teflon-tubing system (Fig. 2.1b). In order to reach the background intensity after a sample injection, tubes were rinsed with 1 M HNO_3 and water for at least 100 sec in the interval of sample injections.

The precipitate was separated from the liquid phase by centrifugation. After drying the solid phase at 60°C , X-ray diffraction patterns were measured using RINT 2000

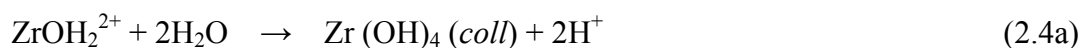
(RIGAKU).

2.3 Results and Discussion

2.3.1 Solubility of Amorphous Zirconium Hydroxide by Oversaturation Method

Solubility in the acidic, neutral and alkaline pH_c range

The colloid precipitation in the sample vessel was formed rapidly when the pH_c was increased at the beginning of the experiment. The solubility data obtained after filtration by 3k Da NMWL membrane filters are plotted as a function of pH_c in Fig. 2.2. The solubility decreases with an increase of pH_c under the acidic condition, and it is not significantly dependent on the standing time up to 6 months nor on the ionic strength. In spite of the careful sample preparation around pH_c 4, the solubility data from oversaturation were scattered. Under this condition, the pH_c shifts to higher and/or lower values. It is considered that the pH_c dependence is affected by the formation of polynuclear/colloidal species as:



The pH_c shift to lower values is due to the formation of polynuclear species and/or colloids (*coll*) by reaction Eq. (2.4a). On the other hand, when disordered and unstable colloids are formed by rapid titration, the pH_c is increased by reaction Eq. (2.4b). However, it is noted that the apparent solubility is not affected significantly by the pH_c shift after 3 months (Fig. 2.2), and it can be considered the chemical equilibrium is established within 3 months.

Recently, Cho et al. reported the solubility obtained by the combination of coulometric titration and LIBD detection of Zr(IV) hydrolysis colloids [10]. They approached the solubility limit taking great care with pH control to avoid local regions of oversaturation. At the pH_c of colloid detection (> 5 nm in size), the solubility for amorphous Zr(OH)₄ was determined at *I* = 0.5 M. The results of their *in-situ* colloid detection were higher than ours as shown in Fig. 2.2. Their *in-situ* LIBD measurement seems to give an upper solubility limit for fresh amorphous Zr(OH)₄.

Ekberg et al. measured the solubility of Zr(OH)₄(s) as the solid phase after using centrifugation rather than ultra-filtration [5]. The solubility after 3 days was much lower than that from our oversaturation experiments. Rai et al. reported that the solubility of crystalline

ThO₂ and UO₂ is several orders lower than that of amorphous solids [11,12]. Such a low solubility may be explained by considering the stability of solid phases and/or the surface reaction mechanism in comparison with that of the amorphous phase [13]. Crystalline solids are dissolved very slowly, and polynuclear and colloidal species may be expected to be less abundant. On the other hand, the present sample solution, which is prepared by the oversaturation method, is considered to contain a mixture of mononuclear, polynuclear, and colloidal species. It is thus important to know the effects of such species on the solubility data obtained from the oversaturation experiments.

Due to low solubility in the order of $<10^{-8}$ M, memory and matrix effects in ICP-MS measurement are significant problems. Since solubility could not be determined in some samples in the neutral pH_c range due to the fairly low concentration of zirconium ($< 1 \times 10^{-8}$ M), the values obtained should be considered as an upper limit of solubility. In Fig. 2.2, plots with down arrows show the solubility data under the detection limit. Reproducible solubility data could not be obtained in the alkaline pH_c (>13.5) region due to a low chemical resistance of regenerated cellulose membrane filters.

Size distributions of colloidal species

The concentration of Zr at a given pH_c after ultrafiltration by 3k, 10k, 30k, 50k and 100k Da NMWL filters is shown in Fig. 2.3. It is obvious that the concentration increases with an increase of the filter pore size in most cases, although it reaches the initial concentration (10^{-2} M) in the lower pH region. Fig. 2.4 shows the size distributions of such species, which are obtained from the concentration data in Table 2.1. It can be recognized that the concentration of the species decreases with increasing pH_c in both solutions at $I = 0.1$ and 1.0 . In the neutral pH_c range, the size distribution cannot be investigated because of very low concentrations of the species.

The size distributions in Fig. 2.4 indicated the possible formation of the considerably large-sized species such as > 7 nm, corresponding about 17-mer hydrolysis species provided that the mononuclear species is 0.4 nm and connected in a line (ca. 0.4 nm for mononuclear species estimated by reference values [14]). In this study, such large species were treated as colloidal species which is different from a polynuclear species. The polynuclear species were defined as a well-ordered species consisting of mononuclear species by double hydroxyl bridges. The detail of the polynuclear species and their contributions are discussed in Chapter 3.

Therefore, it is interesting to compare the observed size distributions with calculated ones, and a simple polymer model of Flory-Schulz [15] is applied here to the data plots in Fig. 2.4. This model has been applied to describe a molecular weight distribution relating with a degree of polymerization in polymer chemistry. It has also been successfully applied in the previous studies to the size distributions of colloidal species such as neptunium (IV) and americium (III) co-precipitated with iron (III) [16,17]. The polymerization phenomenon is dealt with by considering “a probability (P) in which a “monomeric” unit collides and connects with each other.” The monomeric unit is supposed to connect linearly with a certain probability to form a polymer. In the present study, the mononuclear species of Zr^{4+} , ZrOH^{3+} , Zr(OH)_2^{2+} , Zr(OH)_3^+ and $\text{Zr(OH)}_4(\text{aq})$ are treated inclusively as a monomeric unit in the model

The total number, $N(l_1, l_2)$, of unit molecules comprising chain molecules in the range l_1 to l_2 in nm size is given by

$$N(l_1, l_2) = N_0 \frac{1}{P} \left(\frac{1-P}{\ln P} \right)^2 \left\{ P^{(l_2/l_0)} \left(\left(\frac{l_2}{l_0} \right) \ln P - 1 \right) - P^{(l_1/l_0)} \left(\left(\frac{l_1}{l_0} \right) \ln P - 1 \right) \right\} \quad (2.5)$$

where P is the probability that a unit monomeric molecule reacts with a chain molecule to increase the length of the chain, N_0 is the total number of unit molecules present in solution, and l_0 (ca. 0.4 nm [14]) is the length of the unit molecule. The l_1 and l_2 represent the filter pore sizes used in the ultracentrifugation. For example, a subtraction between Zr concentrations filtered through 3k Da and 10k Da filters corresponds to a sum of colloidal species whose size is from 2 nm to 3 nm. The 2 nm-sized and 3 nm-sized colloidal species were treated as 25-mer and 56-mer, respectively, assuming that the species were 2-dimensional. The number of mononuclear species N_1 is a sum of the species up to 0.4 nm and its fractional abundance to N_0 is given by

$$N_1 / N_0 = (1 - P)^2 \quad (2.6)$$

The P values are obtained from the analysis of the observed size distributions (Fig. 2.4) and curves in the figure show the calculated size distributions. It can be seen that the observed size distributions are well explained by the calculated ones. It follows that one can consider the possible presence of colloidal species in this case. As has already been pointed out, there will be various species, including colloidal ones, in oversaturated solutions. When

the size of mononuclear species is assumed to be 0.4 nm, the concentration of the mononuclear species can be calculated as shown in Table 2.1. The data are a few orders lower than those for 3k Da (open squares with a dotted line in Fig. 2.2).

In fact, it is well known that colloidal species are formed in the neutral pH_c region in which the neutral species Zr(OH)₄(aq) is expected to be predominant. In such a case, it is very important to consider the kinetics of the formation of these species, as is often pointed out for titration experiments [4]. Some of the species, which may have charges depending on solution conditions, are small enough to pass through filter pores, and are considered to enhance the measured solubility. In the present study, however, the solubility of “mononuclear-size” species can be estimated from the Flory-Schulz’s model curves.

Solubility product of Zr(OH)₄(am)

The concentrations of mononuclear species ([Zr]_{mono_tot}) calculated from the polymer model can be expressed by the following equation.

$$\begin{aligned} [\text{Zr}]_{\text{mono_tot}} &= [\text{Zr}^{4+}] + [\text{ZrOH}^{3+}] + [\text{Zr(OH)}_2^{2+}] + [\text{Zr(OH)}_3^{+}] + [\text{Zr(OH)}_4(\text{aq})] \\ &= [\text{Zr}^{4+}] (1 + \beta_{1,1}[\text{OH}^-] + \beta_{1,2}[\text{OH}^-]^2 + \beta_{1,3}[\text{OH}^-]^3 + \beta_{1,4}[\text{OH}^-]^4) \\ &= \frac{K_{\text{sp}}}{[\text{OH}^-]^4} (1 + \beta_{1,1}[\text{OH}^-] + \beta_{1,2}[\text{OH}^-]^2 + \beta_{1,3}[\text{OH}^-]^3 + \beta_{1,4}[\text{OH}^-]^4), \end{aligned} \quad (2.7)$$

where K_{sp} denotes the solubility product of Zr(OH)₄(am), that is $K_{\text{sp}} = [\text{Zr}^{4+}][\text{OH}^-]^4$, and $\beta_{1,n}$ the formation constant of 1: n complexes. According to the specific ion-interaction theory (SIT) method, the K_{sp} and $\beta_{1,n}$ are given by

$$\begin{aligned} \log K_{\text{sp}} &= \log K_{\text{sp}}^{\circ} + \log \gamma_{\text{Zr}^{4+}} + 4 \log \gamma_{\text{OH}^-} \\ &= \log K_{\text{sp}}^{\circ} + 20D - [\varepsilon(\text{Zr}^{4+}, \text{ClO}_4^-) + 4\varepsilon(\text{OH}^-, \text{Na}^+)] \cdot I_{\text{m}} \end{aligned} \quad (2.8)$$

$$\begin{aligned} \log \beta_{1,n} &= \log \beta_{1,n}^{\circ} + \log \gamma_{\text{Zr(OH)}_n^{(4-n)+}} - (\log \gamma_{\text{Zr}^{4+}} + n \log \gamma_{\text{OH}^-}) \\ &= \log \beta_{1,n}^{\circ} + \{(4-n)^2 - 16 - n^2\} \cdot D \\ &\quad - \{\varepsilon(\text{Zr(OH)}_n^{(4-n)+}, \text{ClO}_4^-) - \varepsilon(\text{Zr}^{4+}, \text{ClO}_4^-) - n\varepsilon(\text{OH}^-, \text{Na}^+)\} \cdot I_{\text{m}}, \quad (n = 1-4) \end{aligned} \quad (2.9)$$

where $\varepsilon(\text{OH}^-, \text{Na}^+)$, $\varepsilon(\text{Zr}^{4+}, \text{ClO}_4^-)$ and $\varepsilon(\text{Zr(OH)}_n^{(4-n)+}, \text{ClO}_4^-)$ are the ion interaction coefficients, D the Debye-Hückel term at 25°C and I_{m} the molal ionic strength.

In the least squares fitting of the “mononuclear solubility” (concentrations of mononuclear species) data, the $\log K_{sp}^{\circ}$ value was treated as a free parameter and the hydrolysis constants [18] were treated as fixed parameters. The ion interaction parameter values of Zr^{4+} , $ZrOH^{3+}$, $Zr(OH)_2^{2+}$, $Zr(OH)_3^{+}$, and OH^{-} were taken to be 0.84 [5], 0.55 [19], 0.52 [20], 0.23 [20], and 0.04 [21], respectively. The ion product (pK_w) [22] was also used from the literature. Then, the $\log K_{sp}^{\circ}$ value was determined to be -56.9 ± 0.7 (Table 2.2). On the basis of these constants obtained, the solubility curve for mononuclear species at $I = 0.5$ is shown in Fig. 2.2 as the dotted line in the acidic pH_c region. The solubility of $Zr(OH)_4(am)$ with no colloidal contribution were similar to the solubility of $Zr(OH)_4(s)$ prepared by the undersaturation method [5] and the both solubility product values were in agreement within the margin of errors.

2.3.2 Solubility of Amorphous Thorium Hydroxide by Oversaturation Method

Solubility in the acidic, neutral and alkaline pH_c range

Figure 2.5 shows Th(IV) solubility in 0.2-2.0 M $NaClO_4$ solutions obtained by 3k Da NMWL filtration, together with previously reported data. [9,23-26] No significant change of the Th(IV) concentrations was observed between 89 and 104 days, so that the steady state was considered to be achieved at least after 89 days. It is interesting to note that Th(IV) hydroxide is considered to be stable in a wide variety of electrolyte solutions, and the solubility equilibrium has been observed within at least a few days. [25] The present solubility data obtained by 3k Da filtration are in agreement with the literature data obtained by filtration with 5k Da [23] and 2.5k Da [24] NMWL membranes, and are slightly lower than the data with 30k Da NMWL membranes [25]. On the other hand, the solubility by Neck et al. and Östhols et al. [9,26] are lower than the present solubility. In their experiments, amorphous precipitates were dried before starting the sample preparation by the undersaturation method, while Moon, Felmy et al. and Rai et al. [23-25] used wet amorphous precipitates. The difference of the experimental treatments may cause a difference of solid phase and/or colloid formation. Although there was less dependence on filter pore size compared to Zr, Th solubility was observed to slightly increase with increasing filter pore size, indicating the possible presence of a colloidal species (Table 2.3).

Size distributions of colloidal species and solubility product of $Th(OH)_4(am)$

Similarly to the analysis of Zr, the polymer model [15] was applied to the size

distributions of Th species. The size of a Th monomeric unit was taken to be 0.5 nm, assuming a cubic structure [27]. The P values were obtained from analysis of the size distributions using Eq. (2.5), and the solubility of the mononuclear species was then calculated using the obtained P values (Table 2.3) corresponding to the mononuclear solubility ($[\text{Th}]_{\text{mono_tot}}$) as expressed by

$$\begin{aligned} [\text{Th}]_{\text{mono_tot}} &= [\text{Th}^{4+}] + [\text{ThOH}^{3+}] + [\text{Th}(\text{OH})_2^{2+}] + [\text{Th}(\text{OH})_3^+] + [\text{Th}(\text{OH})_4(\text{aq})] \\ &= [\text{Th}^{4+}] (1 + \beta_{1,1}[\text{OH}^-] + \beta_{1,2}[\text{OH}^-]^2 + \beta_{1,3}[\text{OH}^-]^3 + \beta_{1,4}[\text{OH}^-]^4) \\ &= \frac{K_{\text{sp}}}{[\text{OH}^-]^4} (1 + \beta_{1,1}[\text{OH}^-] + \beta_{1,2}[\text{OH}^-]^2 + \beta_{1,3}[\text{OH}^-]^3 + \beta_{1,4}[\text{OH}^-]^4). \end{aligned} \quad (2.10)$$

It is interesting to note that Th colloidal species were assumed to be 1-dementinal due to the better fitting of the size distribution data. Curves in Fig. 2.6 show the calculated size distributions in the range from 0.5 to 7 nm. The concentration of the mononuclear species at $I = 0.6$ is shown as a dashed curve in Fig. 2.5. Similarly to the results of Zr, the calculated solubility of mononuclear species is near to the solubility obtained from dried hydroxide precipitates [9,26]. The solubility of dried amorphous precipitate may include less contribution of the colloidal species.

The solubility product value of $\text{Th}(\text{OH})_4$ (am) was determined in the least square analysis of the mononuclear solubility using Eq. (2.10). In the analysis, values reported in our previous study were used for the hydrolysis constants $\beta_{1,n}$ ($n = 1-4$) of mononuclear species [28] (Table 2.4). The solubility product of $\log K_{\text{sp}}^\circ = -48.1 \pm 0.5$ at $I = 0$ was obtained after correction using SIT method, in which, due to the lack of experimental data, the estimated ion interaction coefficient values of Th^{4+} , ThOH^{3+} , $\text{Th}(\text{OH})_2^{2+}$, $\text{Th}(\text{OH})_3^+$, and OH^- were taken to be 0.67, 0.45, 0.3, 0.15 [29] and 0.04 [21], respectively. The $\log K_{\text{sp}}^\circ$ value obtained in the present study, which is considered to be free from any contribution of the colloidal species, is lower than the values of -45.5 reported by Felmy et al. [24] and -44.9 reported by Rai et al. [25], and near to the values of -47.8 by Neck et al. [9], -48.69 by Östhols et al. [26], and -47.5 for $\text{ThO}_2(\text{am, hyd, aged})$ by NEA-TDB [30].

2.3.3 Solubility of Crystalline Zirconium Oxide and Dehydrated Hydroxide by Undersaturation Method

Solubility in the acidic, neutral and alkaline pH_c range

Solubility of ZrO_2 and $\text{Zr}(\text{OH})_4$ after filtration by 3k Da NMWL membrane filter is

plotted in Fig. 2.7 as a function of pH_c . The solubility data of 0.01 M at complete dissolution of Zr was obtained after 43 and 93 days and those of 0.1 M and 1.0 M was obtained after 21 or 24 days. Since the solubility was independent of the aging time at 0.01 M total Zr, the solubility equilibrium was achieved. In that case, the solubility of ZrO_2 and Zr(OH)_4 was less than 10^{-6} M even under the strong acid condition. At $\text{pH}_c > 2$, the obtained values were kept at around 10^{-8} M as low as the ICP-MS detection limit. Under the alkaline condition, the solubility of Zr(OH)_4 increases with the increasing pH, while that of ZrO_2 is as low as the detection limit. As shown in Fig. 2.8, the obtained data of ZrO_2 and Zr(OH)_4 are independent of the ultrafiltration by the filters of 3k to 100k Da NMWL, indicating no presence of colloidal species in this range.

Figure 2.9 shows the results of the solubility measurements of ZrO_2 and Zr(OH)_4 as a function of the total Zr solute amount added in the solution. In the case of Zr(OH)_4 , its solubility increases with the increasing solute amount as shown in Fig. 2.9. No equilibrium was achieved even after 61 days. In some details, it is noticed that about 0.1% of the added solute is dissolved in the solution in every case by comparing the Zr concentration with the total amount. Considering that the solid phase separated from the aqueous phase would be composed of the larger colloidal species, this amount of 0.1% would be attributed to the possible presence and/or formation of soluble colloidal species on the present Zr(OH)_4 . In this respect, it is interesting to compare the XRD spectra of the Zr(OH)_4 before and after the contact with the solution. As shown in Fig. 2.10, the XRD peaks of Zr(OH)_4 after the contact with the solution are as broad as those of the amorphous precipitate from “oversaturation” and shifted to a higher angle in comparison with those before the contact. This broad peak at $2\theta = 30^\circ$ of the amorphous precipitate was also observed by Keramidas et al [31]. Thus it can be considered that the Zr(OH)_4 is easily transformed into an amorphous phase composing of the colloidal species by incorporating water molecules and that a definite fraction of the smaller colloidal species may be dissolved into the solution. In the case of ZrO_2 , on the other hand, its solubility seems almost independent of the total solute amount, and only a slight increase of the solubility is observed at the higher total solute amounts and the lower pH condition. This increase may be attributed to possible effect of soluble hydroxides contained in the ZrO_2 . The XRD spectrum of the ZrO_2 after contacting with the liquid phase shows the same pattern as that of a crystal ZrO_2 , suggesting that the steady state is achieved between the crystalline and liquid phases in this case.

Solubility product of $\text{ZrO}_2(\text{cr})$

A comprehensive review of the literatures on zirconium hydrous oxides was performed in the NEA-TDB project [32]. The solubility product and hydrolysis constants were selected and a diagram of the stability field distribution was proposed as a function of total zirconium concentration and pH_c . In the diagram, the dominant species are defined as trimeric and tetrameric species of $\text{Zr}_3(\text{OH})_9^{3+}$, $\text{Zr}_4(\text{OH})_{15}^+$, $\text{Zr}_4(\text{OH})_{16}(\text{aq})$ when the zirconium concentration is higher than 10^{-6} M. The mononuclear species are considered to exist only in the low concentration under 10^{-6} M. The present results are considered to be consistent with this diagram; no presence of the larger species is observed in the case of the ZrO_2 of which the solubility is very low.

The obtained solubility data at $\text{pH}_c > 2$ are around the detection limit and are considered to be the upper limit. Therefore, in the analysis the solubility data at $\text{pH}_c < 2$ were used to determine the solubility product of $\text{ZrO}_2(\text{cr})$. As described above, the measured solubility was assumed to represent the concentration of mononuclear species given by Eq. (2.7). Similarly to the analysis of amorphous zirconium solubility, the hydrolysis constants, ion interaction parameters were treated as fix parameters and the solubility product of $\text{ZrO}_2(\text{cr})$ was determined to $\log K_{\text{sp}}^\circ = -62.5 \pm 0.7$. The values obtained and used in the analysis are summarized in Table 2.5 together with the literature value. The obtained solubility product value is in good agreement with that by Pouchon et al [33]. In the solubility analysis of $\text{ZrO}_2(\text{cr})$, little contribution of the colloidal species to the apparent solubility was shown and this may be a reason for less scattering in the solubility product values.

Influence of the formation of colloidal species on solubility

Figure 2.11 shows a comparison of the present solubility data for $\text{ZrO}_2(\text{cr})$ and $\text{Zr}(\text{OH})_4$ with some literature data [5,10,32,34]. It can be seen that the solubility of $\text{ZrO}_2(\text{cr})$ is quite low compared with the others. The $\log K_{\text{sp}}^\circ$ of $\text{ZrO}_2(\text{cr})$ was then evaluated by considering predominant formation of mononuclear species in the present study. In the case of $\text{Zr}(\text{OH})_4$, on the other hand, much higher and different solubility data have been obtained depending on the influence of the formation of colloidal species on the experimental results.

In the measurement of the solubility of amorphous hydroxide ($\text{Zr}(\text{OH})_4(\text{am})$) prepared by the oversaturation method, for example, the formation of colloidal species were observed. In such a case, the size distributions of the species were measured and analyzed by

a simple polymer model of Flory-Schulz to evaluate the concentration of mononuclear species, that is the solubility of the amorphous Zr(OH)_4 . As a result, the $\log K_{\text{sp}}^\circ$ value was determined to be -56.9 ± 0.7 .

It is interesting to note that the solubility of the present Zr(OH)_4 would be low compared with that expected for the amorphous Zr(OH)_4 of which the $\log K_{\text{sp}}^\circ$ is -56.9 . As mentioned above, it seems that the Zr(OH)_4 is easily transformed into an amorphous phase composing of the colloidal species by incorporating water molecules and that a definite fraction of the smaller colloidal species may be dissolved into the solution. Since no equilibrium was observed for the Zr(OH)_4 , however, it might be considered that the dissolution reactions are so slow in the present case. Thus it is important to take into account such a slow kinetics of the reactions involving colloidal species in order to obtain the reliable solubility for the Zr(OH)_4 .

2.4 Conclusion

Considering the results of the present solubility measurements, it is obvious that the sample preparation is one of the most important factors for obtaining reliable and reproducible data. The formation of colloidal species, of which a steady state size distribution was reached within a few months, was observed in oversaturation experiments. From the observed size distributions, it was found that the colloidal species under 3k Da in size may exist even in the acidic solution. Applying a simple polymer model to the size distributions, the “mononuclear” solubility was calculated and the solubility products of $\text{Zr(OH)}_4(\text{am})$ and $\text{Th(OH)}_4(\text{am})$ were determined using only mononuclear hydrolysis constants, which were obtained with sufficient precision in the literatures.

On the other hand, for $\text{ZrO}_2(\text{cr})$, the solubility measured by the undersaturation method showed quite low values even in a strong acid condition. Dominant soluble species were considered to be mononuclear species of Zr^{4+} , ZrOH^{3+} , Zr(OH)_2^{2+} , Zr(OH)_3^+ , $\text{Zr(OH)}_4(\text{aq})$ and the solubility product and hydrolysis constants were determined from the solubility data of $\text{ZrO}_2(\text{cr})$. On the contrary, the solubility of $\text{Zr(OH)}_4(\text{s})$, which is dehydrated dried powder, by the undersaturation method increased with the increasing solute amount and no equilibrium was achieved. This may be due to possible presence and/or formation of soluble colloidal species on the present $\text{Zr(OH)}_4(\text{s})$. It seems to take much longer time to achieve equilibrium of the reactions involving such species.

References

1. Kobayashi, T., Sasaki, T., Takagi, I., Moriyama, H.: Solubility of Zirconium(IV) Hydrous Oxides. *J. Nucl. Sci. Technol.*, **44**, 90 (2007).
2. Sasaki, T., Kobayashi, T., Takagi, I., Moriyama, H.: Solubility measurement of zirconium(IV) hydrous oxide. *Radiochim. Acta* **94**, 489 (2006).
3. Kobayashi, T., Sasaki, T., Takagi, I., Moriyama, H.: Solubility of Thorium(IV) in the Presence of Oxalic and Malonic Acids. *J. Nucl. Sci. Technol.*, **46**, 1085 (2009).
4. Veyland, A., Dupont, L., Pierrad C., Rimbault, J., Aplincourt, M.: Thermodynamic stability of zirconium(IV) complexes with hydroxy ions. *Eur. J. Inorg. Chem.* 1765 (1998).
5. Ekberg, C., Kallvenius, G., Albinsson, Y., Brown, P.: Studies on the hydrolytic behavior of zirconium(IV). *J. Solution Chem.* **33**, 47 (2004).
6. Ekberg, C., Albinsson, Y., Comarmond, M. J., Brown, P. L.: Studies on the complexation behavior of thorium(IV). 1. Hydrolysis equilibria. *J. Sol. Chem.*, **29**, 63 (2000).
7. Walther, C., Roche J., Füss, M., Büchner, S., Koltsov, S., Bergmann, T.: Investigation of polynuclear Zr(IV) hydroxide complexes by nanoelectrospray mass-spectrometry combined with XAFS. *Anal Bioanal Chem.* **388**, 409 (2007).
8. Walther, C., Fuss, M., Böchner, S.: Formation and hydrolysis of polynuclear Th(IV) complexes - a nano-electrospray mass spectrometry study. *Radiochim. Acta* **96**, 411 (2008).
9. Neck, V., Bouby, M., Altmaier, M., Rothe, J., Denecke, M. A., Kim, J. I.: Solubility of amorphous Th(IV) hydroxide - application of LIBD to determine the solubility product and EXAFS for aqueous speciation. *Radiochim. Acta* **90**, 485 (2002).
10. Cho, H., Walther, C., Roche, J., Neck, V., Denecke, M. A., Dardenne, K., Fanghanel, Th.: Combined LIBD and XAFS investigation of the formation and structure of Zr(IV) colloids. *Anal. Bioanal. Chem.* **383**, 28 (2005)
11. Rai, D., Felmy, A. R., Sterner, S. M., Moore, D. A., Mason, M. J.: The Solubility of Th(IV) and U(IV) Hydrous Oxides in Concentrated NaCl and MgCl₂ Solutions. *Radiochim. Acta* **79**, 239 (1997).
12. Rai, D., Moore, D., Oakes, C., Yui, M.: Thermodynamic model for the solubility of

- thorium dioxide in the $\text{Na}^+\text{-Cl}^-\text{-OH}^-\text{-H}_2\text{O}$ system at 23°C and 90°C. *Radiochim. Acta* **88**, 297 (2000).
13. Neck, V., Altmaier, M., Müller, R., Bauer, A., Fanghänel, Th., Kim, J. I.: Solubility of crystalline thorium dioxide. *Radiochim. Acta* **91**, 253 (2003).
 14. Shannon, R.: Revised Effective Ionic Radii and Systematic Studies of Interatomic Distances in Halides and Chalcogenides. *Acta Cryst.*, **32**, 751 (1976).
 15. Flory, P.: *Principles of Polymer Chemistry*, Cornell Univ. Press, New York (1953).
 16. Moriyama, H., Pratopo, M. I., Higashi, K.: The solubility and colloidal behavior of neptunium(IV). *Sci. Total Environ.* **83**, 227 (1989).
 17. Nakayama, S., Moriyama, H., Arimoto, H., Higashi, K.: Behaviors of americium in aqueous-solutions containing iron. *J. Nucl. Sci. Technol.* **23**, 731 (1986).
 18. Sasaki, T., Kobayashi, T., Takagi, I., Moriyama, H.: Hydrolysis Constant and Coordination Geometry of Zirconium(IV). *J. Nucl. Sci. Technol.*, **45**, 735 (2008).
 19. Curti, E.: *Paul Scherrer Institut Rep. TM-44-01-01* (2001).
 20. Fujiwara, K., Yamana, H., Fujii, T., Moriyama, H.: Determination of uranium(IV) hydrolysis constants and solubility product of $\text{UO}_2 \cdot x\text{H}_2\text{O}$. *Radiochim. Acta*, **91**, 345 (2003).
 21. Guillaumont, R., Fanghänel, Th., Fuger, J., Grenthe, I., Neck, V., Palmer, D., Rand, M.: *Update on the Chemical Thermodynamics of Uranium, Neptunium, Plutonium, Americium and Technetium*, In: *Chemical Thermodynamics* (Eds.: F. J. Mompean et al.) Vol. 5. Elsevier, North-Holland, Amsterdam (2003).
 22. Baes, C. F., Mesmer, R. E.: *The Hydrolysis of Cations*. John Wiley & Sons, New York (1976).
 23. Moon, H.: Equilibrium Ultrafiltration of Hydrolyzed Thorium(IV) Solutions. *Bull. Korean Chem. Soc.* **10**, 270 (1989).
 24. Felmy, A. R., Rai, D., Mason, M. J.: The Solubility of Hydrous Thorium(IV) Oxide in Chloride Media: Development of an Aqueous Ion-Interaction Model. *Radiochim. Acta* **55**, 177 (1991).
 25. Rai, D., Moore, D., Oakes, C., Yui, M.: Thermodynamic model for the solubility of thorium dioxide in the $\text{Na}^+\text{-Cl}^-\text{-OH}^-\text{-H}_2\text{O}$ system at 23°C and 90°C. *Radiochim. Acta* **88**, 297 (2000).
 26. Östholts, E., Bruno, J., Grenthe, I.: On the influence of carbonate on mineral dissolution: III. The solubility of microcrystalline ThO_2 in $\text{CO}_2\text{-H}_2\text{O}$ media. *Geochim. Cosmochim.*

- Acta **58**, 613 (1994).
27. Moriyama, H., Sasaki, T., Kobayashi, T., Takagi, I.: Systematics of Hydrolysis Constants of Tetravalent Actinide Ions. , " J. Nucl. Sci. Technol., **42**, 626 (2005).
 28. Sasaki, T., Takaoka, Y., Kobayashi, T., Fujii, T., Takagi, I., Moriyama, H.: Hydrolysis constants and complexation of Th(IV) with carboxylates. Radiochim. Acta **96**, 799 (2008).
 29. Neck, V., Kim, J. I.: Solubility and hydrolysis of tetravalent actinides. Radiochim. Acta **89**, 1 (2001).
 30. Rand, R., Fuger, J., Grenthe, I., Neck, V., Rai, D.: *Chemical Thermodynamics of Thorium*, In: *Chemical Thermodynamics* (Eds.: F. J. Mompean et al.) Vol. 11, Elsevier, North-Holland, Amsterdam (2009).
 31. Keramidas, V., White, W.: Raman scattering study of the crystallization and phase transformations of ZrO₂. J. Am. Ceram. Soc., **57**, 22 (1974).
 32. Brown, P., Curti, E., Grambow, B., Ekberg, C.: *Chemical Thermodynamics of Zirconium*, In: *Chemical Thermodynamics* (Eds.: F. J. Mompean et al.) Vol. 8. Elsevier, North-Holland, Amsterdam (2005).
 33. Pouchon, M. A., Curti, E., Degueldre, C., Tobler, L.: The influence of carbonate complexes on the solubility of zirconia: new experimental data. Progress in Nuclear Energy, **38**, 443 (2001).
 34. Kovalenko, P. N., Bagdsarov, K. N.: The solubility of zirconium hydroxide. Russ. J. Inorg. Chem., **6**, 272 (1961).
 35. Neck, V., Kim, J. I.: An electrostatic approach for the prediction of actinide complexation constants with inorganic ligands-application to carbonate complexes. Radiochim. Acta, **88**, 815 (2000).

Table 2.1 Size distributions in Zr colloidal particles in the acidic pH_c region, and *P* values obtained by polymer model fitting.

<i>I</i> (M)	pH _c	<i>P</i> ^{a)}	log [Zr]					
			"mononuclear" ^{a)}	< 3k Da	3k - 10k Da	10k - 30k Da	30k - 50k Da	50k - 100k Da
0.1	1.97	0.969	-5.01	-2.94	-2.17	-2.70	-	-
	2.22	0.989	-5.89	-3.64	-2.67	-	-3.14	-
	3.07	0.999	-8.14	-	-4.78	-4.20	-4.87	-3.74
1.0	1.59	0.930	-4.31	-2.54	-2.24	-3.22	-	-
	2.24	0.991	-6.13	-3.86	-2.81	-	-3.11	-
	2.62	0.999	-7.83	-	-4.12	-4.10	-4.44	-3.84

a) Values were obtained assuming that $l_0 = 0.4$ nm.

Table 2.2 Summary of solubility products of amorphous hydroxide ($\text{Zr(OH)}_4(\text{am})$) and hydrolysis constants for Zr(IV) reported in the literature.

		This Work	Ekberg et al. [5]	Cho et al [10]	Baes et al [22]
$\text{Zr(OH)}_4(\text{am})$	$\log K_{\text{sp}}^\circ$	$-56.9 \pm 0.7^{\text{a)}$	-57.14 ± 0.84	-53.1 ± 0.5	-
ZrOH^{3+}	$\log \beta_{1,1}^\circ$	$14.29^{\text{b)}$	14.29 ± 0.06	14.3	14.3 ± 0.05
Zr(OH)_2^{2+}	$\log \beta_{1,2}^\circ$	$26.66^{\text{b)}$	27.7 ± 0.2	$27.6^{\text{c)}$	26.3
Zr(OH)_3^+	$\log \beta_{1,3}^\circ$	$35.85^{\text{b)}$	40.1 ± 0.3	$38.1^{\text{c)}$	36.9
$\text{Zr(OH)}_4(\text{aq})$	$\log \beta_{1,4}^\circ$	$43.12^{\text{b)}$	52.1 ± 0.3	$45.4^{\text{c)}$	46.3

a) Calculated using the values of hydrolysis constants and “mononuclear” solubility in Tables 2.2 and 2.1, respectively.

b) Obtained from an electrostatic model described in Chapter 3.

c) Estimated by applying the ligand repulsion model of Ref.[35].

Table 2.3 Size distributions in Th colloidal particles in the acidic pH_c region, and P values obtained by polymer model fitting.

I (M)	pH _c	$P^{a)}$	"mononuclear" ^{b)}	< 3k Da	log [Th]			
					3k - 10k Da	10k - 30k Da	30k - 50k Da	50k - 100k Da
0.2	4.73	0.956	-4.72	-3.63	-	-3.66	-3.87	-3.26
	5.57	0.997	-7.17	-5.23	-6.51	-	-6.37	-5.83
	4.00	0.971	-5.07	-4.09	-4.48	-3.52	-	-3.76
	4.63	0.987	-5.74	-4.78	-	-4.37	-	-4.44
	5.60	0.997	-7.05	-5.48	-	-5.76	-5.80	-6.16
0.6	4.04	0.969	-5.01	-4.24	-4.24	-3.60	-	-
1.0	5.82	0.995	-6.53	-5.51	-5.02	-	-	-5.61
	4.71	0.976	-5.24	-4.30	-5.11	-	-	-
	5.45	0.995	-6.56	-5.49	-5.40	-	-	-5.31
	4.15	0.943	-4.49	-3.75	-3.62	-	-3.27	-
	3.72	0.906	-4.05	-3.10	-	-3.29	-	-
2.0	4.94	0.995	-6.58	-5.41	-7.74	-5.66	-	-7.15
	5.15	0.998	-7.31	-5.86	-	-6.54	-6.15	-

a) Values were obtained in the least square analysis.

b) Values were obtained assuming that $l_0 = 0.5$ nm.

Table 2.4 Summary of solubility products of amorphous hydroxide ($\text{Th(OH)}_4(\text{am})$) and hydrolysis constants for Th(IV) reported in the literature.

		This Work	Neck [29]	Rai [12]	NEA-TDB [30]
$\text{Th(OH)}_4(\text{am})$	$\log K_{\text{sp}}^\circ$	$-48.1 \pm 0.5^{\text{a}}$	-47.8 ± 0.3	-44.9 ± 0.5	$-46.7 \pm 0.9^{\text{b}}$, $-47.5 \pm 0.9^{\text{c}}$
ThOH^{3+}	$\log \beta_{1,1}^\circ$	12.2 [28]	11.8 ± 0.2	-	11.5 ± 0.5
Th(OH)_2^{2+}	$\log \beta_{1,2}^\circ$	23.0 [28]	22.0 ± 0.6	-	21.8 ± 0.5
Th(OH)_3^+	$\log \beta_{1,3}^\circ$	32.7 [28]	31.0 ± 1.0	-	-
$\text{Th(OH)}_4(\text{aq})$	$\log \beta_{1,4}^\circ$	39.1 [28]	38.5 ± 0.5	-	38.6 ± 0.5

a) Calculated using “mononuclear” solubility in Table 2.1.

b) Value for $\text{ThO}_2(\text{am}, \text{hyd}, \text{fresh})$.

c) Value for $\text{ThO}_2(\text{am}, \text{hyd}, \text{aged})$.

Table 2.5 Summary of solubility products of crystalline oxide ($\text{ZrO}_2(\text{cr})$) and hydrolysis constants for Zr(IV) reported in the literature.

		This Work	Pouchon [33]
$\text{ZrO}_2(\text{cr})$	$\log K_{\text{sp}}^\circ$	$-62.5 \pm 0.7^{\text{a)}$	-63.0 ± 1.6
ZrOH^{3+}	$\log \beta_{1,1}^\circ$	$14.29^{\text{b)}$	-
$\text{Zr}(\text{OH})_2^{2+}$	$\log \beta_{1,2}^\circ$	$26.66^{\text{b)}$	-
$\text{Zr}(\text{OH})_3^+$	$\log \beta_{1,3}^\circ$	$35.85^{\text{b)}$	-
$\text{Zr}(\text{OH})_4(\text{aq})$	$\log \beta_{1,4}^\circ$	$43.12^{\text{b)}$	-

a) Calculated using the values of hydrolysis constants in Table 2.5.

b) Obtained from an electrostatic model described in Chapter 3.

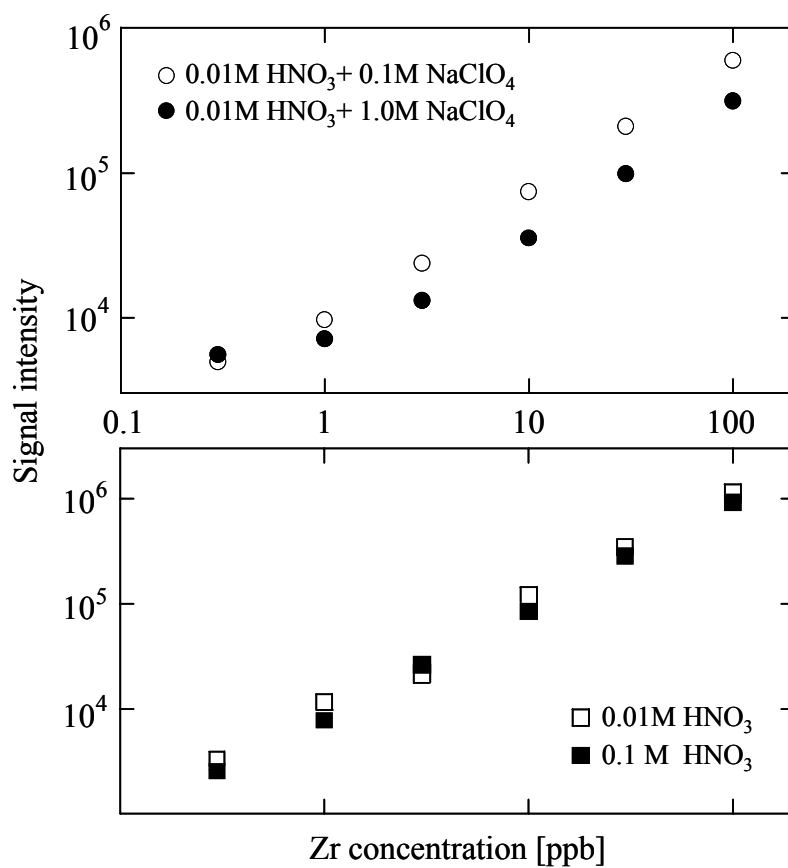


Fig. 2.1 Observation of matrix effect for the ICP-MS signal intensity in the presence of sodium perchlorate (upper) and nitric acid (lower).

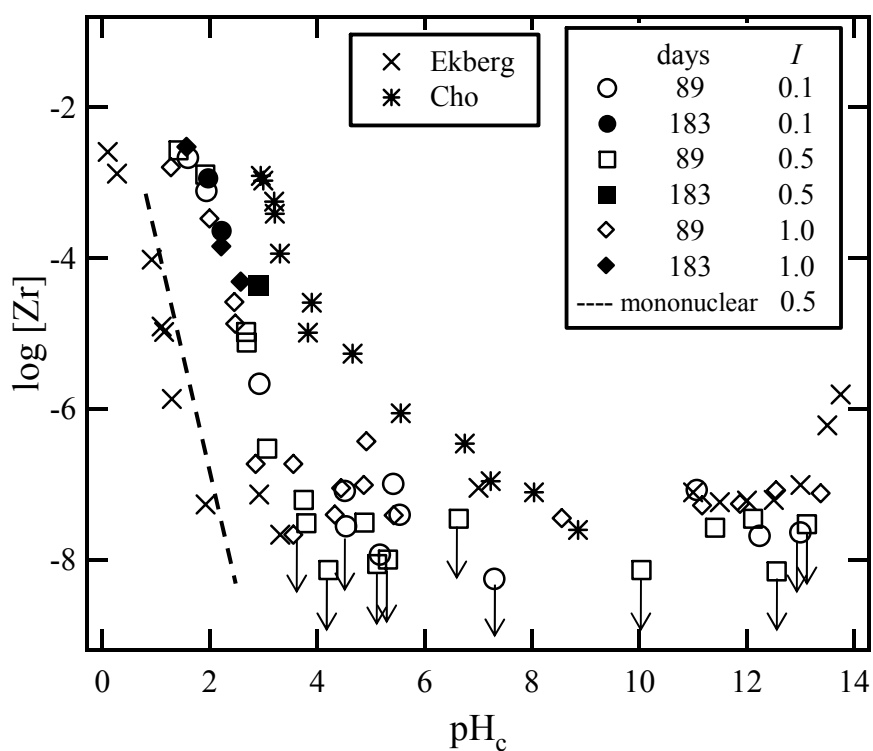


Fig. 2.2 Solubility of $\text{Zr(OH)}_4(\text{am})$ at $I = 0.1$ to 1.0 M after 3 kDa filtration as a function of pH_c . Plots with down arrows indicate levels under the detection limit $1 \times 10^{-8} \text{ M}$. The dashed curve represents the mononuclear solubility obtained using a simple polymer model. See text for details.

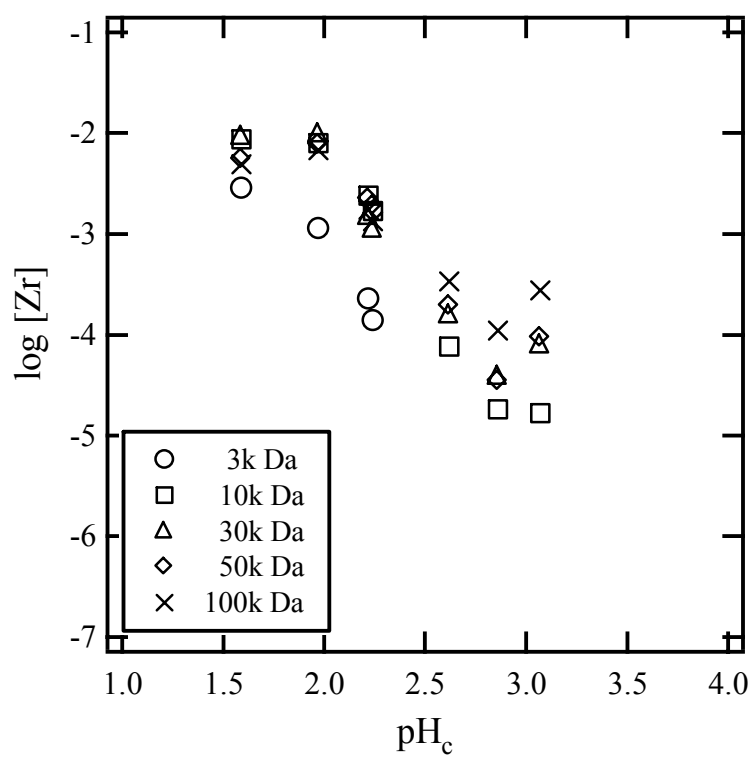


Fig.2.3 pH dependence of solubility of zirconium hydroxide after filtration by 3k - 100k Da NMWL membrane filters.

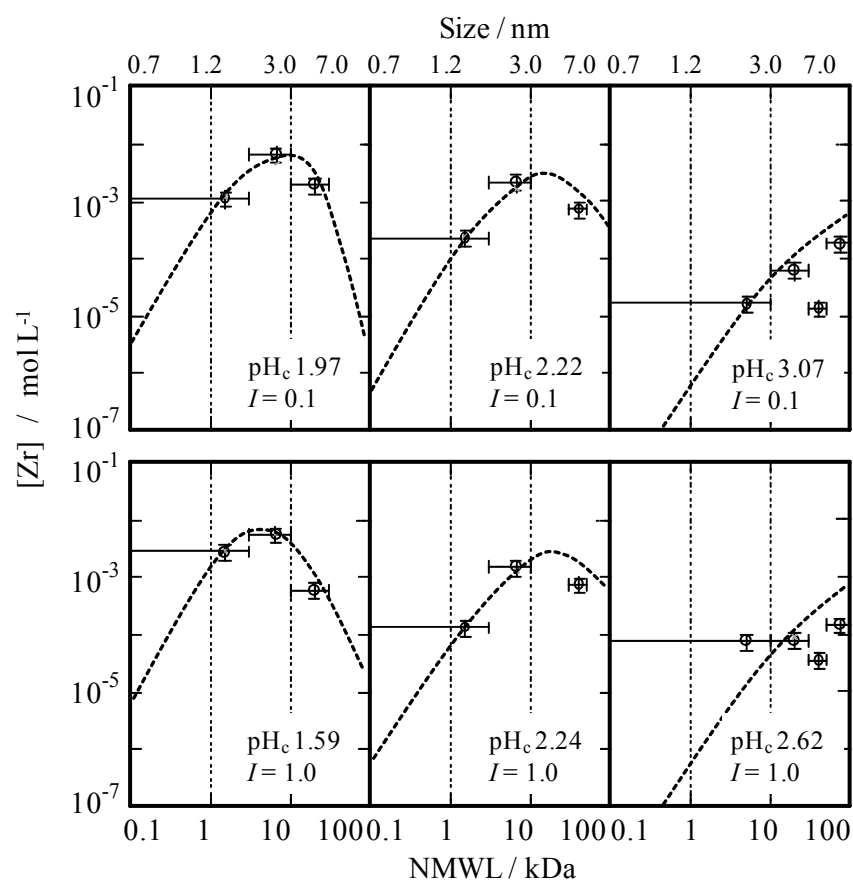


Fig. 2.4 Size distributions of Zr colloidal particles in the supernatant of sample solutions after 6 months. Curves show the calculated size distributions from 0.1k to 100k Da NMWL. Size scale in nm shows an index of the molecular size filtered.

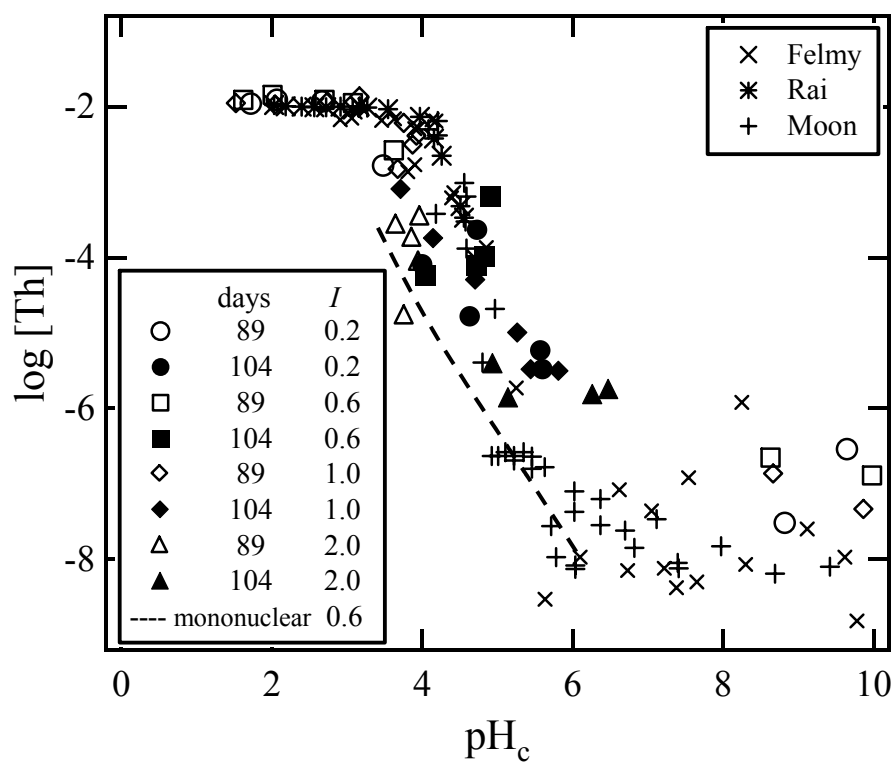


Fig. 2.5 Solubility of $\text{Th}(\text{OH})_4$ (am) at $I = 0.2$ to 2.0 M after 3k Da filtration as a function of pH_c . The dashed curve represents the mononuclear solubility obtained using a simple polymer model. See text for details.

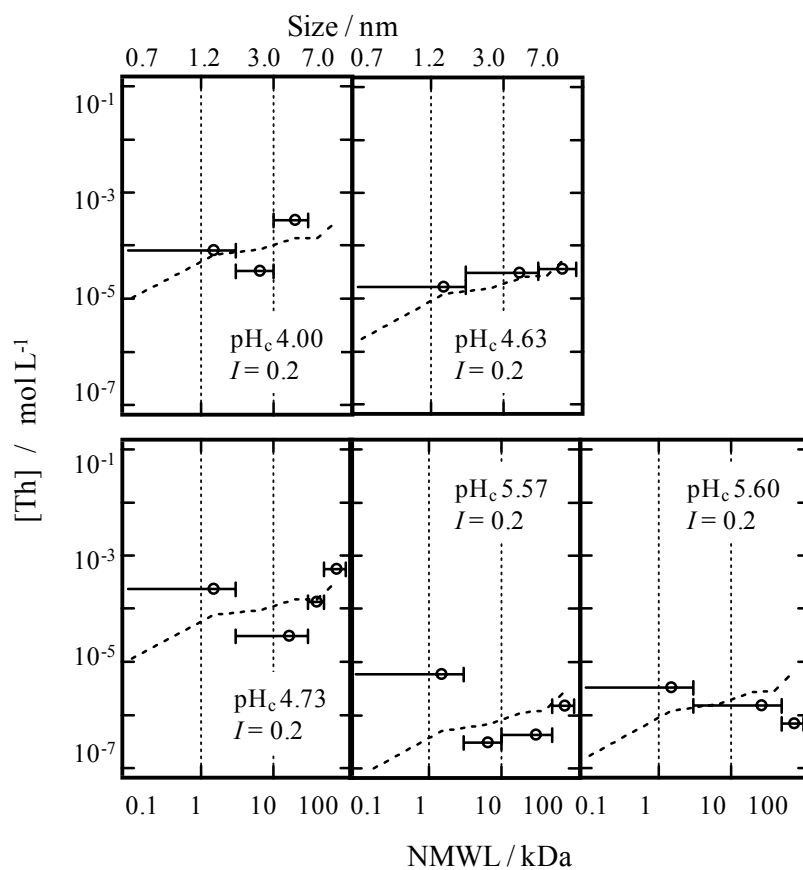


Fig. 2.6 Size distributions of Th colloidal particles in the supernatant of sample solutions after 104 days. Curves show the calculated size distributions from 0.1k to 100k Da NMWL. Size scale in nm shows an index of the molecular size filtered.

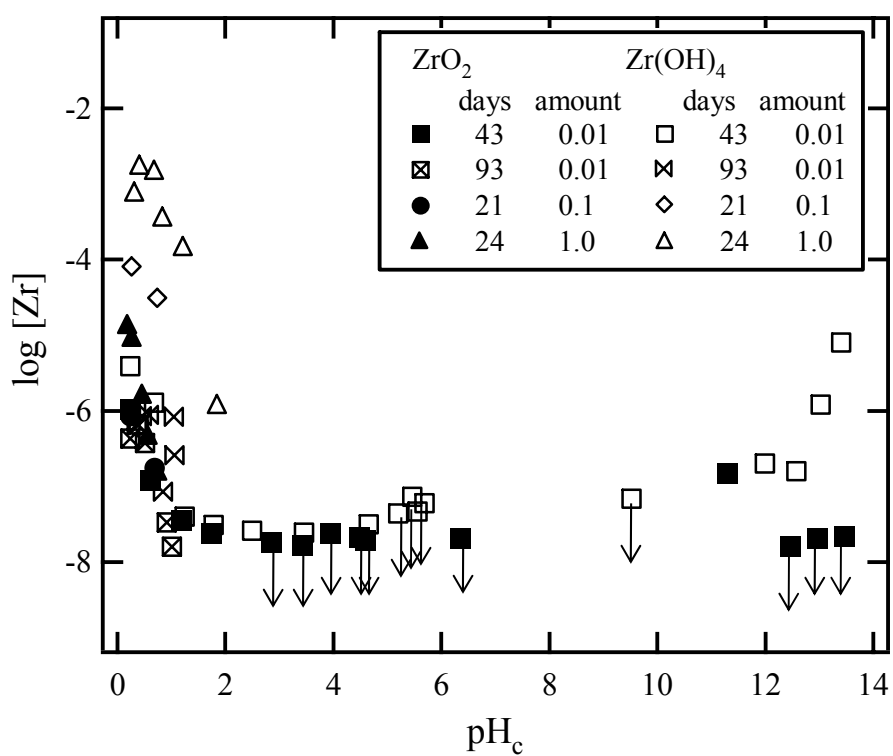


Fig. 2.7 Solubility of ZrO_2 and Zr(OH)_4 at $I = 0.1$ to 1.0 M after 3 kDa filtration as a function of pH_c . Plots with down arrows indicate levels under the detection limit 1×10^{-8} M. The value of “amount” means Zr concentration (M) when the solute added is dissolved completely.

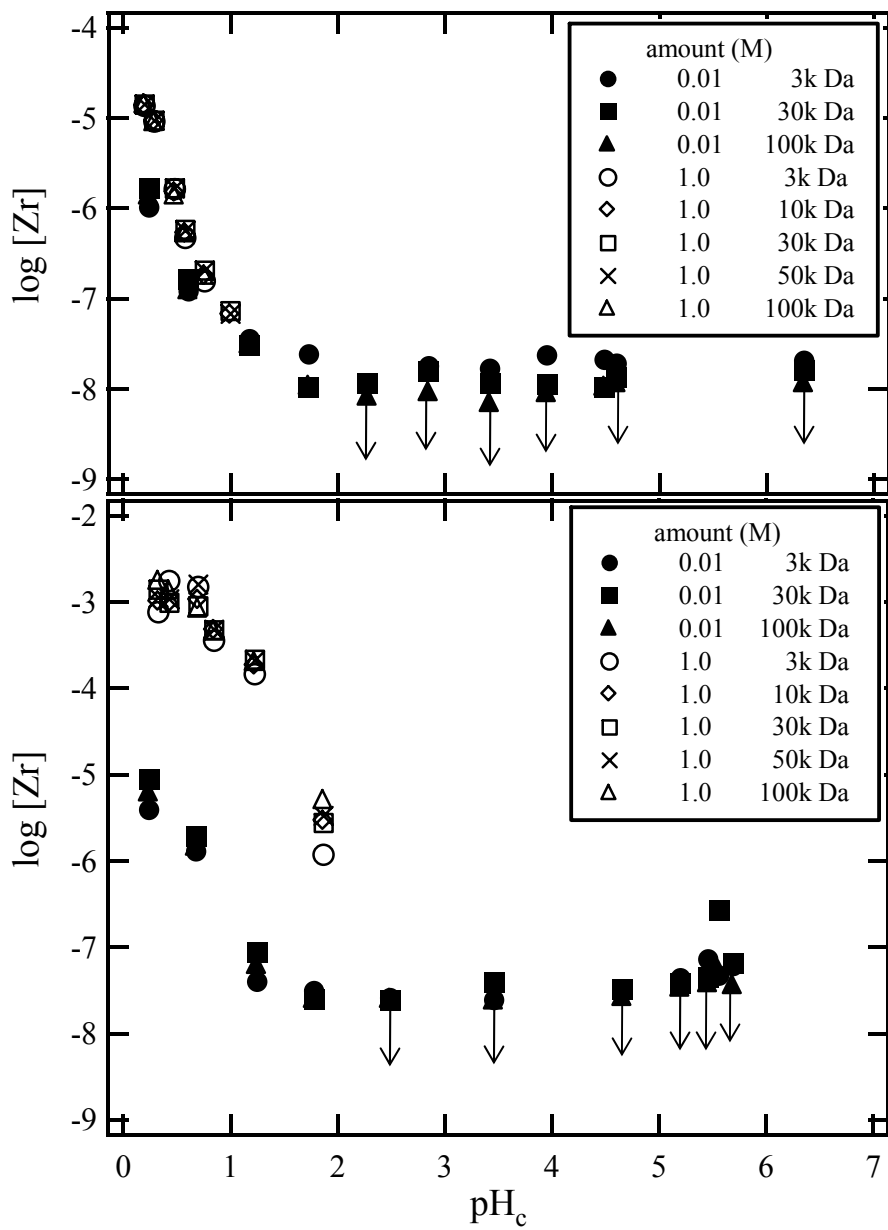


Fig.2.8 Solubility of ZrO_2 and Zr(OH)_4 after filtration by 3k - 100k Da NMWL membrane filters at 0.01 M (after 43 days) and 1.0 M (after 24 days) total solute amount in the solution ($I = 1.0$).

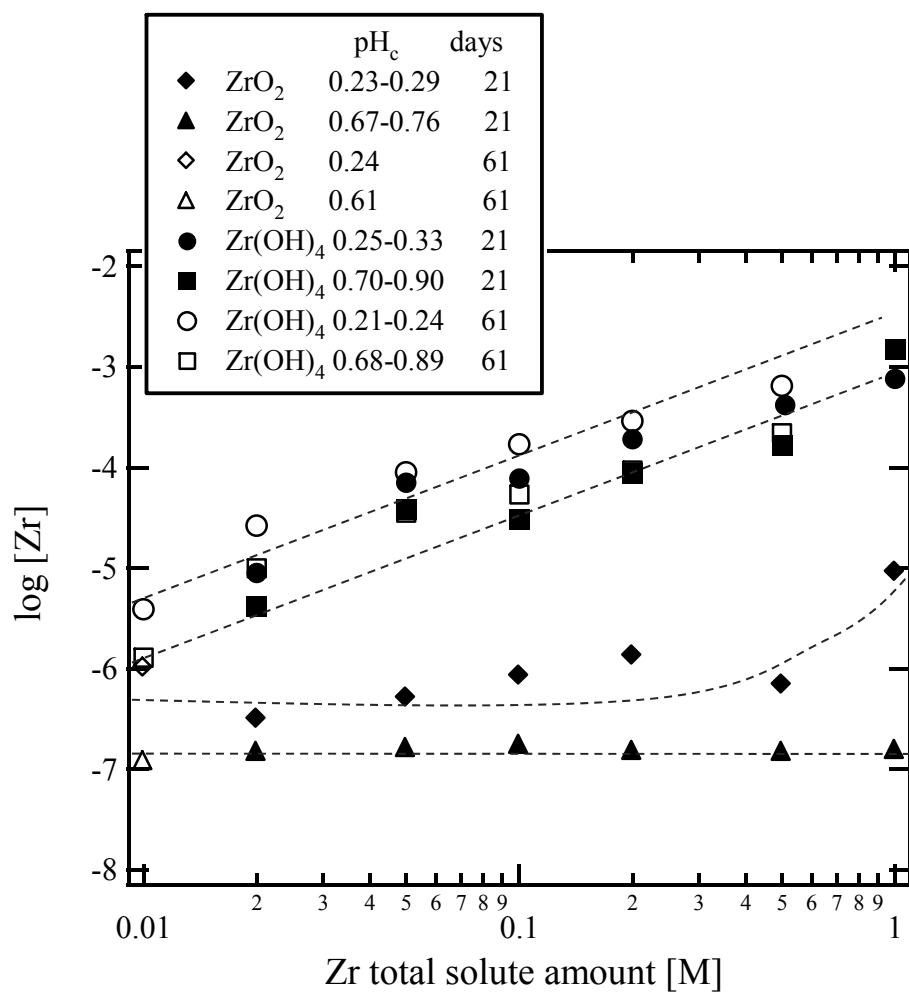


Fig. 2.9 Solubility of Zr(OH)_4 and ZrO_2 after 21 and 61 days as a function of the Zr total solute amount at complete dissolution ($I = 1.0$). Curves are drawn for the aid of the eyes.

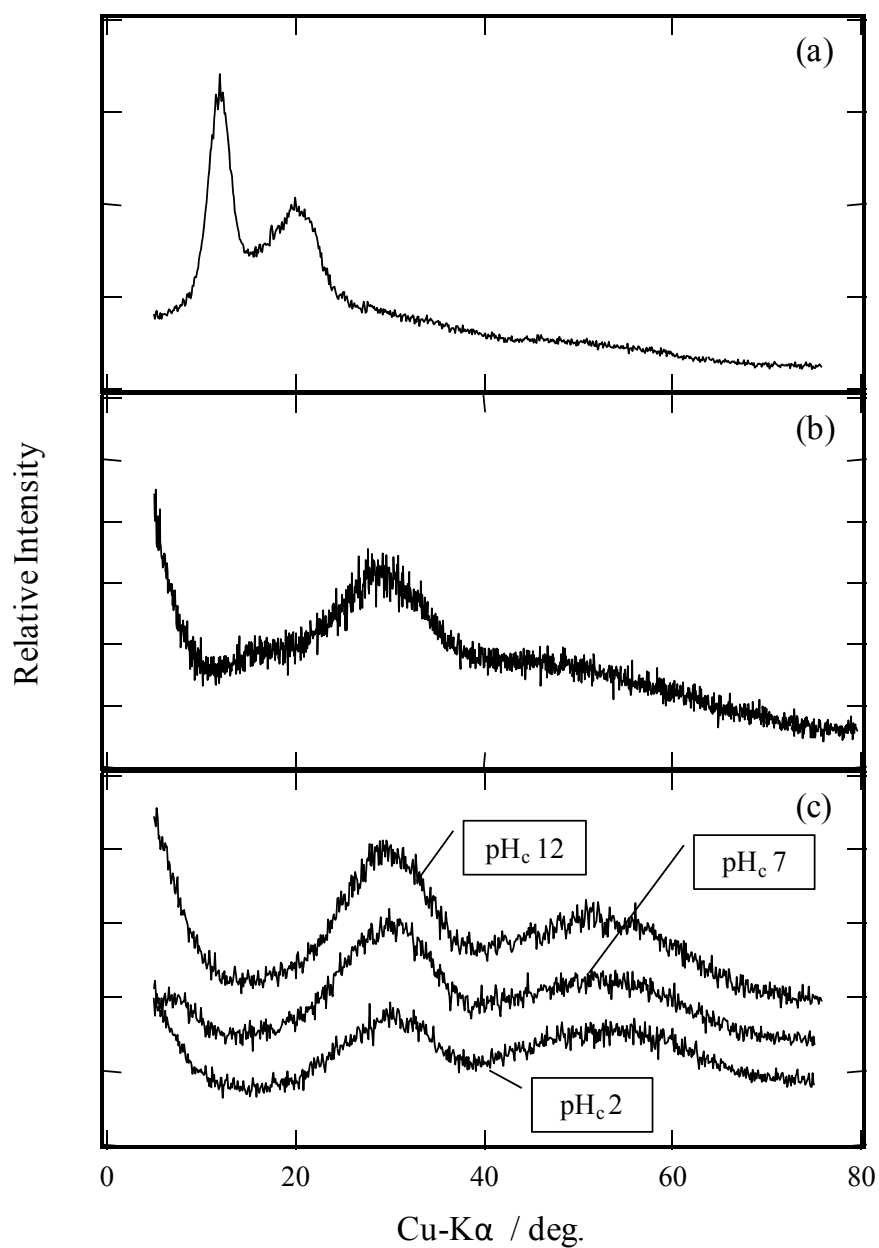


Fig. 2.10 X-ray diffraction patterns of (a) Zr(OH)_4 reagent before contacting the liquid phase, (b) amorphous precipitate from the oversaturation at pH_c 7, and (c) the solid phases of Zr(OH)_4 at pH_c 2, 7 and 12.

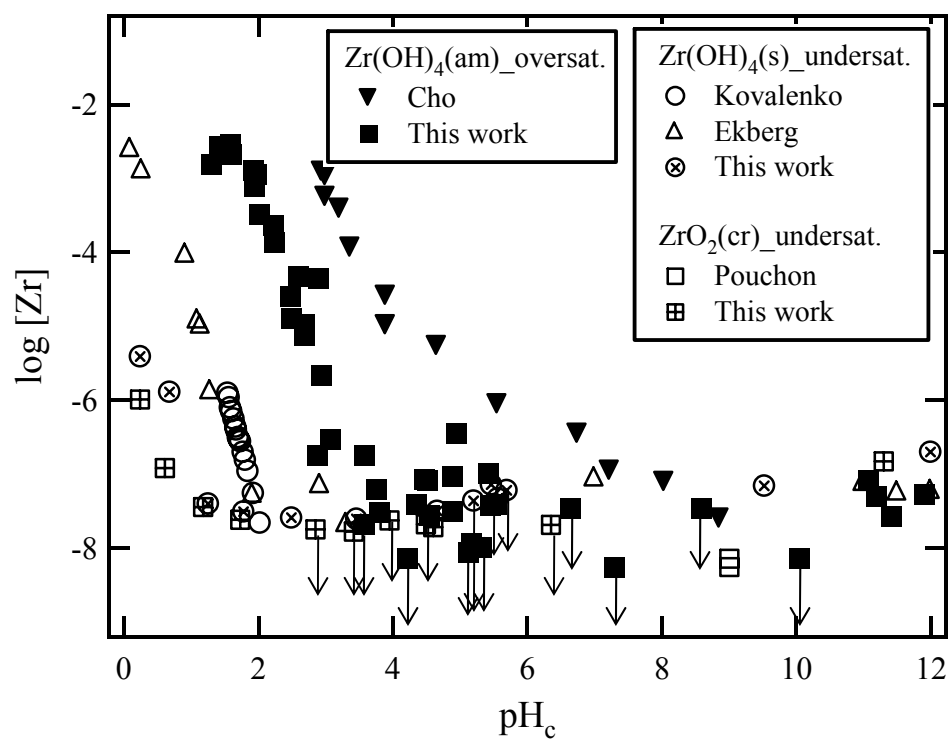


Fig. 2.11 The obtained solubility of ZrO₂ and Zr(OH)₄ compared with the literature solubility data.

Chapter 3 Hydrolysis Constant of Zirconium and Thorium

3.1 Introduction

The present chapter deals with mononuclear and polynuclear hydrolysis constant of zirconium and thorium [1,2]. In order to reveal contributions of these species to the apparent solubility, hydrolysis constant is required but there is still lack of the data, especially the constant of polynuclear species. As described in Chapter 1, it is quite difficult to obtain reliable polynuclear hydrolysis constants by experimental methods and the constants have been obtained based on some assumptions in literatures. The scatter in the reported values may be caused by the difference in assuming dominant species in solutions. In the present study, a semiempirical thermodynamic model was introduced and the hydrolysis constants of the polynuclear species were calculated from a systematic point of view. Although the obtained values depend on some model parameters, the values can be regarded as criteria.

Tetravalent ions of zirconium and thorium are hard acids, and hydroxyl ions are hard bases. The dominant interaction between these ions can be considered as an ion interaction. The stabilities of metal complexes formed by the ion interaction have been discussed in terms of a charge and ionic radius in many literatures [3-9]. The unified theory proposed by Brown and Sylva was one of the most successful models that could explain a trend of complex formation constants by considering an electrostatic effect between a metal cation and anionic ligands [9]. This model has provided many complex formation constants for the safety assessment of geological disposal [10], but in the case of a complex which has many binding ligands, the estimated values tended to be higher than the experimental ones. It was thought that the difference arose from the effect of electrostatic repulsions between anionic ligands binding to the central metal ion.

Therefore, the term of the electrostatic repulsion was introduced in the Ligand Repulsion Model and the Hard Sphere Model [11-14], and the tetravalent hydrolysis constants were well reproduced. In the Ligand Repulsion Model proposed by Neck and Kim, one semiempirical parameter that describes the shielding effect between water molecules and hydroxyl ions binding with a metal ion was introduced [11,12]. In the Hard Sphere Model, a central metal ion, coordinating water molecules and hydroxyl ions were treated as simple hard spheres and electrostatic interactions between the hard spheres were considered to

explain the hydrolysis constant. Dielectric constant and effective charges of the ions were introduced to represent a shielding effect and the additional interaction of $5f$ orbital [13,14]. Analyzing the known hydrolysis constants, the parameters were determined and unknown hydrolysis constants were estimated using the obtained parameters. In the present chapter, the Hard Sphere Model was improved to predict the hydrolysis constants of polynuclear species.

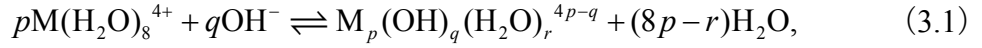
3.2 Hard Sphere Model for polynuclear species

3.2.1 The structure and formation reaction of polynuclear hydrolysis species

Zirconium and thorium can easily release four electrons from $4d$, $5s$ orbital (Zr) and $6d$, $7s$ orbitals (Th) and exist as stable tetravalent ions in aqueous solution. It is well known that thorium oxide has a stable cubic fluorite structure [15]. On the other hand, zirconium oxide has 3 well-defined polymorphs, the monoclinic baddeleyite, tetragonal, and cubic structures [16-18]. The monoclinic phase is stable up to around 1100 °C and then transforms to the tetragonal phase. Both these structures are related to the cubic fluorite structure. Zirconium hydrolysis species may have a similar structure to those of oxide. However, recent EXAFS study has been suggested that Zr(IV) ion in aqueous solution had an antiprismatic structure [19]. This is possibly due to its shorter ionic radius than that of thorium.

In the present study, hydrolysis species of thorium and other tetravalent actinides was assumed to have a cubic structure with eight-coordination based on the structure of the oxide, although an octahedral structure was assumed in the previous study [13]. In the case of zirconium, an antiprismatic structure was assumed to be as Zr hydrolysis species. The eight corners of the cubic and antiprismatic structure are occupied by water molecules and/or hydroxyl ions to form hydrolysis species.

A polymerization process to the case of thorium and zirconium ions is shown in Fig. 3.1. Thomas was one of the first to interpret the polymerization phenomena [20]. He suggested that some irreversible elimination of water molecules, which is accompanied by the formation of oxygen bridges, may occur under appropriate conditions of high temperature, prolonged aging and high pH. For simplicity, however, the formation of oxygen bridges is not taken into account in this study. The polymerization reaction for the (p, q) species with $p \geq 2$ is written as



where $r = 2 - q + 9p/2 + [1 - (-1)^{p-1}]/4$. The hydroxyl ions coordinate so that the electrostatic repulsion becomes the smallest. The potential energy change ΔE in Eq. (3.1) is given by

$$\Delta E_{p,q} = E_{p,q} - pE_{1,0} + [(8p-r) - q]E' \quad (3.2)$$

where $E_{p,q}$ denotes the contribution of $\text{M}_p(\text{OH})_q(\text{H}_2\text{O})_r^{4p-q}$ to the potential energy change and $E_{1,0}$ the contribution of $\text{M}(\text{H}_2\text{O})_8^{4+}$, and E' the contribution of a free water molecule released from the hydroxyl bridges. In the present case, the formation of polynuclear species with $p \leq 4$ are considered, and the number of free water molecules is 0, 2, 4, and 8 for $p = 1, 2, 3$, and 4, respectively.

By considering the coulombic interactions between hard spheres, the electrostatic potential energy $E_{p,q}$ of each species is given by

$$E_{p,q} = \sum_{i \neq j}^N \left(\frac{Z_i Z_j}{\epsilon d_{ij}} \right) \quad (3.3)$$

where N denotes the total number of hard spheres in the (p,q) species, Z_i and Z_j are the electric charges of the hard spheres i and j , respectively, ϵ is the dielectric constant, and d_{ij} is the distance between the hard spheres i and j .

Accordingly, the standard state hydrolysis constant $\beta_{p,q}^\circ$ of each species is expressed by

$$\beta_{p,q}^\circ = \exp(-\Delta E_{p,q} / RT) \quad (3.4)$$

where R and T denote the gas constant and absolute temperature, respectively.

3.2.2 Model parameters and analytical procedure

Dielectric constant

As for the dielectric constant, an improvement was introduced in the present model although a single constant has been assumed in the previous study [13,14]. In their

electrostatic repulsion model, for example, Neck and Kim have used the geometry dependent dielectric constant by considering possible dependence of the electrostatic shielding on geometry [11,12]. Such dependence may be due to different effects of water molecules in different geometries. Since all the effects of water molecules are included in the dielectric constant, in their model, it seems critically important to take the geometry dependent dielectric constant. In the present model, on the other hand, some of the neighboring water molecules were taken into account as hard spheres, and then much less effect may be expected due to the others. In order to minimize the number of free parameters, two types of the dielectric constant were used in the present study. One is the dielectric constant ϵ_1 for two ligands holding the central actinide ions between them. In this geometry, the electrostatic interaction between ligands is less affected by water molecules. The other denoted as ϵ_2 is for all other geometries in the coordination sphere.

Effective charges of ions

In the previous study, systematic trends of hydrolysis constants were well explained by the Hard Sphere Model, and the effective charges of the central actinide ion were discussed considering the additional interaction of $5f$ orbital [13,14]. Similar to the previous study, the effective charges of tetravalent actinides were used. On the other hand, no contribution of non-electrostatic interaction of Zr^{4+} was assumed. In the analysis, the charges of thorium and zirconium are assumed to be +4, and that of OH^- to be -1 as fixed parameters and the effective charge of water molecules (Z_{H_2O}) was treated as a fitting parameter (Table 3.1). In the analysis of Th hydrolysis constant, because of the lack of known data, reported data of uranium was also used in the least square analysis. The effective charge of uranium was supposed to be a fitting parameter similar to the previous study [13,14].

Hydrolysis constants

In literatures and our previous work, several hydrolysis constants were determined with sufficient precision from the experimental data [21-23]. In the case of tetravalent actinide, the mononuclear hydrolysis constants of thorium and uranium were determined by a solvent extraction method at considerably low thorium and uranium concentration [21,22]. In the present analysis, the values of $\log \beta_{1,1}^o = 12.2$, $\log \beta_{1,2}^o = 23.0$, $\log \beta_{1,3}^o = 32.7$ [21] for Th(IV) and $\log \beta_{1,1}^o = 13.71$, $\log \beta_{1,2}^o = 26.12$, $\log \beta_{1,3}^o = 36.85$, $\log \beta_{1,6}^o = 47.0$ [22] for U(IV) were treated as fixed parameters. In the analysis, thorium and uranium species were

assumed to have the same Z_{H_2O} , ε_1 and ε_2 , and the parameters were obtained from both thorium and uranium mononuclear hydrolysis constants using a relationship between tetravalent hydrolysis constant and ionic radii [13]. Concerning polynuclear hydrolysis constants, the values reported by Neck and Kim [12] were used in the analysis as fixed parameters. They selected a several kinds of hydrolysis constants based on the review of experimental values and estimation using the Ligand Repulsion Model. Although there is little number of data which are comparable to their values, the selected data are relatively in good agreement with reported values [23-25] (see Table 1.3).

On the other hand, in the case of zirconium, the only value of $\log \beta_{1,1}^{\circ} = 14.29 \pm 0.06$ obtained by a potentiometry using relative low concentration zirconium [26] were used from the literature. As discussed in Chapter 1, although the reported values of $\log \beta_{1,1}^{\circ}$ are in good agreement with each other in spite of the different experimental procedures, other reported constants involving highly hydrolyzed species and polynuclear ones are scattered [27-33]. In the present analysis, therefore, the values of $\log \beta_{1,6}^{\circ} = 48$ and $\log \beta_{4,8}^{\circ} = 112$ were assumed so that the solubility calculated from the obtained hydrolysis constants as a sum of the concentrations of mononuclear and polynuclear species agree with the experimental data in Chapter 2. The hydrolysis constants used in the analysis are summarized in Table 3.2 and Table 3.3.

Analytical procedure

In the case of thorium, the dielectric constants (ε_1 , ε_2) and the effective charges (Z_{H_2O} , $Z_M(U^{4+})$) were determined in the least square analysis of mononuclear hydrolysis constants of thorium and uranium using Eqs. (3.2) - (3.4). The ionic radius of 1.08×10^{-10} m for Th(IV), 1.04×10^{-10} m for U(IV) [11,12] and 1.38×10^{-10} m [34,35] for O^{2-} and H_2O were used. The parameter E' which denotes the contribution of a free water molecule released in the polymerization process were determined in the least square fitting of $\log \beta_{2,2}^{\circ} = 22.3$, $\log \beta_{4,8}^{\circ} = 91.6$, $\log \beta_{4,12}^{\circ} = 141.3$ for thorium [12]. It is note that other model parameters obtained from the analysis of mononuclear hydrolysis constants were fixed when E' was obtained. The obtained parameter values and hydrolysis constants are summarized in Table 3.1 and Table 3.2.

The dielectric constants (ε_1 , ε_2), the effective charge (Z_{H_2O}) and E' values were determined in the analysis of zirconium hydrolysis constants. The ionic radius of 0.89×10^{-10} m for Zr(IV), which was the minimum value calculated from the antiprismatic

structure was a little larger than the values of 0.84×10^{-10} m, which was the ionic radius of eight-coordination Zr(IV) in a crystal structure [36]. The obtained values are summarized in Table 3.1 and Table 3.3.

3.3 Discussion

3.3.1 Obtained parameters and hydrolysis constants

The effective charges of U^{4+} and water molecules were determined to be 4.30 ± 0.05 and -0.13 ± 0.13 from the analysis of thorium and uranium mononuclear hydrolysis constants. Concerning the effective charge of uranium ion, the effect of the $5f$ electrons was observed similar to the previous analysis [13,14]. The dielectric constants were obtained to be 21.9 ± 7.8 and 13.9 ± 5.1 for ϵ_1 and ϵ_2 , respectively. The difference between the values in the present study and previous study [13,14] may be due to the differences of structures of hydrolysis species, ionic radius and hydrolysis constants used in the analysis. The value of E' was determined to be 7.7 ± 0.3 kJ/mol (Table 3.1).

In the case of zirconium, the parameter values of Z_{H_2O} , ϵ_1 and E' were determined to be -0.07 , 25.7 and 18.8 kJ·mol⁻¹, respectively (Table 3.1). The value of $\epsilon_2 = 20$ was fixed because of lacking fixed parameters. The solubility as a sum of the concentrations from mononuclear to tetranuclear species can be calculated from the obtained hydrolysis constants and solubility product value. It should be note that when the reported constants of highly hydrolyzed or polynuclear species were used as fixed parameters to obtain the sequence of hydrolysis constants, the calculated solubility showed considerably higher values compared to the experimental data. The effective charge of water molecules in the Zr species is less negative than that in the Th species and the dielectric constants of Zr species are larger than those of Th species, indicating the less repulsion between ligands in Zr species than those in Th species. This is due to a difference in hydrolysis constants used in the analysis.

The Zr(IV) and Th(IV) mononuclear and polynuclear hydrolysis constants shown in Table 3.2 and Table 3.3 are summarized in Fig 3.2 and compared with literature values [32,37]. The calculated zirconium hydrolysis constants are much lower than the reported values, especially in the polynuclear species [32]. Although the calculated constants are dependent to a large extent on the selected structures, ionic radii and hydrolysis constants used in the analysis, the present model is expected to provide a basis not only to check abnormal experimental data, but also to systematically predict unknown values.

3.3.2 Contributions of polynuclear species to the solubility

Figure 3.3 shows a comparison of the predicted solubility curve with the experimental results for zirconium amorphous hydroxide ($\text{Zr}(\text{OH})_4(\text{am})$) after filtration through 3k Da filters. The components of polynuclear and mononuclear (1, q) - (4, q) hydrolysis species, which are considered to pass through the 3k Da filters, were calculated from the constants in Table 3.2. The contribution of colloidal species under 3k Da was calculated using the polymer model in Chapter 2. The value of $\log K_{\text{sp}}^{\circ} = -56.9$ obtained in Chapter 2 was taken as the solubility product of $\text{Zr}(\text{OH})_4(\text{am})$ with no contribution of the colloidal species. In Fig. 3.3, it can be seen that the contributions of polynuclear species such as $\text{Zr}_4(\text{OH})_{10}^{6+}$ and $\text{Zr}_4(\text{OH})_{12}^{4+}$ are considerably large in the acidic pH region. In the region of $\text{pH}_c \geq 3$, the contribution of colloidal species becomes predominant.

In Fig. 3.4, the predicted solubility curve with the experimental results for crystalline oxide ($\text{ZrO}_2(\text{cr})$) are shown. The predicted solubility curve and its component concentrations were similarly calculated by taking the solubility product value of $\log K_{\text{sp}}^{\circ} = -62.5$ in Chapter 2. As shown in Fig. 3.4, no significant contribution of the polynuclear species was predicted in this case. It is also noticed that there was no significant contribution of the colloid formation to the observed solubility data in the acidic pH region.

Figure 3.5 shows a comparison of the predicted solubility curve with the experimental results for thorium amorphous hydroxide ($\text{Th}(\text{OH})_4(\text{am})$). The predicted solubility and its component concentrations were calculated by taking the hydrolysis constants in Table 3.3 and the solubility product value of $\log K_{\text{sp}}^{\circ} = -48.1$. As shown in Fig. 3.5, the contributions of polynuclear species are not significant even in the acidic pH region, contrary to zirconium. As above, the calculated hydrolysis constants significantly depend on the hydrolysis constants used in the analysis as fixed parameters. For further confirmation of the contribution of polynuclear species to the apparent solubility, reliable experimental values involving polynuclear species are needed.

3.4 Conclusion

The systematic trends of hydrolysis constants of zirconium and thorium were investigated using the improved Hard Sphere Model. A polymerization process accompanied by the formation of double hydroxyl bridges was assumed, considering antiprismatic and

cubic structures as Zr and Th mononuclear hydrolysis species, respectively. The parameter values such as effective charge, dielectric constant were determined by analyzing the known hydrolysis constants. Due to the lack of the known hydrolysis constants of polynuclear species, some values were temporarily assumed to explain the experimental solubility plots. Although the calculated hydrolysis constants depend on the selected structures, ionic radii, and selected hydrolysis constants, the present model provides a basis not only to check abnormal experimental data but also to predict unknown values.

Using the polynuclear hydrolysis constants obtained by this model, the contributions of polynuclear species to the observed solubility were examined, together with the contribution of the colloidal species by the polymer model in Chapter 2. In the $\text{Zr(OH)}_4(\text{am})$ solubility, the contributions of polynuclear species were considered to be high under the acidic condition. With an increase of pH_c , the dominant species converted to the colloidal species, while in the near neutral pH region, the apparent solubility was controlled by the mononuclear species. Contrary to $\text{Zr(OH)}_4(\text{am})$ solubility, no significant contribution of the polynuclear and colloidal species was predicted in the solubility of $\text{ZrO}_2(\text{cr})$. In the case of thorium, the contributions of polynuclear species were not significant possibly due to the low hydrolysis constants. Although reliable experimental values are indispensable for the better prediction, the present model could provide a criterion of polynuclear hydrolysis constant from a systematic point of view.

References

1. Moriyama, H., Sasaki, T., Kobayashi, T., Takagi, I.: Systematics of Hydrolysis Constants of Tetravalent Actinide Ions. *J. Nucl. Sci. Technol.*, **42**, 626 (2005).
2. Sasaki, T., Kobayashi, T., Takagi, I., Moriyama, H.: Hydrolysis Constant and Coordination Geometry of Zirconium(IV). *J. Nucl. Sci. Technol.*, **45**, 735 (2008).
3. Davies, C. W.: Electrolytic dissociation of metal hydroxide. *J. Chem. Soc.*, 1256 (1951).
4. Irving, H., Williams, R. J. P.: Stability of transition-metal complexes. *J. Chem. Soc.*, 3192 (1953).
5. Williams, R. J. P.: Stability of the complexes of the group IIA metal ions. *J. Chem. Soc.*, 3770 (1952).
6. Baes, C. F., Mesmer, R. E.: *The Hydrolysis of Cations*. John Wiley and Sons, New York, (1976).

7. Huheey, J. E.: *Inorganic Chemistry, 2nd ed.*, Harper and Row, New York, (1976).
8. Grenthe, I., Puigdommenech, I.: *Modelling in Aquatic Chemistry*, OECD-NEA, Paris, (1997).
9. Brown, P. L., Sylva, R. N.: Unified theory of metal-ion-complex formation constants. J. Chem. Res., (S)4-5, (M)0110 (1987).
10. Brown, P. L., Wanner, H.: *Predicted Formation Constants Using the Unified Theory of Metal Ion Complexation*. OECD-NEA, Paris, (1987).
11. Neck, V., Kim, J. I.: An electrostatic approach for the prediction of actinide complexation constants with inorganic ligands-application to carbonate complexes. Radiochim. Acta, **88**, 815 (2000).
12. Neck, V., Kim, J. I.: Solubility and hydrolysis of tetravalent actinides. Radiochim. Acta, **89**, 1 (2001).
13. Moriyama, H., Kitamura, A., Fujiwara, K., Yamana, H.: Analysis of Mononuclear Hydrolysis Constants of Actinide Ions by Hard Sphere Model. Radiochim. Acta, **87**, 97 (1999).
14. Moriyama, H., Fujiwara, K., Yamana, H.: Systematics of Complexation Constants of Actinide Ions with Inorganic Ligands. J. Nucl. Sci. Technol., Supplement **3**, 246 (2002).
15. Katz, J. J., Seaborg, G. T., Morss, L. R.: *The Chemistry of the Actinide Elements 2nd Ed.* Chapman and Hall, London (1986).
16. McCullough, J. D., Trueblood, K. N.: Crystal Structure of Baddeleyite (Monoclinic ZrO_2). Acta Crystallogr., **12**, 507 (1959).
17. Teufer, G.: Crystal Structure of Tetragonal ZrO_2 . Acta Crystallogr., **15**, 1187 (1962).
18. Smith, D. K., Newkirk, H. W.: Crystal Structure of Baddeleyite (Monoclinic ZrO_2) and Its Relation to the Polymorphism of ZrO_2 . Acta Crystallogr., **18**, 982 (1965).
19. Hagfeldt, C., Kessler, V., Persson, I.: Structure of the hydrated, hydrolysed and solvated zirconium(IV) and hafnium(IV) ions in water and aprotic oxygen donor solvents. A crystallographic, EXAFS spectroscopic and large angle X-ray scattering study. J. Chem. Soc. Dalton Trans. Inorg. Chem., **14**, 2142 (2004).
20. Thomas, A. W., Whitehead, T. H.: Ion interchanges in aluminum oxychloride hydrosols. J. Phys. Chem., **35**, 27 (1931).
21. Sasaki, T., Takaoka, Y., Kobayashi, T., Fujii, T., Takagi, I., Moriyama, H.: Hydrolysis constants and complexation of Th(IV) with carboxylates. Radiochim. Acta, **96**, 79 (2008).

22. Fujiwara, K., Yamana, H., Fujii, T., Moriyama, H.: Determination of uranium(IV) hydrolysis constants and solubility product of $\text{UO}_2 \cdot x\text{H}_2\text{O}$. *Radiochim. Acta*, **91**, 345 (2003).
23. Baes, C. F., Meyer, N. J., Roberts, C. E.: Hydrolysis of thorium(IV) at 0 and 95°C. *J. Inorg. Chem.* **4**, 518 (1965).
24. Grenthe, I., Lagerman, B.: Studies on metal carbonate equilibria .23. Complex — formation in the Th(IV)-H₂O-CO₂(g) system. *Acta Chem. Scand.* **45**, 231(1991).
25. Ekberg, C., Albinsson, Y., Comarmond, M. J., Brown, P. L.: Studies on the complexation behavior of thorium(IV). 1. Hydrolysis equilibria. *J. Sol. Chem.*, **29**, 63 (2000).
26. Ekberg, C., Kallvenius, G., Albinsson, Y., Brown, P.: Studies on the hydrolytic behavior of zirconium(IV). *J. Solution Chem.* **33**, 47 (2004).
27. Zielen, A. J., Connick, R. E.: The hydrolytic polymerization of zirconium in perchloric acid solutions. *J. Amer. Chem. Soc.* **78**, 5785 (1956).
28. Tribalat, S., Schriver, L.: Zirconium(IV) thiocyanate complex. Its use as an indicator of thiocyanate or free zirconium. *C. R. Séances Acad. Sci., Ser. C*, **274**, 849 (1972).
29. Baes, C. F., Mesmer, R. E.: *The Hydrolysis of Cations*. John Wiley & Sons, New York (1976).
30. Veyland, A., Dupont, L., Pierrad, C., Rimbault, J., Aplincourt, M.: Thermodynamic stability of zirconium(IV) complexes with hydroxy ions. *Eur. J. Inorg. Chem.* 1765 (1998).
31. Ekberg, C., Kallvenius, G., Albinsson, Y., Brown, P.: Studies on the hydrolytic behavior of zirconium(IV). *J. Solution Chem.* **33**, 47 (2004).
32. Brown, P., Curti, E., Grambow, B., Ekberg, C.: *Chemical Thermodynamics of Zirconium*, In: *Chemical Thermodynamics* (Eds.: F. J. Mompean et al.) *Vol. 8*. Elsevier, North-Holland, Amsterdam (2005).
33. Walther, C., Roche, J., Füss, M., Büchner, S., Koltsov, S., Bergmann, T.: Investigation of polynuclear Zr(IV) hydroxide complexes by nanoelectrospray mass-spectrometry combined with XAFS. *Anal Bioanal Chem.* **388**, 409 (2007).
34. Marcus, Y: *Ion Solvation*. Wiley-Interscience, Chichester (1985).
35. Marcus, Y: Ionic radii in aqueous solutions. *Chem Rev.*, **88**, 1475 (1988).
36. Shannon, R.: Revised Effective Ionic Radii and Systematic Studies of Interatomic Distances in Halides and Chalcogenides. *Acta Cryst.*, **32**, 751 (1976).

37. Rand, R., Fuger, J., Grenthe, I., Neck, V., Rai, D.: *Chemical Thermodynamics of Thorium*, In: *Chemical Thermodynamics* (Eds.: F. J. Mompean et al.) *Vol. 11*, Elsevier, North-Holland, Amsterdam (2009).

Table 3.1 Parameter values used and obtained in the analysis of hydrolysis constants.

M(IV)	Zr(IV)	Th(IV) ^{b)}	U(IV) ^{b)}
Z_M	4	4	4.3±0.13
Z_{OH}	−1	−1	
Z_{H_2O}	−0.07	−0.13±0.13	
r_M (nm)	0.089	0.108	0.104
r_{OH} (nm)	0.138	0.138	
r_{H_2O} (nm)	0.138	0.138	
ε_1	25.7	21.9±7.8	
ε_2	20 ^{a)}	13.9±5.1	
E' (kJ/mol)	18.8	7.7±0.3	

a) Fixed due to the lack of data.

b) Calculated using hydrolysis constants of thorium and uranium [21, 22].

Table 3.2 Zr hydrolysis constants predicted in the present study.

Species (<i>p,q</i>)	Selected $\log \beta^{\circ}_{p,q}$	Calculated $\log \beta^{\circ}_{p,q}$	NEA-TDB [32]	Species (<i>p,q</i>)	Selected $\log \beta^{\circ}_{p,q}$	Calculated $\log \beta^{\circ}_{p,q}$	NEA-TDB [32]
(1,1)	14.29 [26]	14.29	14.32	(2,2)		25.33	
(1,2)		26.66	28.98	(2,4)		56.13	
(1,3)		35.85		(2,6)		80.01	
(1,4)		43.12	53.81	(2,8)		95.85	
(1,5)		46.52		(2,10)		102.09	
(1,6)	48 ^{a)}	48	55	(2,12)		98.65	
(3,4)		45.32	56.4	(4,8)	112 ^{a)}	112	118.52
(3,6)		80.05		(4,10)		145.81	
(3,8)		109.21		(4,12)		172.63	
(3,10)		131.00		(4,14)		194.61	
(3,12)		145.41		(4,16)		207.57	232.39
(3,14)		152.93		(4,18)		213.49	
(3,16)		150.21		(4,20)		214.17	

a) Assumed so that the solubility calculated from the obtained constants agree with the experimental data.

Table 3.3 Th hydrolysis constants predicted in the present study.

Species (<i>p,q</i>)	Selected $\log \beta^{\circ}_{p,q}$	Calculated $\log \beta^{\circ}_{p,q}$ ^{a)}	NEA-TDB [37]	Species (<i>p,q</i>)	Selected $\log \beta^{\circ}_{p,q}$	Calculated $\log \beta^{\circ}_{p,q}$ ^{a)}	NEA-TDB [37]
(1,1)	12.2 [21]	12.88	11.5	(2,2)	22.3 [12]	20.87	22.1
(1,2)	23.0 [21]	23.09	21.8	(2,4)		46.10	
(1,3)	32.7 [21]	32.42		(2,6)		63.72	
(1,4)		39.08	38.6	(2,8)		76.67	
(1,5)		40.52		(2,10)		79.07	
(1,6)		39.28		(2,12)		80.12	
(3,4)		37.31		(4,8)	91.6 [12]	91.28	91.6
(3,6)		65.29		(4,10)		117.87	
(3,8)		86.05		(4,12)	141.3 [12]	141.98	141.4
(3,10)		103.61		(4,14)		157.03	
(3,12)		113.99		(4,16)		167.69	
(3,14)		117.73		(4,18)		169.04	
(3,16)		114.29		(4,20)		166.02	

a) Calculated using the obtained parameters in Table 3.1.

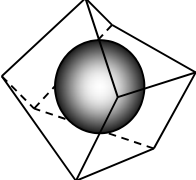
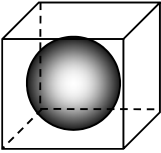
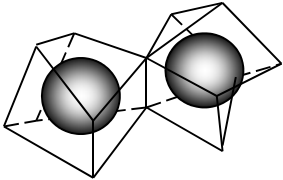
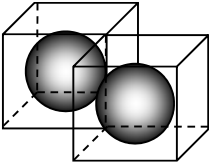
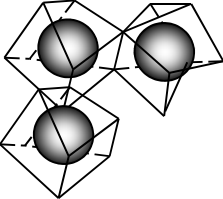
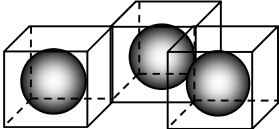
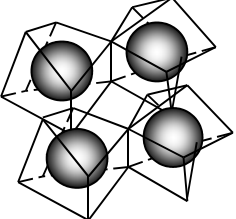
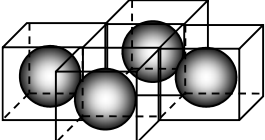
	Zr: antiprismatic	Th: cubic
$(1,q)$		
$(2,q)$		
$(3,q)$		
$(4,q)$		

Fig. 3.1 Formation of polynuclear hydrolysis species of zirconium and thorium.

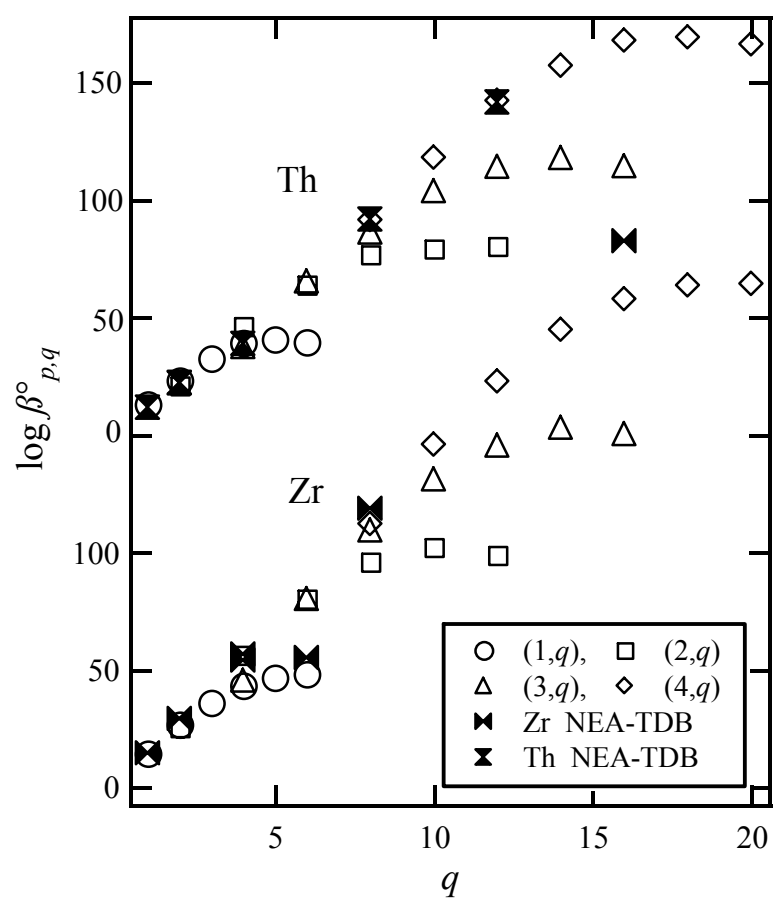


Fig. 3.2 Hydrolysis constants of zirconium and thorium.

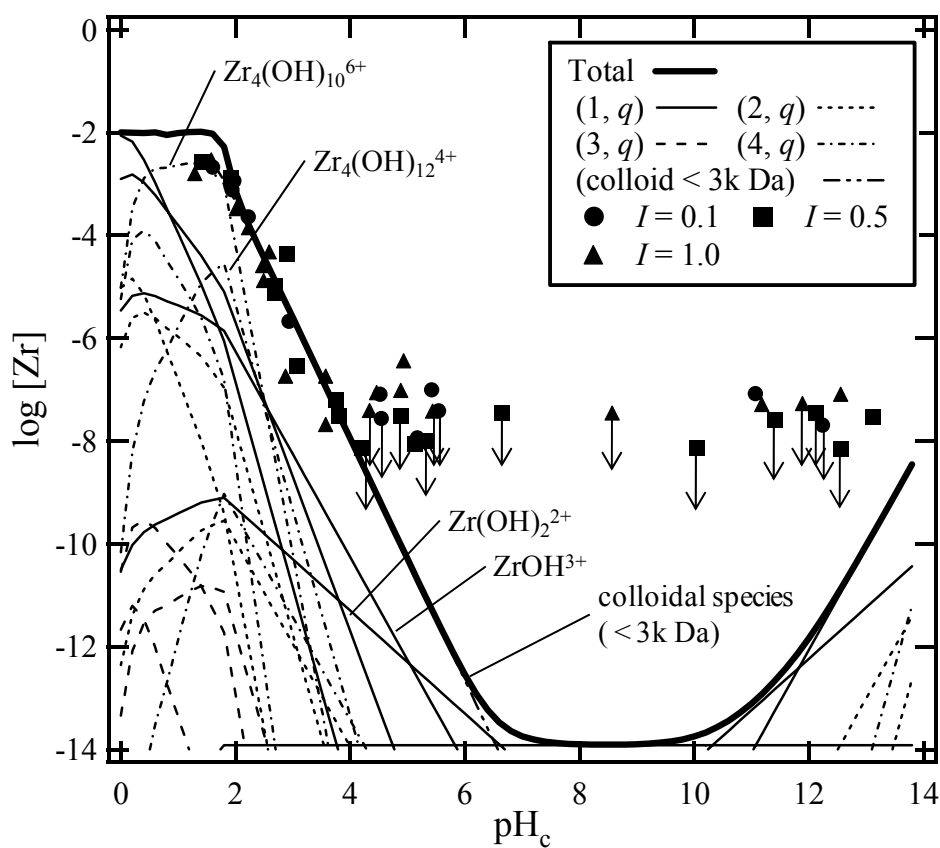


Fig. 3.3 Solubility and component concentrations of $Zr(OH)_4(am)$ at $I = 1.0$ as a function of pH_c . The bold line curve denotes the total solubility, including the (p, q) polynuclear species of $p \leq 4$ and colloidal species $< 3k Da$. Plots were obtained after $3k Da$ filtration and those with downward arrows indicate the levels below the detection limit of ICP-MS from Fig. 2.2.

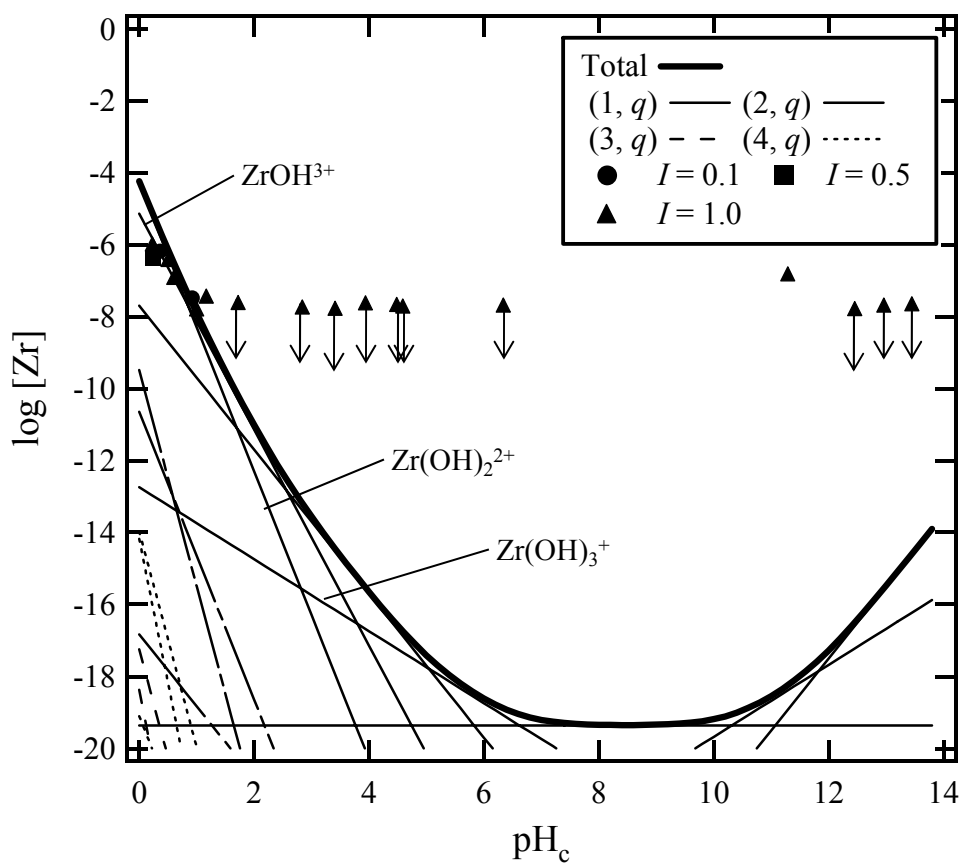


Fig. 3.4 Solubility and component concentrations of $\text{ZrO}_2(\text{cr})$ at $I = 1.0$ as a function of pH_c . The bold line curve denotes the total solubility, including the (p, q) species of $p \leq 4$. Plots were obtained after 3k Da filtration and those with downward arrows indicate the levels below the detection limit of ICP-MS from Fig. 2.7.

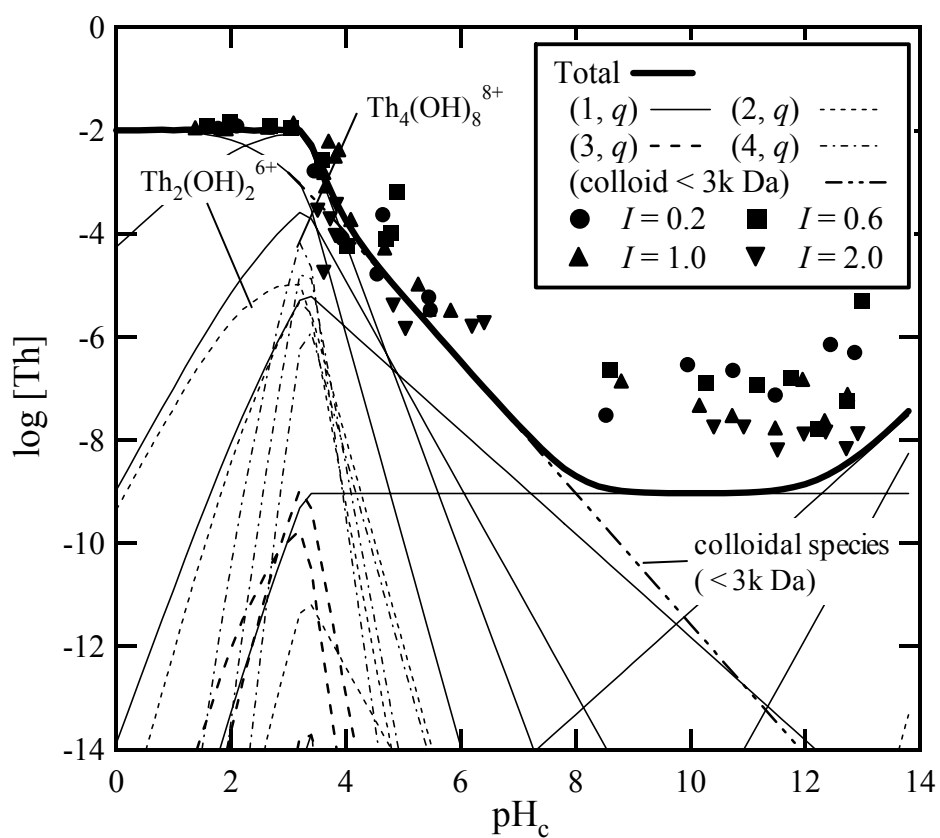


Fig. 3.5 Solubility and component concentrations of $\text{Th}(\text{OH})_4(\text{am})$ at $I = 1.0$ as a function of pH_c . The bold line curve denotes the total solubility, including the (p, q) species of $p \leq 4$ and colloidal species $< 3\text{k Da}$. Plots were obtained after 3k Da filtration from Fig. 2.5.

Chapter 4 Solubility in the presence of organic acid

4.1 Introduction

In this chapter, zirconium(IV) and thorium(IV) solubility in the presence of oxalic and malonic acids are discussed [1-3]. The tetravalent ions are considered to form not only hydrolysis species but also stable compounds and complexes with organic acids in groundwater [4]. Therefore, thermodynamic data such as complex formation constant and solubility product are required for a quantitative understanding of the effects of organic acids to the apparent solubility. However, a lack of knowledge and thermodynamic data remains regarding dominant soluble species and solid phases, and the reactions of tetravalent metal ions with organic acids that must be considered with respect to competing hydrolysis reaction.

Among many kinds of organic acids, multidentate chelating ligand is one of the most important ligands, due to its strong coordination capability. Oxalic ((COOH)₂, C20) and malonic (CH₂(COOH)₂, C21) acids, which are considered as simple model ligands of various organic acids [5,6], can form stable and strong bidentate complexes with tetravalent ions. For example, bidentate oxalic acid is known to strongly coordinate with zirconium ions to form 1:1, 1:2, 1:3, and 1:4 complexes and with thorium ions to form 1:1, 1:2, and 1:3 complexes in aqueous solutions [7-14]. Although the formation constants in these reactions should be very high, experimental data resulted in scattered values across several orders of magnitude, possibly affected by the complicated hydrolysis reaction.

It is also known that precipitates form on adding oxalic and malonic acid to solutions of zirconium and thorium [15-21]. However, the composition of the solid phase seems to depend on the competing hydrolysis and complexation reactions. For Instance, thorium ions precipitate as Th(C20)₂ under acidic conditions [18-21], while zirconium ions were considered to precipitate as Zr(OH)₂(C20), not Zr(C20)₂ [16,17]. In both cases, the precipitates were prepared mainly in the acidic region in the literatures and the solubility-limiting solid phase in near neutral pH region, where the hydrolysis reaction is thought to be superior, has not been revealed.

In the present study, the thorium and zirconium solubility in the presence of oxalic and malonic acid was measured in a wide range of hydrogen ion concentration (pH_c) and

carboxylic acid concentration. Similar to the case in the absence of the carboxylic acid, size distributions of soluble species were obtained by sequential filtration. Solid phases precipitated under various conditions were investigated using elemental analysis, X-ray diffraction patterns (XRD), thermogravimetric analysis (TGA) and differential thermal analysis (DTA). Based on the results of the analysis of the solubility, soluble species and solid phases, the solubility-limiting solid phase was discussed and their solubility products were determined.

4.2 Experimental

4.2.1 Sample preparation

Zr(IV) sample solutions in the presence of oxalic and malonic acids by an oversaturation method: A stock solution of zirconium was prepared from perchlorate salt which was obtained from ZrCl_4 (Aldrich, <99.9%) by perchloric acid fuming in a Teflon beaker covered with a watch glass. Aliquots of the stock solution were added to oxalic acid $((\text{HOOC})_2 \cdot 2\text{H}_2\text{O})$, Wako Pure Chem., <99.5%) or malonic acid $((\text{CH}_2(\text{COOH})_2)$, Aldrich, <99%) solutions such that the initial Zr concentration was 0.01 mol/dm^3 (M). The ionic strength (I) was set as 0.5 by the addition of NaClO_4 , and the pH_c value was adjusted by adding $\text{HClO}_4/\text{NaOH}$ while stirring continuously with a magnetic stirrer.

Th(IV) sample solutions in the presence of oxalic and malonic acids by an oversaturation method: The reagent of Th(IV) nitrate ($\text{Th}(\text{NO}_3)_4 \cdot 4\text{H}_2\text{O}$ (Nakalai Chemicals Ltd.)) was dissolved in 0.1 M perchlorate acid and 3% aqueous NH_3 was quickly added to neutralize and precipitate thorium hydroxide. The precipitate was washed with deionized distilled water several times and finally dissolved in a concentrated solution of perchlorate acid. The solution was then filtered with a $0.25 \mu\text{m}$ filter to remove any residue, resulting in a stock solution of thorium perchlorate ($[\text{Th}] = 0.25 \text{ M}$). Th sample solutions in the presence of oxalic and malonic acids were prepared in a similar manner. The ionic strength was set at 0.5 by the addition of NaClO_4 , and the pH_c value was adjusted.

4.2.2 Solubility measurement

The sample solutions were divided in quantities of 10 mL in polypropylene tubes and allowed to stand for a given aging period, and sometimes agitated by hand. After aging the sample solutions at 25°C , the pH_c values of the supernatants were measured using

combination glass electrodes (9611-10D Horiba Ltd.). All chemicals used were reagent grade. The supernatants were filtered through Microcon (Millipore) centrifugal filters with a nominal molecular weight limit (NMWL) of 3k Da and approximately 2 nm pore sizes. In order to investigate the dependence of the apparent solubility on the filter pore size, some supernatants were also filtered through 10k, 30k, 50k and 100k Da NMWL membranes. Aliquots of the filtrate were acidified with 0.1 M nitric acid to determine the Zr and Th concentration by ICP-MS with a detection limit of approximately 10^{-8} M.

4.2.3 Solid phase analysis

The samples for solid phase analysis were prepared by the oversaturation method in a similar manner. The reagent of NaClO_4 was not added for simplicity of the analysis. After aging for a given period, the pH_c of the solutions were measured and Zr and Th precipitate was separated from the liquid phase and dried at 90°C .

X-ray diffraction patterns of the solid phases were measured using RINT 2000 (RIGAKU). The TGA/DTA7 system (Perkin Elmer) was used for thermogravimetric analysis (TGA) and differential thermal analysis (DTA) experiments. The TGA and DTA measurement was performed under the Ar atmosphere. The heating rate was $+5^\circ\text{C}$ per minute and the maximum temperature was about 700°C . Elemental analysis revealed that the weight percentages of carbon and hydrogen in the solid phase were performed using a CHN coder MT-2 (Yanaco). After dissolution of the precipitate by a mixture of perchloric and nitric acids at 180°C and 120 psi for 60min, the concentrations of metal and sodium ions were measured by ICP-AES (ICPS-5000, Shimadzu).

It is note that the “total” concentrations of zirconium, thorium, oxalic acid, and malonic acid were distinguished from their “initial” concentrations in this study. The “initial” concentrations were calculated by considering the amounts of zirconium, thorium and the carboxylic acids added during sample preparation and by assuming that no solid phases were formed. On the other hand, the “total” concentrations were the concentrations of zirconium, thorium and the carboxylic acids in the liquid phase. Therefore, when some of the zirconium, thorium and carboxylic acid precipitate as solid phases, the “total” concentrations will be lower than the “initial” concentrations.

4.3 Results and Discussion

4.3.1 Zirconium solubility in ternary aqueous system of Zr(IV)-OH-carboxylate

Solubility in the presence of oxalic and malonic acids

Figures 4.1 and 4.2 show the plots of zirconium solubility after filtration with 3k Da NMWL membranes in the presence of oxalic (C20) and malonic (C21) acids, respectively. The solubility of amorphous zirconium hydroxide ($\text{Zr}(\text{OH})_4(\text{am})$) in the absence of the carboxylic acids is also shown for the purpose of comparison (broken line). The plotted values with downward facing arrows in Fig. 4.2 indicate the solubility data near the detection limit. No significant change was observed in the zirconium solubility even after a few months, indicating that steady state was achieved. Since there was no significant difference between the solubility after filtrated through 3 kDa, 30 kDa, and 100 kDa NMWL (Fig. 4.3), it was assumed that the dominant species were “mononuclear” species. In the presence of C21 at pH_c 5.8, on the other hand, the solubility would increase with the increasing pore size of the filters. The formation of colloids by hydrolysis reaction might occur under this condition.

In the presence of 0.1 M oxalic acid below pH_c 6.0, no precipitate was observed, indicating that the precipitate was dissolved due to the formation of anionic species. As shown in Fig. 4.1, the zirconium solubility in this case was observed to be higher than that in the absence of oxalic acid under weakly acidic and near neutral conditions. In the presence of 0.02 M oxalic acid, the solubility at about pH_c 7 was lower than that below pH_c 6. This can be explained by the strong hydrolysis reaction in the high pH region. However, in the presence of 0.1 M oxalic acid, no decrease of the solubility at the same pH_c was observed due to the strong complex formation of zirconium oxalate. Similarly to the C20 system under weakly acidic conditions, the solubility in the presence of C21 was found to be higher than that in the absence of C21 but was lower than that in the presence of oxalic acid. This suggests the possible formation of anionic malonate complexes. In the presence of 0.005 M oxalic and malonic acids, in which the concentration of the carboxylic acids was quite low, no increase of the zirconium solubility was observed compared to that in the absence of the carboxylic acids. On the other hand, the zirconium solubility with C21 under acidic conditions was obviously lower than that of hydroxide, as shown by the broken curve in Fig. 4.2. The solubility of zirconium in the presence of malonic acid under acidic conditions might be controlled by a zirconium-malonate in the solid phase instead of $\text{Zr}(\text{OH})_4(\text{am})$.

Solid phase in the presence of oxalic and malonic acids

In the presence of twice the initial concentration of zirconium, oxalic acid was observed to form a white amorphous precipitate under the acidic and neutral pH conditions. Figure 4.4a shows the X-ray diffraction patterns of the solid phase precipitated at pH_c 1.1 and 5.1, together with that of Zr(OH)₄ (Aldrich, 97%) for comparison. All peaks are broad corresponding to amorphous materials. In detail, the minor peaks in the spectrum at pH_c 1.1 may suggest the existence of a different composition compared with the amorphous Zr(OH)₄.

The results of the TGA and DTA are shown in Fig. 4.5 together with that for Zr(OH)₄. The broad endothermic peak around 100°C and the sharp exothermic peak around 420°C for the Zr(OH)₄ were attributed to the dehydration reaction and the crystallization, respectively. The observed peaks are consistent with the literature data [22]. There are at least two stages of the decomposition of the zirconium-oxalate precipitate in Fig. 4.5. The percentage of weight loss below 300°C corresponds to the dehydration, and the decomposition of oxalate salt and crystallization of zirconium oxide is thought to occur at 300 - 500°C. The TGA curves for the precipitates formed at pH_c 3.5 and 5.1 are similar over the entire temperature range (Fig. 4.5). On the other hand, a greater weight loss for the precipitate at pH_c 1.1 was shown. This suggests that the original precipitate at pH_c 1.1 contains a larger amount of oxalic acid.

Results of the elemental analysis of the solid phases precipitated under various experimental conditions are listed in Table 4.1, together with the total weight percentages of samples after heated at 600°C in the TGA measurement. Assuming that the solid phase consists of Zr, OH, C₂x, H₂O and residual NaClO₄ and that the solid phase converted to ZrO₂ and NaCl after the TGA measurement, its composition was estimated to fit the experimental results. As shown in Table 4.1, the calculated weight percentages of Zr, C, H and Na from the estimated compositions are in good agreement with the experimental values in most samples. In Chapter 2, zirconium hydroxide did not precipitate at pH_c < 2 when [Zr]_{ini} was 10⁻² M in the absence of oxalic acid [23]. However, under the present conditions at a similar pH_c, the solid phase was observed and found to consist of a mixture of oxalate and OH ions.

This observation was consistent with the other findings reported in the literature. Zaitsev and Bochkarev assumed that the solid phase was Zr(OH)₂(C₂O₄) under similar

conditions at pH_c 1 to 2 [16], and Kvashenko and Bortun found that the composition ratio was $\text{Zr} : \text{C20} = 1:1$ in the solid phase prepared from a solution of oxalic acid and zirconium chloride at elevated temperature [17]. It is notable that the value of n in $\text{Zr}(\text{OH})_n(\text{C20})_{(4-n)/2}$ in the solid phase decreases gradually with the decreasing pH_c . In the presence of an excess of oxalic acid, no precipitate was observed at pH_c 1 to 6, and zirconium formed soluble species such as 1:3 and 1:4 complexes with oxalate ion [8]. As shown in Table 4.1, the composition of the precipitate formed at pH_c 7.4 was similar to that of the hydroxide with less oxalate.

Similar to the oxalate system, the Zr precipitate was observed in the acidic to neutral pH region in the presence of twice and ten times the initial concentration of malonic acid to zirconium. The X-ray diffraction patterns of the solid phase prepared at pH_c 2.0, 3.5 and 5.0 were supposed to be amorphous, similar to the oxalate system (Fig. 4.4b). Three decomposition stages in the TGA curve were observed in Fig. 4.6. With the aid of the results from DTA, the weight loss is thought to correspond to the dehydration reaction at $< 200^\circ\text{C}$, the decomposition of malonate salt at $300 - 400^\circ\text{C}$, and the crystallization of zirconium oxide at $400 - 500^\circ\text{C}$. The compound at 400°C may be zirconium carbonate formed in the decomposition of the zirconium oxalate system [17]. In the acidic region, the ratio of OH to Zr was almost constant at 2 under the presence of twice malonic acid to zirconium. Compared with the above Zr-OH-oxalate system, the binary malonate complex $\text{Zr}(\text{C21})_2$ is not stable. This is thought to be because the coordination power of malonic acid to the tetravalent metal ion is weaker than that of oxalic acid [23]. The composition of the solid phase under near neutral condition seems close to that of hydroxide with much less malonate. Thus, the pH_c dependence on the compositions of the solid phases may be estimated, as shown in Table 4.1.

In the zirconium-oxalate system the anionic complexes $\text{Zr}(\text{C20})_3^{2-}$ and $\text{Zr}(\text{C20})_4^{4-}$ formed due to their high constants of formation, therefore, the precipitate was easily re-dissolved. In the presence of excess malonic acid, on the other hand, the amorphous solid phase of zirconium was formed over the entire pH_c range. The complexation of Zr with malonate ion is not considered to be strong enough to form anionic species. The composition ratio n in the presence of malonic acid decreases to less than 2 with decreasing pH_c (Table 4.1).

4.3.2 Solubility products in Zr(IV)-OH-carboxylate system

Formation constants and solubility products in Zr-OH-oxalate system

From the results in Table 4.1, it was suggested that the solid phases consist of zirconium and the carboxylic acids. Therefore, the total oxalic and malonic concentrations in the liquid phase ($[C20]_{\text{tot}}$, $[C21]_{\text{tot}}$) were calculated by subtracting the amount in the solid phase from the initial amount added. The $[C20]_{\text{tot}}$ and $[C21]_{\text{tot}}$ values of all samples were deduced by using the results in Table 4.1.

In the present analysis, the Zr-OH-oxalate ternary solid phase in the acidic pH region was assumed to be $\text{Zr}(\text{OH})_2(\text{C20})(\text{s})$ in the stoichiometric form. On the other hand, at higher pH conditions, the composition of the solid phase was considered to be near $\text{Zr}(\text{OH})_4(\text{am})$ as shown in Table 4.1. Thus, by assuming the presence of solubility-limiting solid phases such as $\text{Zr}(\text{OH})_2(\text{C20})(\text{s})$ and $\text{Zr}(\text{OH})_4(\text{am})$, the equilibrium reactions and the solubility products can be described as



$$K_{\text{sp,OH,C20}} = [\text{Zr}^{4+}][\text{OH}^-]^2[\text{C20}^{2-}], \quad (4.2)$$



$$K_{\text{sp4}} = [\text{Zr}^{4+}][\text{OH}^-]^4. \quad (4.4)$$

As shown in the above equations, the composition of the solubility-limiting solid phase is dependent on the pH_c value and the oxalic acid concentration. Moreover, by assuming the formation of hydrolysis species and complex species, the total zirconium concentration ($[\text{Zr}]_{\text{tot}}$) and the total oxalic acid concentration ($[C20]_{\text{tot}}$) can be defined as

$$\begin{aligned} [\text{Zr}]_{\text{tot}} &= [\text{Zr}^{4+}] + [\text{ZrOH}^{3+}] + [\text{Zr}(\text{OH})_2^{2+}] + [\text{Zr}(\text{OH})_3^+] + [\text{Zr}(\text{OH})_4(\text{aq})] \\ &\quad + [\text{Zr}(\text{C20})^{2+}] + [\text{Zr}(\text{C20})_2(\text{aq})] + [\text{Zr}(\text{C20})_3^{2-}] + [\text{Zr}(\text{C20})_4^{4-}] \\ &= [\text{Zr}^{4+}](1 + \beta_{1,1}[\text{OH}^-] + \beta_{1,2}[\text{OH}^-]^2 + \beta_{1,3}[\text{OH}^-]^3 + \beta_{1,4}[\text{OH}^-]^4 \\ &\quad + \beta_{1,1}[\text{C20}^{2-}] + \beta_{1,2}[\text{C20}^{2-}]^2 + \beta_{1,3}[\text{C20}^{2-}]^3 + \beta_{1,4}[\text{C20}^{2-}]^4), \end{aligned} \quad (4.5)$$

$$\begin{aligned}
[\text{C20}]_{\text{tot}} = & [\text{H}_2\text{C20}] + [\text{HC20}^-] + [\text{C20}^{2-}] \\
& + [\text{Zr}(\text{C20})^{2+}] + 2[\text{Zr}(\text{C20})_2(\text{aq})] + 3[\text{Zr}(\text{C20})_3^{2-}] + 4[\text{Zr}(\text{C20})_4^{4-}] \\
= & 4\beta_{\text{L4}}[\text{Zr}^{4+}][\text{C20}^{2-}]^4 + 3\beta_{\text{L3}}[\text{Zr}^{4+}][\text{C20}^{2-}]^3 + 2\beta_{\text{L2}}[\text{Zr}^{4+}][\text{C20}^{2-}]^2 \\
& + \left\{ \beta_{\text{L1}}[\text{Zr}^{4+}] + \frac{[\text{H}^+]^2}{10^{\text{pKa1}+\text{pKa2}}} + \frac{[\text{H}^+]}{10^{\text{pKa2}}} + 1 \right\} [\text{C20}^{2-}], \tag{4.6}
\end{aligned}$$

where pK_{a1} and pK_{a2} , $\beta_{1,n}$ ($n = 1-4$), and β_{Lm} ($m = 1-4$) are the dissociation constants, the hydrolysis constants, and formation constants, respectively, of zirconium oxalate $\text{Zr}(\text{C20})_{\text{m}}^{4-2m}$. The designator (aq) is used for uncharged aqueous species.

Equations (4.5) and (4.6) were used in the least square fitting analysis of the solubility data in Fig. 4.1 in order to determine the solubility product of $\text{Zr}(\text{OH})_2(\text{C20})(\text{s})$ and the complex formation constants of $\text{Zr}(\text{C20})_3^{2-}$ and $\text{Zr}(\text{C20})_4^{4-}$. In the analysis, the values of the solubility product of $\text{Zr}(\text{OH})_4(\text{am})$ and the formation constants of the hydrolysis species were taken from the previous chapter [23,24]. The experimental data obtained by Caletka et al. [9] were considered while evaluating the complex species [4], and the $\beta_{\text{C20,1}}$ and $\beta_{\text{C20,2}}$ values were recalculated using the values of the hydrolysis constants obtained in this study [24]. The data obtained by Caletka et al. were derived from the sorption of 10^{-6} M zirconium on silica gel in the presence of oxalic acid in nitric acid media; however, the values of the hydrolysis constants used in their analysis were relatively higher than recently reported values [24-28]. Therefore, in the present study, the digitized data obtained by Caletka et al. [9] for 1 M HNO_3 was recalculated. The formation constants of $\text{Zr}(\text{C20})^{2+}$ and $\text{Zr}(\text{C20})_2(\text{aq})$, the hydrolysis constants [24], the solubility product of $\text{Zr}(\text{OH})_4(\text{am})$ [23], and the dissociation constants [29] were considered to be fixed parameters (Table 4.2). These fixed parameters were used after correction at $I = 0.5$ by SIT. The ion interaction parameter values of Zr^{4+} , ZrOH^{3+} , $\text{Zr}(\text{OH})_2^{2+}$, $\text{Zr}(\text{OH})_3^+$, and OH^- were taken to be 0.84 [26], 0.55 [30], 0.52 [31], 0.23 [31], and 0.04 [32], respectively. The ion interaction parameter values of zirconium oxalates were assumed to be 0, and the value $\varepsilon(\text{CH}_3\text{COO}^-, \text{Na}^+) = 0.08$ [32] was used for oxalic acid due to lack of other data. The free parameters of the complex formation constants of $\text{Zr}(\text{C20})_3^{2-}$ and $\text{Zr}(\text{C20})_4^{4-}$ and the solubility product of $\text{Zr}(\text{OH})_2(\text{C20})$ were fitted as shown in Table 4.2.

Figures 4.7 and 4.8 show the solubility curve in the presence of 0.02 M and 0.1 M oxalic acid and the contributions of the soluble species, as calculated using the equilibrium constants in Table 4.2. The experimental data (●, ■) were well reproduced and the dominant species across the wide range of pH_c values considered in this study was found to be

$\text{Zr}(\text{C20})_4^{4-}$. The dominant solubility-limiting solid phases are shown at the bottom of each figure. The solid phases determined from the results of the zirconium solubility seem to be consistent with the results of the solid phase analysis given in Table 4.1. However, the results of the solid phase analysis suggest that the composition of the solid phase depends on the pH value and changes continuously in a manner similar to that of nonstoichiometric compounds.

Formation constants and solubility products in Zr-OH-malonate system

Similarly to the zirconium oxalate system, zirconium malonate precipitate was observed for acidic pH values (Fig. 4.2). If one assumes two solid phases, $\text{Zr}(\text{OH})_4(\text{am})$ and $\text{Zr}(\text{OH})_2(\text{C21})(\text{s})$, the equilibrium reaction and the solubility product of $\text{Zr}(\text{OH})_2(\text{C21})(\text{s})$ can be given as



$$K_{\text{sp,OH,C21}} = [\text{Zr}^{4+}][\text{OH}^-]^2[\text{C21}^{2-}]. \quad (4.8)$$

Also, the total zirconium concentration ($[\text{Zr}]_{\text{tot}}$) in the malonate system and the total malonic acid concentration ($[\text{C21}]_{\text{tot}}$) in the liquid phase can be described by

$$\begin{aligned} [\text{Zr}]_{\text{tot}} &= [\text{Zr}^{4+}] + [\text{ZrOH}^{3+}] + [\text{Zr}(\text{OH})_2^{2+}] + [\text{Zr}(\text{OH})_3^+] + [\text{Zr}(\text{OH})_4(\text{aq})] \\ &\quad + [\text{Zr}(\text{C21})^{2+}] + [\text{Zr}(\text{C21})_2(\text{aq})] + [\text{Zr}(\text{C21})_3^{2-}] \\ &= [\text{Zr}^{4+}](1 + \beta_{1,1}[\text{OH}^-] + \beta_{1,2}[\text{OH}^-]^2 + \beta_{1,3}[\text{OH}^-]^3 + \beta_{1,4}[\text{OH}^-]^4 \\ &\quad + \beta_{1,1}[\text{C21}^{2-}] + \beta_{1,2}[\text{C21}^{2-}]^2 + \beta_{1,3}[\text{C21}^{2-}]^3), \end{aligned} \quad (4.9)$$

$$\begin{aligned} [\text{C21}]_{\text{tot}} &= [\text{H}_2\text{C21}] + [\text{HC21}^-] + [\text{C21}^{2-}] + [\text{Zr}(\text{C21})^{2+}] + 2[\text{Zr}(\text{C21})_2(\text{aq})] + 3[\text{Zr}(\text{C21})_3^{2-}] \\ &= 3\beta_{1,3}[\text{Zr}^{4+}][\text{C21}^{2-}]^3 + 2\beta_{1,2}[\text{Zr}^{4+}][\text{C21}^{2-}]^2 \\ &\quad + \left\{ \beta_{1,1}[\text{Zr}^{4+}] + \frac{[\text{H}^+]^2}{10^{\text{pKa1}+\text{pKa2}}} + \frac{[\text{H}^+]}{10^{\text{pKa2}}} + 1 \right\} [\text{C21}^{2-}], \end{aligned} \quad (4.10)$$

where β_{Lm} ($m = 1-3$) are the formation constants of zirconium malonate $\text{Zr}(\text{C21})_m^{4-2m}$. In this case, the contribution of $\text{Zr}(\text{C21})_4^{4-}$ is not considered since the coordination power of malonic acid to Zr ion is not so strong as that of oxalic acid due to the strain energy of the

chemical bridge between two carboxyl groups. The strain energy for carboxylic acid coordinating bidentate is stronger as it increases with the alkyl chain length [5].

The solubility data in Fig. 4.2 were analyzed using least square fitting. Similarly to the C20 system, the solubility product of the ternary solid phase and the formation constants of zirconium malonates were treated as free parameters. As a result of the lack of literature data, the β_{L1} and β_{L2} values were correlated with the β_{L3} value using an electrostatic model [33]. The hydrolysis constants [24], the solubility product of $\text{Zr}(\text{OH})_4(\text{am})$, and the dissociation constants [29] were considered to be fixed parameters and the ion interaction parameter values were also used in the SIT correction of the oxalate system. As shown in Table 4.2, the obtained value of $\log K_{\text{sp,OH,C21}}^\circ$ was similar to that of $\log K_{\text{sp,OH,C20}}^\circ$. Thus, it appears that the stabilities of these amorphous solid phases are quite similar to each other.

Figures 4.9 and 4.10 show the solubility curve in the presence of 0.02 M and 0.1 M malonic acid and the concentration of the soluble species, as calculated from the constants in Table 4.2. The solubility-limiting solid phase of the system was found to be $\text{Zr}(\text{OH})_4(\text{am})$ for $\text{pH}_c > 5$. (Figs. 4.9 and 4.10) The solid phase deduced from the analysis of the zirconium solubility in the presence of C21 was almost consistent with the results of the solid phase analysis in Table 4.1.

4.3.3 Thorium solubility in ternary aqueous system of Th(IV)-OH-carboxylates

Solubility in the presence of oxalic and malonic acids

Th(IV) solubility in the presence of oxalic and malonic acids, which were obtained by filtration with 3k Da NMWL membranes, are shown in Figs. 4.11 and 4.12, respectively. The solubility of thorium hydroxide in the absence of the carboxylic acids is also shown for comparison. Similarly to the solubility of the hydroxide, no significant change in the Th concentrations is shown after different periods at a given pH_c , indicating that steady-state concentrations were reached within a few months. However, in the presence of oxalic acid at around pH_c 6, the solubility after 237 days was observed to be higher than that after 20-202 days. The solubility increased with increasing aging time, although the sample solutions were prepared by the oversaturation method. Therefore, the solid phase precipitated after 20-202 days in the near neutral pH region in the presence of oxalic acid may not be stable.

Under acidic pH conditions, the Th solubility in the presence of oxalic acid is lower than that in the absence of the acid, which implies the formation of a Th oxalate solid phase as a solubility-limiting solid phase (Fig. 4.11), while no precipitate was observed in the

presence of malonic acid (Fig. 4.12). In the weakly acidic and near neutral pH regions, the Th solubility in the presence of oxalic and malonic acids is higher than that in the absence of the acids, due to the formation of soluble carboxylate complexes. It is interesting to note that there are only minor contributions of the colloidal species in the presence of carboxylic acids; As shown in Fig. 4.13, the species of < 3k Da were found to be predominantly formed in the presence of oxalic acid, differently from the case in the absence of oxalic acid. The formation of the colloidal species may be suppressed by the competing reactions to form soluble carboxylate complexes. Thus it was assumed that the dominant species were "mononuclear" species in the presence of the carboxylic acids, similarly to the analysis of zirconium.

Solid phase in the presence of oxalic and malonic acids

The solid phase formed in the presence of oxalic acid was estimated to be $\text{Th}(\text{C20})_2 \cdot 2\text{H}_2\text{O}$, and not ternary precipitate by analysis of the TGA and DTA curves in Fig. 4.14. Similarly, Aybers [21] synthesized $\text{Th}(\text{C20})_2 \cdot 2\text{H}_2\text{O}$ in 0.5 M thorium nitrate solution. There were three decomposition stages corresponding to dehydration (200°C), formation of $\text{Th}(\text{CO}_3)_2$ (300°C) and formation of ThO_2 (400°C). In the present case, the TGA and DTA curves at pH_c 2.9 were similar to those at pH_c 0.8, indicating formation of $\text{Th}(\text{C20})_2 \cdot 2\text{H}_2\text{O}$. Since the constant of formation of thorium complex with oxalate ion is lower than that of zirconium [8,9,34], Th oxalate precipitate could not be re-dissolved. On the other hand, the Zr oxalate precipitate was re-dissolved as shown in Fig. 4.1.

At pH_c 1 to 6, the different behavior between the oxalate and malonate systems may be attributed to the stability of $\text{Th}(\text{C20})_2$ and $\text{Th}(\text{C21})_2$ in the solid phase; the $\text{Th}(\text{C20})_2$ precipitate is not easily re-dissolved compared to that of $\text{Th}(\text{C21})_2$. From the TGA and DTA analysis (Fig. 4.15), two stages of decomposition correspond to the dehydration at < 250°C and the decomposition of the malonate complex at 250 - 500°C. The total weight loss indicates the ratio n in $\text{Th}(\text{OH})_n(\text{C21})_{(4-n)/2}$ was almost 2. However, since the hydroxide $\text{Th}(\text{OH})_4$ precipitates at pH_c 8.9 in the absence of malonic acid, $\text{Th}(\text{OH})_4$ may also precipitate in the presence of malonic acid. It is difficult to characterize the solid phase, the ternary $\text{Th}(\text{OH})_2(\text{C21})$ or the mixture of $\text{Th}(\text{OH})_4$ and $\text{Th}(\text{C21})_2$, at this stage.

4.3.4 Solubility products in Th(IV)-OH-carboxylate system

Formation constants and solubility products in Th-OH-oxalate/malonate system

The hydrolysis and binary carboxylate complexes were assumed as the dominant soluble species for simplicity, similar to the approach used in the case of zirconium. The total Th concentration ($[Th]_{tot}$) and the total carboxylic acid concentration ($[C2x]_{tot}$, $x = 0, 1$) are then described as

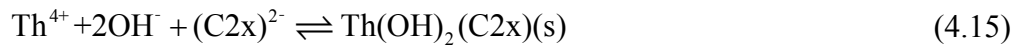
$$\begin{aligned}
 [Th]_{tot} &= [Th^{4+}] + [ThOH^{3+}] + [Th(OH)_2^{2+}] + [Th(OH)_3^+] + [Th(OH)_4(aq)] \\
 &\quad + [Th(C2x)^{2+}] + [Th(C2x)_2(aq)] + [Th(C2x)_3^{2-}] \\
 &= [Th^{4+}] (1 + \beta_{1,1}[OH^-] + \beta_{1,2}[OH^-]^2 + \beta_{1,3}[OH^-]^3 + \beta_{1,4}[OH^-]^4 \\
 &\quad + \beta_{L1}[(C2x)^{2-}] + \beta_{L2}[(C2x)^{2-}]^2 + \beta_{L3}[(C2x)^{2-}]^3),
 \end{aligned} \tag{4.11}$$

$$\begin{aligned}
 [C2x]_{tot} &= [H_2(C2x)] + [H(C2x)^-] + [(C2x)^{2-}] \\
 &\quad + [Th(C2x)^{2+}] + 2[Th(C2x)_2(aq)] + 3[Th(C2x)_3^{2-}] \\
 &= 3\beta_{L3}[Th^{4+}][C2x]^{2-}]^3 + 2\beta_{L2}[Th^{4+}][C2x]^{2-}]^2 \\
 &\quad + \left\{ \beta_{L1}[Th^{4+}] + \frac{[H^+]^2}{10^{pKa1+pKa2}} + \frac{[H^+]}{10^{pKa2}} + 1 \right\} [(C2x)^{2-}],
 \end{aligned} \tag{4.12}$$

where pK_{a1} and pK_{a2} , $\beta_{1,n}$ ($n = 1-4$), and β_{Lm} ($m = 1-3$) are the dissociation constants, the hydrolysis constants, and the formation constants of Th carboxylate $Th(C2x)_m^{4-2m}$, respectively. In addition, two types of Th carboxylate solid phases, $Th(C2x)_2(s)$ and $Th(OH)_2(C2x)(s)$ are assumed to be the solubility-limiting phase in the acidic pH region, as given by



$$K_{sp,C2x} = [Th^{4+}][C2x]^{2-}]^2, \tag{4.14}$$



$$K_{sp,OH,C2x} = [Th^{4+}][OH^-]^2[(C2x)^{2-}]. \tag{4.16}$$

Due to the strong hydrolysis reaction, the solubility-limiting solid phase in the higher pH region was assumed to be $Th(OH)_4(am)$, similar to the case of the Zr-OH-carboxylate system. Equations (4.11) and (4.12) were used in the least squares fitting analysis of the solubility data shown in Figs. 4.11 and 4.12 in order to determine the

solubility product value of the Th carboxylate solid phase. In the analysis, the solubility data at $[C2x]_{ini} = 0.1$ M were used considering $[C2x]_{tot} \approx [C2x]_{ini} = 0.1$ M. The complex formation constants [34], hydrolysis constants [34], dissociation constants [29], and the solubility product of $Th(OH)_4(am)$ were taken as fixed parameters (Table 4.3) and used after the SIT correction to $I = 0.5$. The ion interaction parameter values of the Th carboxylates were all assumed to be 0, and the value of $\epsilon(CH_3COO^-, Na^+) = 0.08$ [32] was used for carboxylic acid, due to the lack of data.

In the presence of oxalic acid, an interesting time dependence of the solubility data was observed. Comparing the results in Fig. 4.11, it is found that the experimental solubility data at around pH 6.0 increase with increasing aging time even in the oversaturation experiments. This may suggest possible formation of a ternary solid phase in the early stage of the experiments. However, its formation seemed temporal, and the solubility data obtained after 237 days under neutral conditions were used in the analysis by assuming the solubility-limiting solid phases of $Th(C20)_2(s)$ and $Th(OH)_4(am)$ (Fig. 4.16), which were consistent with the thermal analysis results of the solid phase. The obtained solubility product value of $Th(C20)_2$ ($\log K_{sp,C20}^\circ = -24.3 \pm 0.2$) was found to be smaller than the value of -22.4 ($I = 0$ M), which was corrected from the value of 20.47 at $I = 3.0$ M [20] using the SIT. The value reported in the literature was obtained by assuming a negligible contribution of oxalate complexes to a very low oxalate concentration, and the concentration of free oxalate ions may have been overestimated.

In the case of malonic acid, the experimental data are well reproduced only by assuming $Th(OH)_4(am)$ as a solubility-limiting solid phase (Fig. 4.17), and neither $Th(C21)_2(s)$ nor $Th(OH)_2(C21)(s)$ is found to contribute to the data in the analysis. Although the solid phase is considered to contain both OH and malonate from the results of the thermal analysis, the solubility-limiting solid phase is $Th(OH)_4(am)$ in the presence of 0.1 M malonic acid.

4.4 Conclusion

The effect of oxalic (C20) and malonic (C21) acids on the formation of soluble species, solid phase and solubility of Th and Zr under the competitive hydrolysis reaction was investigated. In the presence of oxalic and malonic acids, the apparent solubility was observed to change due to the formation of soluble oxalate and malonate complexes and

insoluble precipitates. There was no dependence of the apparent solubility on filter pore size contrary to that in the absence of the acids, indicating no contribution of colloidal species in the presence of oxalic and malonic acids. The formation of the colloidal species may be suppressed by forming soluble carboxylate complexes. The higher solubility in weakly acidic pH region was due to the formation of Zr, Th oxalate and malonate complexes.

From the elemental analysis and thermal analysis of the precipitates, a possible existence of ternary solid phase $\text{Zr}(\text{OH})_2(\text{C20})(\text{s})$ and $\text{Zr}(\text{OH})_2(\text{C21})(\text{s})$ under acidic condition was implied, while the formation of $\text{Th}(\text{C20})_2(\text{s})$ was indicated and no solid phase was observed under acidic condition in Th/OH/C21 system. Such difference probably arose from the different ionic radii between Zr and Th ions.

The solubility product values of $\text{Zr}(\text{OH})_2(\text{C2x})$ were similar to each other while the complex formation constants differ from each other. No significant dependence of the alkyl chain length on the solubility product values was observed. It is supposed that the dicarboxylate in these ternary solid phases may bridge two Zr ions with a monodentate configuration, as proposed by Bilinski and Brničević [15].

Thus, the present study revealed the relationship between the coordination strength and the solid phase composition as a result of the competition between complexation and hydrolysis reactions. Assuming that the Zr and Th solubility in the neutral pH region was controlled by $\text{Zr}(\text{OH})_4(\text{am})$ and $\text{Th}(\text{OH})_4(\text{am})$, the solubility in the presence of the acids were analyzed and the solubility product values of the ternary and binary carboxylate solid phases were obtained.

References

1. Kobayashi, T., Sasaki, T., Takagi, I., Moriyama, H.: Solid phase precipitates in (Zr, Th)-OH-(oxalate, malonate) ternary aqueous system. *Radiochim. Acta* **97**, 237 (2009).
2. Kobayashi, T., Sasaki, T., Takagi, I., Moriyama, H.: Zirconium Solubility in Ternary Aqueous System of Zr(IV)-OH -carboxylates. *J. Nucl. Sci. Technol.*, **46**, 142 (2009)
3. Kobayashi, T., Sasaki, T., Takagi, I., Moriyama, H.: Solubility of Thorium(IV) in the Presence of Oxalic and Malonic Acids. *J. Nucl. Sci. Technol.*, **46**, 1085 (2009).
4. Hummel, W., Anderegg, G., Rao, L., Puigdomènech, I., Tochiyama, O.: *Chemical Thermodynamics of Compounds and complexes of U, Np, Pu, Am, Tc, Se, Ni and Zr with selected organic ligands*, In: *Chemical Thermodynamics* (Eds.: F. J. Mompean et al.)

Vol. 9, Elsevier, North-Holland, Amsterdam (2005).

5. Sasaki, T., Kubo, S., Kobayashi, T., Takagi, I., Moriyama, H.: Measurement and Analysis of Formation Constants of Europium with Carboxylates. *J. Nucl. Sci. Technol.*, **42**, 724 (2005).
6. Sasaki, T., Kobayashi, T., Takagi, I., Moriyama, H.: Discrete Fragment Model for Complex Formation of Europium(III) with Humic Acid. *J. Nucl. Sci. Technol.*, **45**, 718(2008).
7. Babko, A. K., Dubovenko, L. I.: Zirconium oxalate complexes, *Izv. Vyssh. Uchebn. Zaved., Khim. Khim. Tekhnol.*, **3**, 226 (1960).
8. Shvedov, V., Maslov, E.: Determination of the composition and stability constants of complex compounds by electromigration. I. Determination of the composition and stability constants of oxalate complexes of zirconium, *Sov. Radiochem.* **4**, 376 (1962).
9. Caletka, R., Kyrs, M., Rais, J.: Sorption of Zirconium by Silica Gel from Nitrate Medium in the presence of Oxalic Acid, EDTA and Arsenazo I, *J. Inorg. Nucl. Chem.*, **26**, 1443 (1964).
10. Grinberg, A., Astapovich, V.: Complex zirconium oxalates, *Russ. J. Inorg. Chem.* **6**, 164 (1961).
11. Bagawde, S. V., Ramakrishna, V. V., Patil, S. K.: Oxalate complexing of tetravalent actinides. *J. Inorg. Nucl. Chem.* **38**, 1669 (1976).
12. Erten, H. N., Mohammed, A. K., Choppin, G. R.: Variation of stability constants of thorium and uranium oxalate complexes with ionic strength. *Radiochim Acta* **66/67**, 123 (1994).
13. Bernardo, P. Di., Dinapoli, V., Cassol, A., Magon, L.: Thermodynamic properties of actinide complexes. 4. Thorium(IV)-malonate system and uranyl(VI)-malonate system. *J. Inorg. Nucl. Chem.* **39**, 1659 (1977).
14. Tomat, G., Magon, L., Portanova, R., Cassol, A.: Complexes of Thorium(IV). *Z.Anorg.Allq.Chem.***393**.184 (1972).
15. Bilinski, H., Brničević, N.: Precipitation and Complex Formation of Zirconium(IV) with Malonic, Succinic and Adipic Acids at 298K. *Croatica Chemica Acta* **56**, 53 (1983).
16. Zaitsev, L. M., Bochkarev, G.S.: Solubility product of zirconium oxide oxalate. *Russ. J. Inorg. Chem.* **9**, 1147 (1964).
17. Kvashenko, A., Bortun, A.: Study of zirconium oxalates by thermography. *J. Appl. Chem. USSR* **61**, 1699 (1988).

18. D'Eye, R. W. M., Sellman, P. G.: The thermal decomposition of thorium oxalate. *J. Inorg. Nucl. Chem.* **1**, 143 (1955).
19. Padmanabhan, V. M., Saraiya, S. C., Sundaram, A. K.: Thermal decomposition of some oxalates. *J. Inorg. Nucl. Chem.* **12**, 356 (1960).
20. Pazukhin, E., Smirnova, E., Pazurkhina, Y., Kiselev, P.: Optimization of Conditions for Precipitation of Thorium Oxalate. 4. State of Thorium in Oxalate Solutions. *Soviet Radiochim.* **30**, 308 (1988).
21. Aybers, M.: Kinetic study of the thermal decomposition of thorium oxalate dihydrate. *J. Nucl. Mater.* **252**, 28 (1998).
22. Štefanić, G., Popović, S., Musić, S.: Influence of pH on the hydrothermal crystallization kinetics and crystal structure of ZrO₂. *Thermochim. Acta* **303**, 31 (1997).
23. Sasaki, T., Kobayashi, T., Takagi, I., Moriyama, H.: Solubility measurement of zirconium(IV) hydrous oxide. *Radiochim. Acta* **94**, 489 (2006).
24. Sasaki, T., Kobayashi, T., Takagi, I., Moriyama, H.: Hydrolysis Constant and Coordination Geometry of Zirconium(IV). *J. Nucl. Sci. Technol.*, **45**, 735 (2008).
25. Baes, C. F., Mesmer, R. E.: *The Hydrolysis of Cations*. John Wiley & Sons, New York (1976).
26. Ekberg, C., Kallvenius, G., Albinsson, Y., Brown, P.: Studies on the hydrolytic behavior of zirconium(IV). *J. Solution Chem.* **33**, 47 (2004).
27. Cho, H., Walther, C., Roche, J., Neck, V., Denecke, M. A., Dardenne, K., Fanghänel, Th.: Combined LIBD and XAFS investigation of the formation and structure of Zr(IV) colloids. *Anal. Bioanal. Chem.* **383**, 28 (2005)
28. Brown, P., Curti, E., Grambow, B., Ekberg, C.: *Chemical Thermodynamics of Zirconium*, In: *Chemical Thermodynamics* (Eds.: F. J. Mompean et al.) Vol. 8. Elsevier, North-Holland, Amsterdam (2005).
29. Choppin, G. R., Chen, J.: Complexation constants of Am(III) by oxalate in NaClO₄ media. *Radiochim. Acta* **74**, 105 (1996).
30. Curti, E.: *Paul Scherrer Institut Rep. TM-44-01-01* (2001).
31. Fujiwara, K., Yamana, H., Fujii, T., Moriyama, H.: Determination of uranium(IV) hydrolysis constants and solubility product of UO₂·xH₂O. *Radiochim. Acta*, **91**, 345 (2003).
32. Guillaumont, R., Fanghänel, Th., Fuger, J., Grenthe, I., Neck, V., Palmer, D., Rand, M.: *Update on the Chemical Thermodynamics of Uranium, Neptunium, Plutonium,*

Americium and Technetium, In: *Chemical Thermodynamics* (Eds.: F. J. Mompean et al.)
Vol. 5. Elsevier, North-Holland, Amsterdam (2003).

33. Neck, V., Kim, J. I.: An electrostatic approach for the prediction of actinide complexation constants with inorganic ligands-application to carbonate complexes. *Radiochim. Acta*, **88**, 815 (2000).
34. Sasaki, T., Takaoka, Y., Kobayashi, T., Fujii, T., Takagi, I., Moriyama, H.: Hydrolysis constants and complexation of Th(IV) with carboxylates. *Radiochim. Acta*, **96**, 79 (2008).

Table 4.1 The results of elemental analysis, TGA and estimated compositions of the solid phase.

Sample		Elemental Analysis					TGA	Estimated composition					Calculated from the estimated composition				
pH _c	[C2x] _{ini} / [Zr] _{ini}	Zr	Weight %		Na	Weight % after heated	Molar ratio of each fragment per Zr					Weight %			Weight % after heated		
			C ^{a)}	H ^{a)}			Zr	OH	C2x	Na	ClO ₄	H ₂ O	Zr	C		H	Na
Oxalic acid (C20)																	
1.1	2	-	10.33±0.02	1.54±0.06	1.9	47.5	1.0	1.5	1.2	0.3	0.3	1.6	30.9	10.0	1.6	2.6	48.2
3.5	2	23.5	8.75±0.03	1.49±0.01	3.3	52.4	1.0	2.0	1.2	1.1	0.6	2.3	25.3	8.1	1.8	6.8	50.8
5.1	2	24.1	6.80±0.12	1.11±0.03	4.2	54.4	1.0	2.6	0.9	1.1	0.7	2.3	25.9	6.3	2.1	7.3	52.9
3.8	2	25.1	7.37±0.13	1.64±0.02	5.1		1.0	1.8	1.1	0.8	0.8	2.4	25.1	7.4	1.8	5.2	47.2
6.6	2	36.5	5.28±0.11	1.37±0.04	5.1		1.0	3.0	0.5	0.6	0.4	0.2	36.5	5.3	1.4	5.1	61.9
7.4	10	39.6	6.07±0.11	1.31±0.01	6.6		1.0	3.3	0.6	0.7	0.2	0.0	39.5	6.1	1.5	6.6	69.0
Malonic acid (C21)																	
0.8	2	40.7	12.66±0.06	2.25±0.09	0.0		1.0	2.4	0.8	0.0	0.0	0.6	40.7	12.7	2.3	0.0	55.1
1.3	2	38.4	12.36±0.13	2.12±0.02	0.7		1.0	2.4	0.8	0.1	0.1	0.7	38.4	12.4	2.3	0.8	53.9
2.8	2	34.5	12.49±0.04	1.88±0.00	1.4		1.0	2.2	0.9	0.2	0.2	1.0	34.6	12.6	2.3	1.7	50.9
5.6	2	41.7	7.04±0.00	1.90±0.05	0.8		1.0	3.1	0.4	0.1	0.1	0.8	41.8	7.2	2.6	1.2	59.6
2.3	2	32.7	11.49±0.06	2.21±0.04	0.6		1.0	2.2	0.9	0.1	0.1	2.3	32.8	11.7	3.1	1.1	47.1
3.5	2	31.0	10.68±0.14	2.08±0.01	2.4		1.0	2.2	0.9	0.4	0.4	1.8	31.1	10.8	2.6	2.7	49.0
5.6	2	30.6	7.35±0.13	1.84±0.08	5.1		1.0	2.7	0.6	0.7	0.7	0.7	30.6	7.4	1.8	5.1	55.1
2.0	10	30.0	14.23±0.10	2.25±0.03	0.7		1.0	1.6	1.2	0.1	0.1	2.4	23.6	8.2	3.3	4.4	43.1
3.9	10	23.5	8.01	2.27	3.8		1.0	2.2	0.9	0.7	0.7	4.2	30.1	14.4	3.0	1.1	43.5
8.0	10	36.1	6.52±0.14	1.91±0.03	5.5		1.0	3.3	0.5	0.6	0.4	0.3	36.1	6.5	1.9	5.5	58.0
2.0	10	16.2	8.16±0.12	1.64±0.04	6.0	37.3	1.0	1.3	1.4	2.0	2.0	2.5	16.8	9.0	1.7	8.5	44.3
3.5	10	16.7	8.07±0.02	1.69±0.09	7.2	31.8	1.0	1.5	1.3	2.0	2.0	2.6	17.0	8.6	1.7	8.6	44.7
5.0	10	19.6	6.66±0.00	0.96±0.00	9.7	46.8	1.0	2.3	0.9	2.0	2.0	0.2	19.6	6.7	1.0	9.8	51.4

a) The obtained values with error were the average from two portions of the solid phase sample.

Table 4.2 Solubility products and complex formation constants in Zr-OH-C20 and Zr-OH-C21 systems at $I = 0$.

	Species		This work	Babko [7]	Shevedov [8]	Caletka [9]
	Zr(OH) ₄ (am)	$\log K_{\text{sp}4}^{\circ}$	-56.9			
	ZrOH ³⁺	$\log \beta_{1,1}^{\circ}$	14.29			
	Zr(OH) ₂ ²⁺	$\log \beta_{1,2}^{\circ}$	26.66			
	Zr(OH) ₃ ⁺	$\log \beta_{1,3}^{\circ}$	35.85			
	Zr(OH) ₄ (aq)	$\log \beta_{1,4}^{\circ}$	43.12			
C20 ^{a)}	Zr(OH) ₂ (C20)(s)	$\log K_{\text{sp,C20,21}}^{\circ}$	-42.1±0.2 ^{c)}			
	Zr(C20) ₂ ²⁺	$\log \beta_{\text{L}1}^{\circ}$	11.5 ^{d)}	11.65 ^{e)}	11.13 ^{e)}	12.92 ^{e)}
	Zr(C20) ₂ (aq)	$\log \beta_{\text{L}2}^{\circ}$	20.8 ^{d)}	20.05 ^{e)}	20.31 ^{e)}	23.19 ^{e)}
	Zr(C20) ₃ ²⁻	$\log \beta_{\text{L}3}^{\circ}$	27.2±0.4 ^{c)}	23.2 ^{e)}	26.97 ^{e)}	
	Zr(C20) ₄ ⁴⁻	$\log \beta_{\text{L}4}^{\circ}$	29.7±0.1 ^{c)}	21.31 ^{e)}	33.04 ^{e)}	
C21 ^{b)}	Zr(OH) ₂ (C21)(s)	$\log K_{\text{sp,C21,21}}^{\circ}$	-41.9±0.2 ^{c)}			
	Zr(C21) ₂ ²⁺	$\log \beta_{\text{L}1}^{\circ}$	10.4 ^{f)}			
	Zr(C21) ₂ (aq)	$\log \beta_{\text{L}2}^{\circ}$	17.9 ^{f)}			
	Zr(C21) ₃ ²⁻	$\log \beta_{\text{L}3}^{\circ}$	22.2±0.2 ^{c)}			

a) $\text{pK}_{\text{a}1} = -1.10$ [29] and $\text{pK}_{\text{a}2} = -3.62$ [29] at $I = 0.5$.

b) $\text{pK}_{\text{a}1} = -2.54$ [29] and $\text{pK}_{\text{a}2} = -5.06$ [29] at $I = 0.5$.

c) Standard error.

d) Obtained by recalculation of digitized data in 1M HNO₃ by Caletka et al. [9] using the hydrolysis constants in Chapter 3.

e) Corrected to $I = 0$ by SIT.

f) Depending on $\beta_{\text{L}3}^{\circ}$ by electrostatic model [33].

Table 4.3 Solubility products and complex formation constants in Th-OH-C20 and Th-OH-C21 systems at $I = 0$.

			This work	Bagawde, Erten [11,12]	Bernardo [13]	Pazukhin [20]
Species						
	Th(OH) ₄ (am)	$\log K_{\text{sp}4}^{\circ}$	-48.1			
	ThOH ³⁺	$\log \beta_{1,1}^{\circ}$	12.2 [34]			
	Th(OH) ₂ ²⁺	$\log \beta_{1,2}^{\circ}$	23.0 [34]			
	Th(OH) ₃ ⁺	$\log \beta_{1,3}^{\circ}$	32.7 [34]			
	Th(OH) ₄ (aq)	$\log \beta_{1,4}^{\circ}$	39.1 [34]			
C20 ^{a)}	Th(C20) ₂ (s)	$\log K_{\text{sp,C20}}^{\circ}$	-24.3±0.2 ^{c)}			-22.4 ^{d)}
	Th(OH) ₂ (C20)(s)	$\log K_{\text{sp,C20,21}}^{\circ}$	not determined			
	Th(C20) ₂ ²⁺	$\log \beta_{\text{L1}}^{\circ}$	9.7 [34]	9.79 ^{d)}		
	Th(C20) ₂ (aq)	$\log \beta_{\text{L2}}^{\circ}$	16.0 [34]	17.1 ^{d)}		
	Th(C20) ₃ ²⁻	$\log \beta_{\text{L3}}^{\circ}$	22.2 [34]	22.4 ^{d)}		
C21 ^{b)}	Th(C21) ₂ (s)	$\log K_{\text{sp,C21}}^{\circ}$	not determined			
	Th(OH) ₂ (C21)(s)	$\log K_{\text{sp,C21,21}}^{\circ}$	not determined			
	Th(C21) ₂ ²⁺	$\log \beta_{\text{L1}}^{\circ}$	9.2 [34]		9.4 ^{d)}	
	Th(C21) ₂ (aq)	$\log \beta_{\text{L2}}^{\circ}$	15.7 [34]		15.8 ^{d)}	
	Th(C21) ₃ ²⁻	$\log \beta_{\text{L3}}^{\circ}$	19.7 [34]		18.7 ^{d)}	

a) $\text{p}K_{\text{a1}} = -1.10$ [29] and $\text{p}K_{\text{a2}} = -3.62$ [29] at $I = 0.5$.

b) $\text{p}K_{\text{a1}} = -2.54$ [29] and $\text{p}K_{\text{a2}} = -5.06$ [29] at $I = 0.5$.

c) Standard error.

d) Corrected to $I = 0$ by SIT.

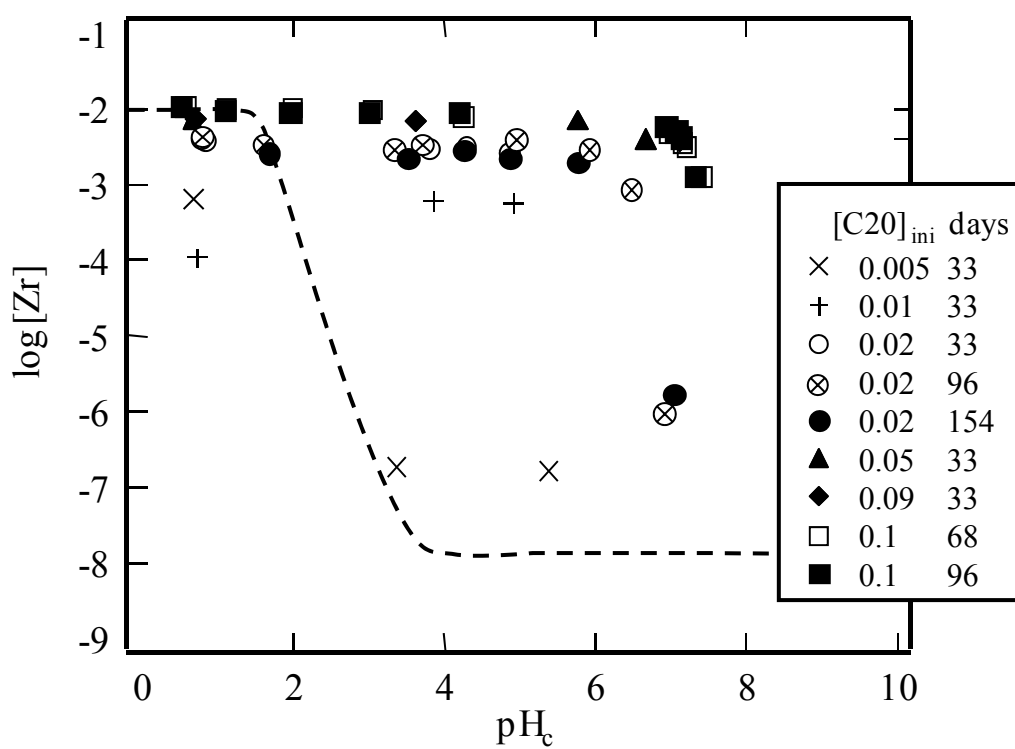


Fig. 4.1 Zirconium solubility after 3k Da filtration in the presence of oxalic acid (C20) prepared by the oversaturation method ($I = 0.5$). The dashed curve represents the solubility of zirconium hydroxide without oxalic acid.

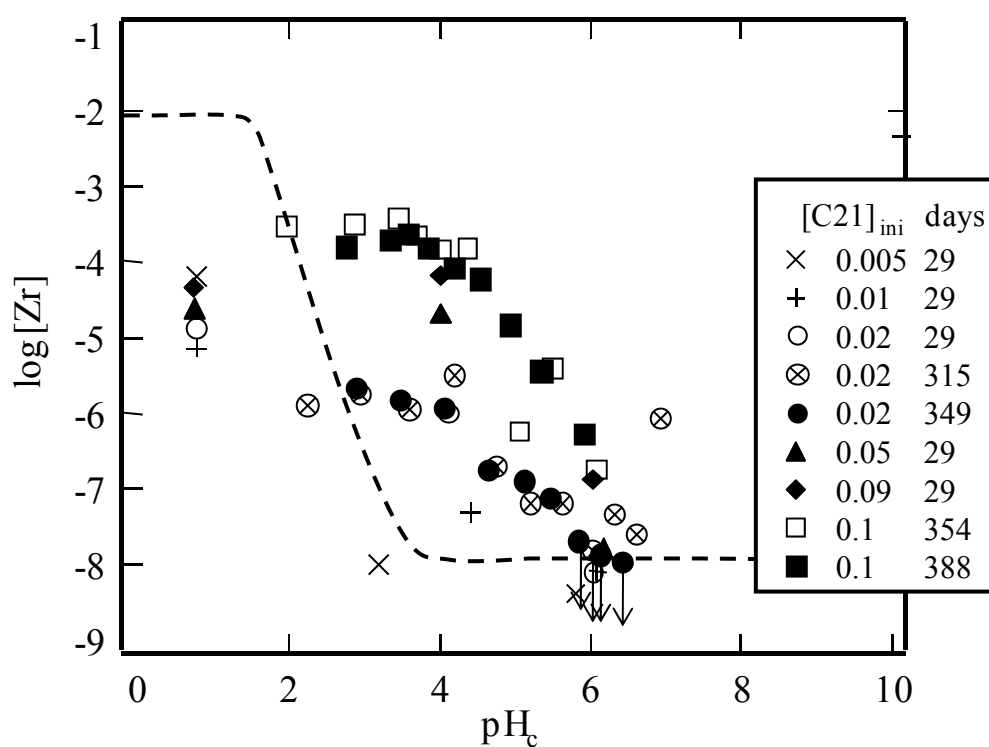


Fig. 4.2 Zirconium solubility after 3k Da filtration in the presence of malonic acid (C21) prepared by the oversaturation method ($I = 0.5$). Plots with down arrows indicate levels under the detection limit 1×10^{-8} M. The dashed curve represents the solubility of zirconium hydroxide without malonic acid.

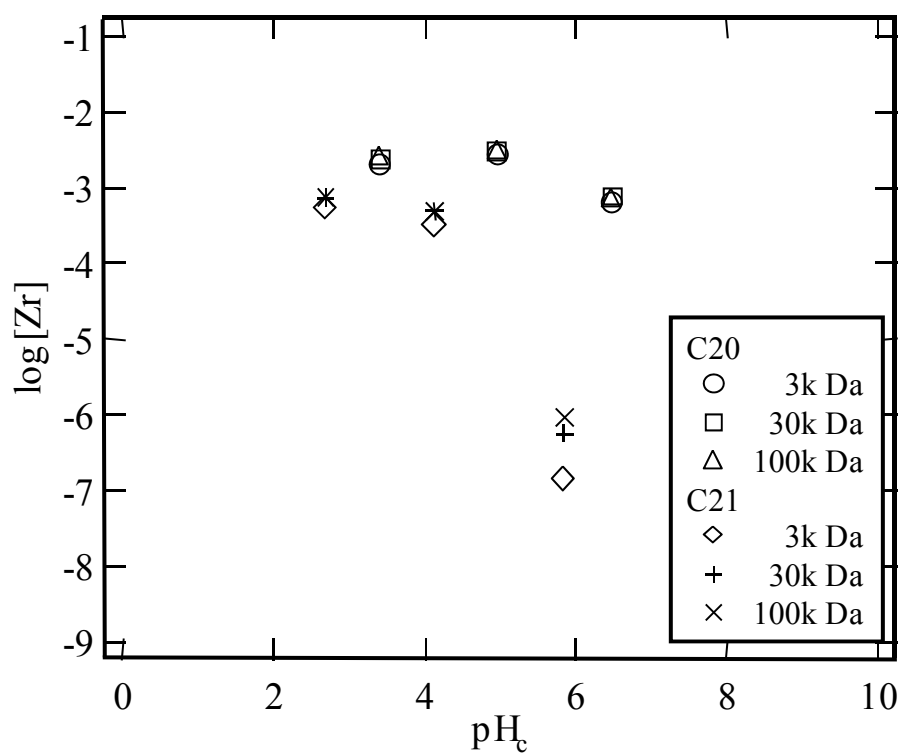


Fig. 4.3 Zirconium solubility after 3k - 100k Da filtrations in the presence of oxalic (C20) and malonic (C21) acids ($I = 0.5$). The initial concentration of the oxalic and malonic acids is 0.02 M.

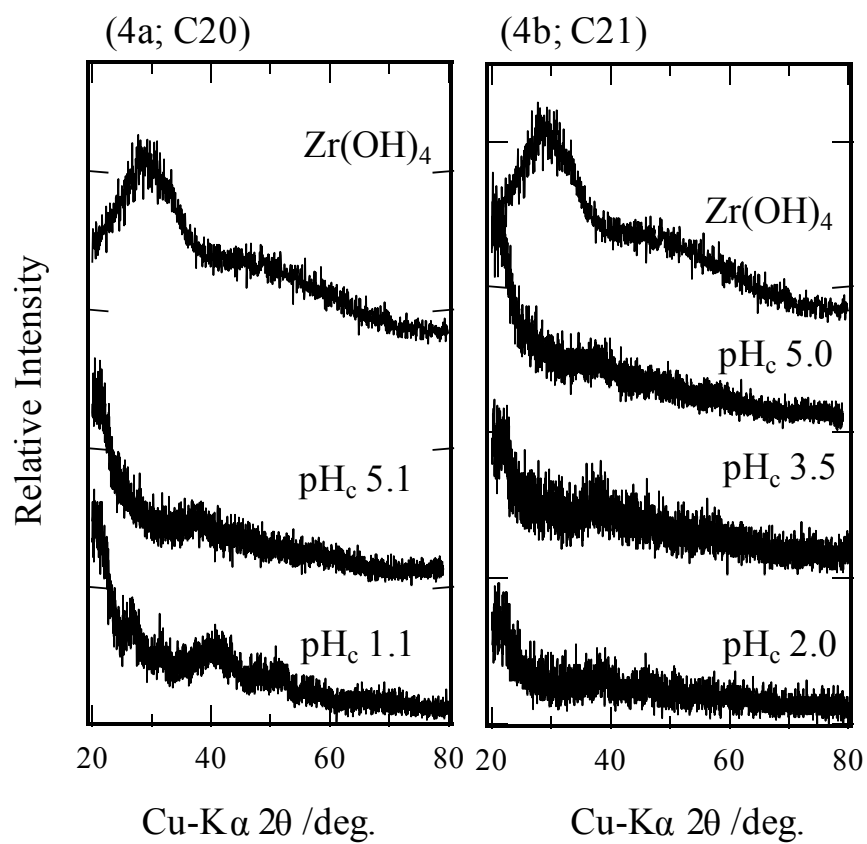


Fig. 4.4 X-ray diffraction patterns of the zirconium solid phase precipitated in the presence of oxalic (4a; C20) and malonic (4b; C21) acids, compared with that of Zr(OH)_4 .

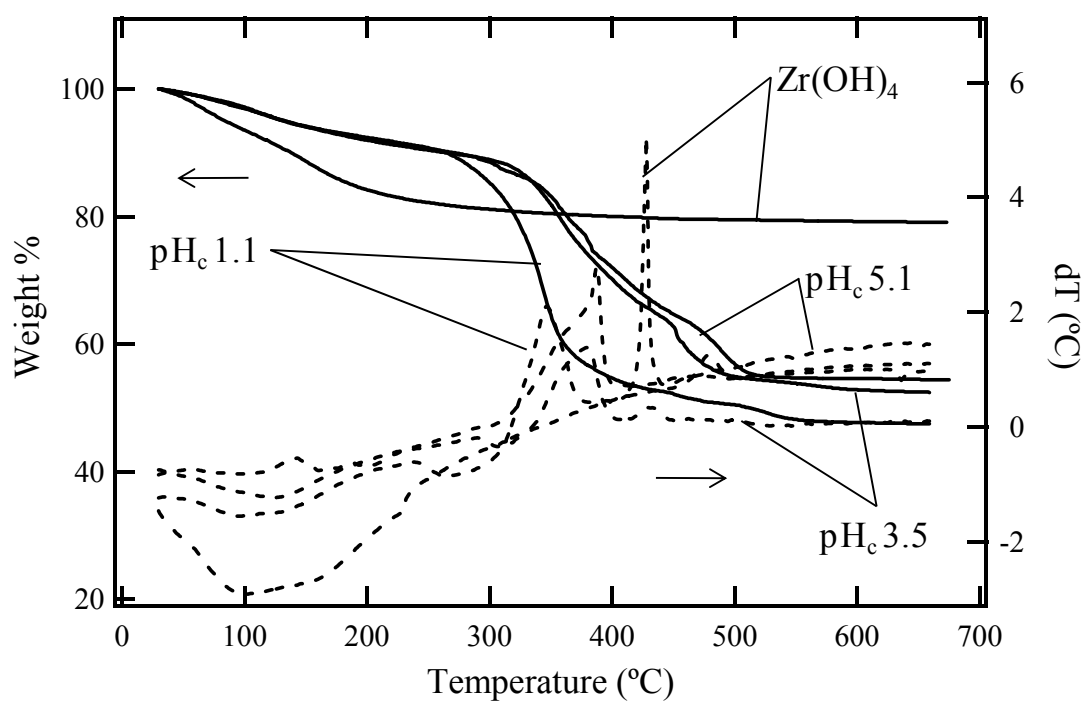


Fig. 4.5 TGA and DTA curves of zirconium solid phase precipitated in the presence of oxalic acids, compared with that of Zr(OH)_4 .

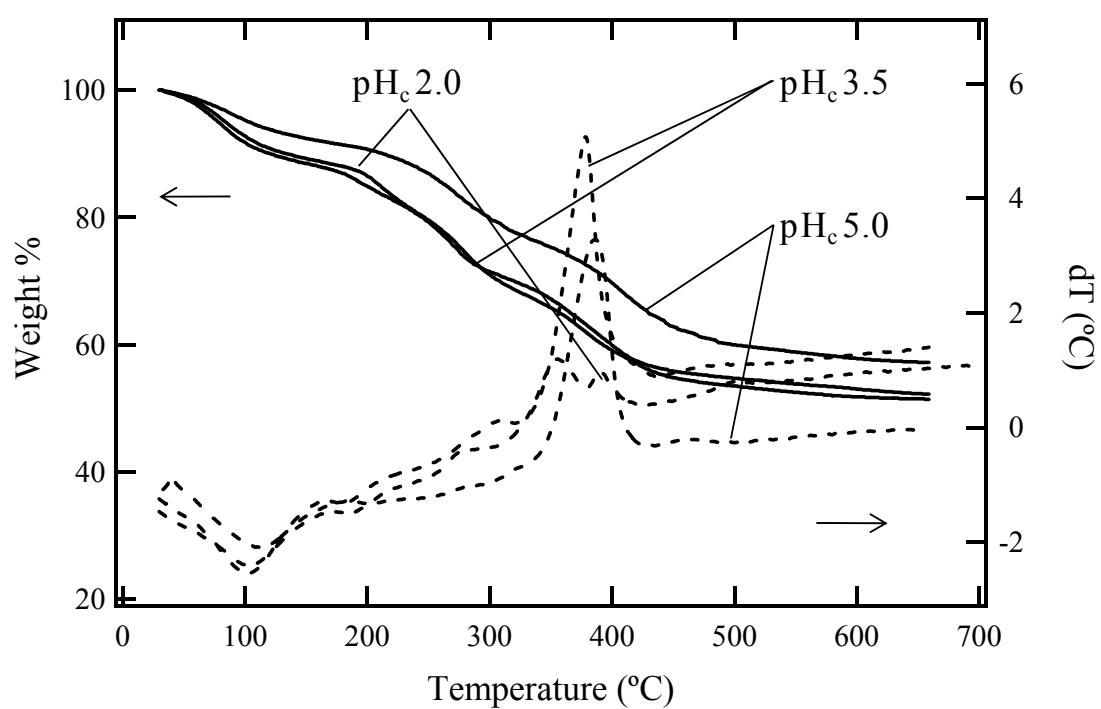


Fig. 4.6 TGA and DTA curves of zirconium solid phase precipitated in the presence of malonic acids.

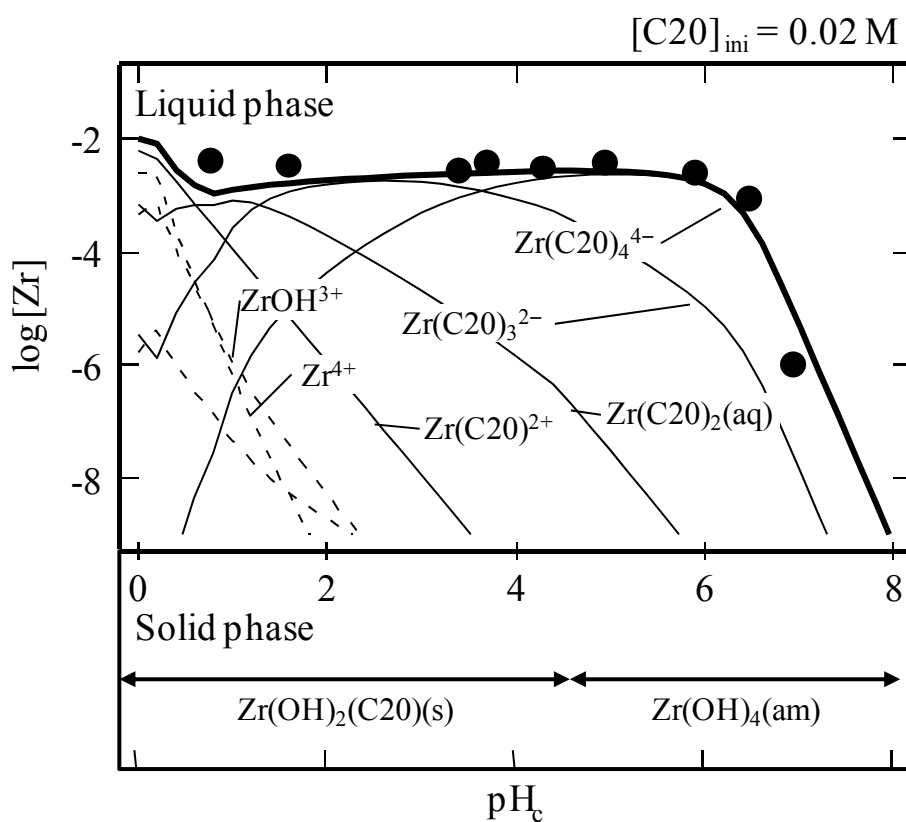


Fig. 4.7 Solubility curve, soluble species and solubility-limiting solid phase in the presence of 0.02 M initial concentration of oxalic acid ($I = 0.5$). The plots show the experimental values and the broken, solid, and bold curves represent the hydrolytic species, oxalate complexes, and the zirconium solubility calculated from the constants in Table 4.2. The solid phase at the bottom column was determined in the solubility analysis.

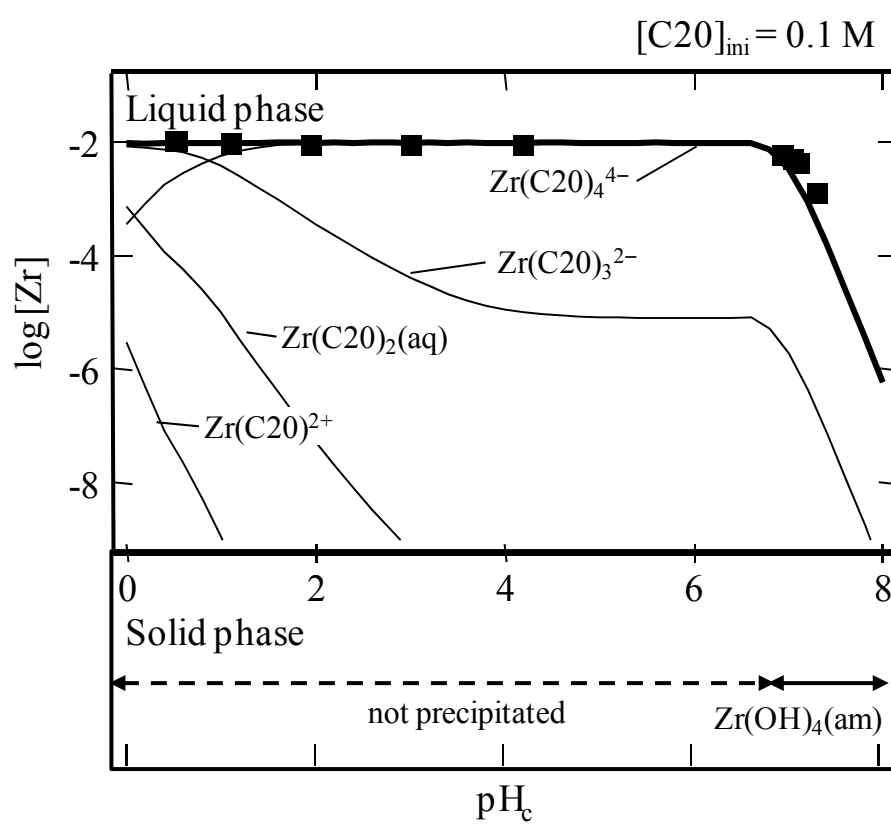


Fig. 4.8 Solubility curve, soluble species and solubility-limiting solid phase in the presence of 0.1 M initial concentration of oxalic acid ($I = 0.5$). See also Fig. 4.7 caption.

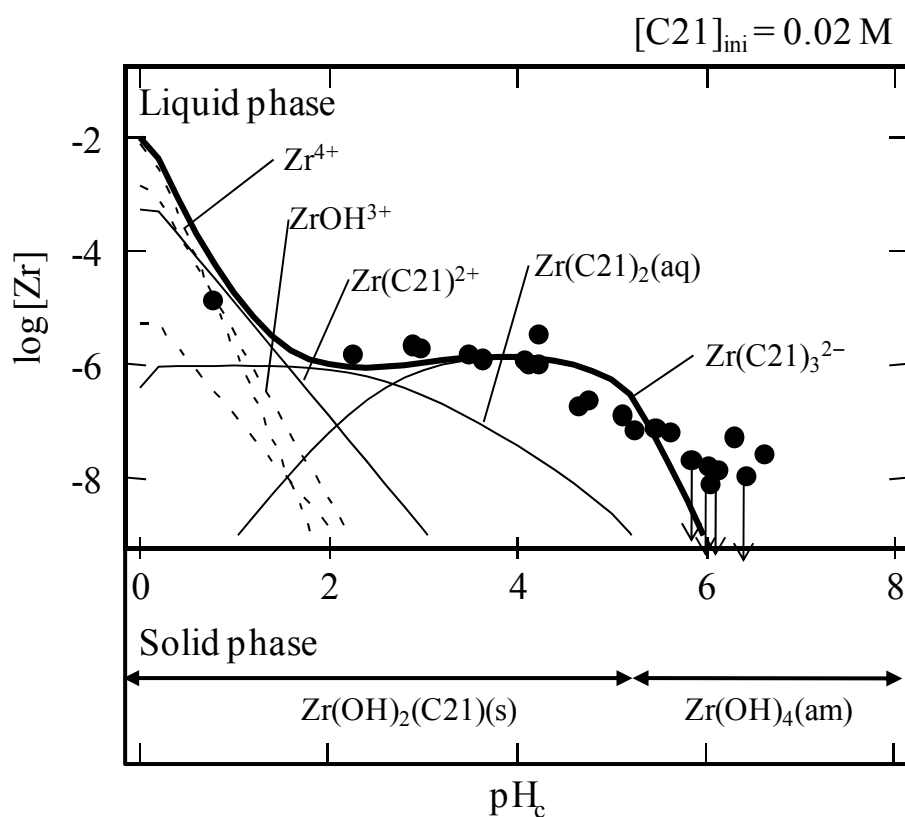


Fig. 4.9 Solubility curve, soluble species and solubility-limiting solid phase in the presence of 0.02 M initial concentration of malonic acid ($I = 0.5$). The plots show the experimental values and the broken, solid, and bold curves represent the hydrolytic species, the malonate complexes, and the zirconium solubility calculated from the constants in Table 4.2. The solid phase at the bottom column was determined in the solubility analysis.

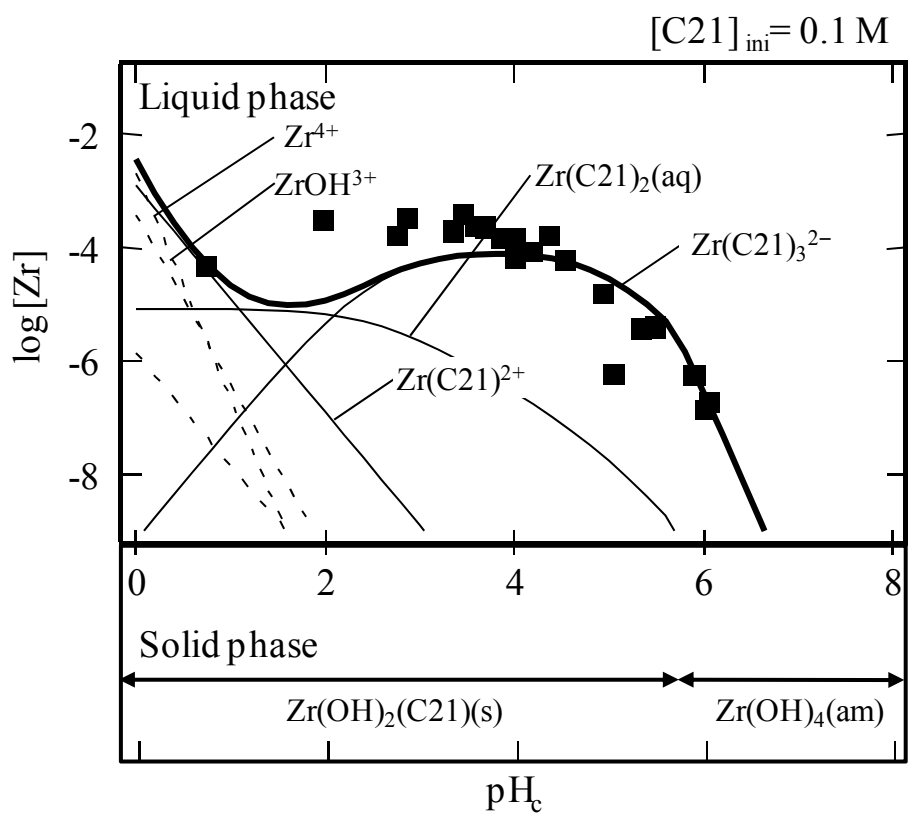


Fig. 4.10 Solubility curve, soluble species and solubility-limiting solid phase in the presence of 0.1 M initial concentration of malonic acid ($I = 0.5$). See also Fig. 4.9 caption.

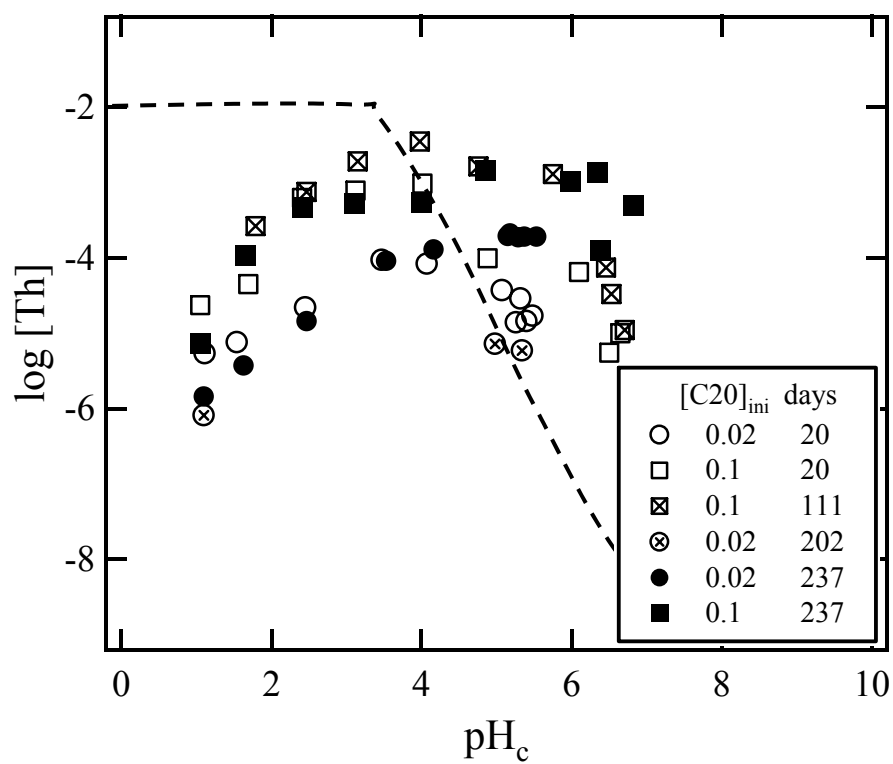


Fig. 4.11 Thorium solubility after 3k Da filtration in the presence of oxalic acid (C20) ($I = 0.5$). The dashed curve represents the solubility of $\text{Th}(\text{OH})_4(\text{am})$ in the absence of oxalic acid.

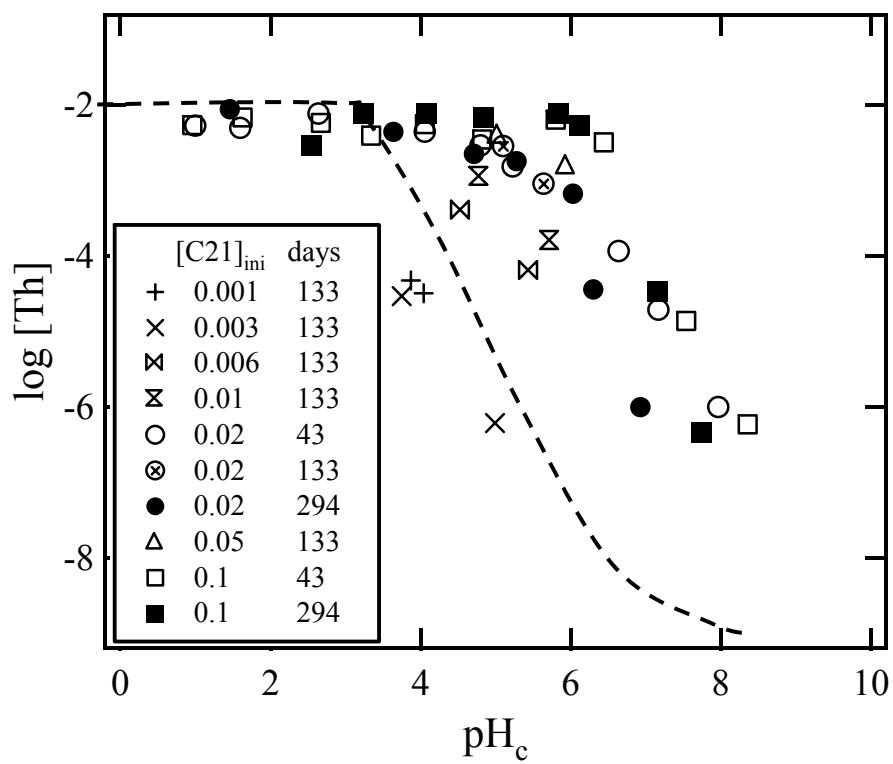


Fig. 4.12 Thorium solubility after 3k Da filtration in the presence of malonic acid (C21) ($I = 0.5$). The dashed curve represents the solubility of Th(OH)₄(am) in the absence of malonic acid.

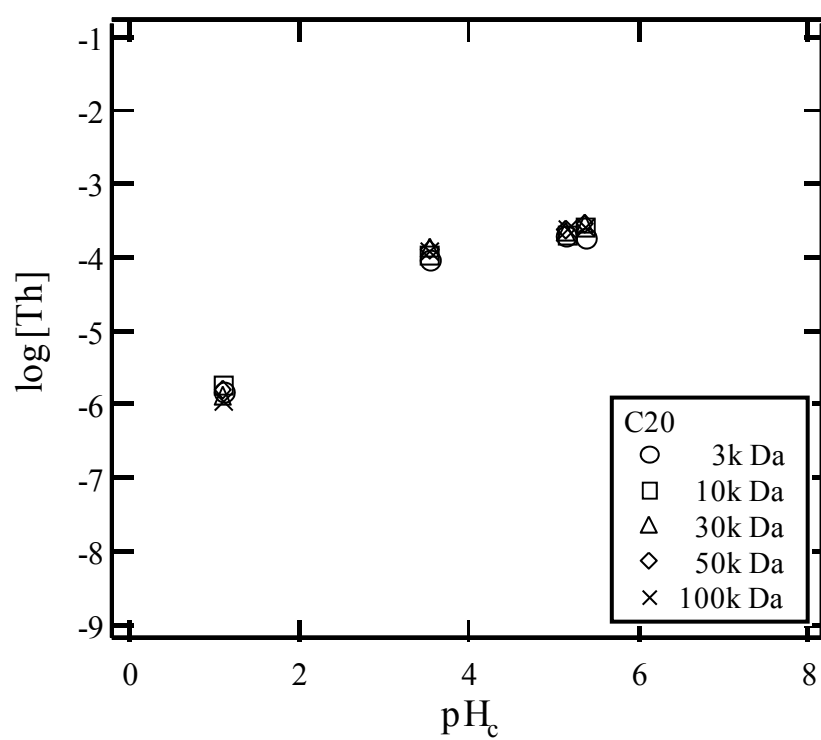


Fig. 4.13 Thorium solubility after 3k - 100k Da filtrations in the presence of oxalic (C20) acid ($I = 0.5$). The initial concentration of the oxalic acid is 0.02 M.

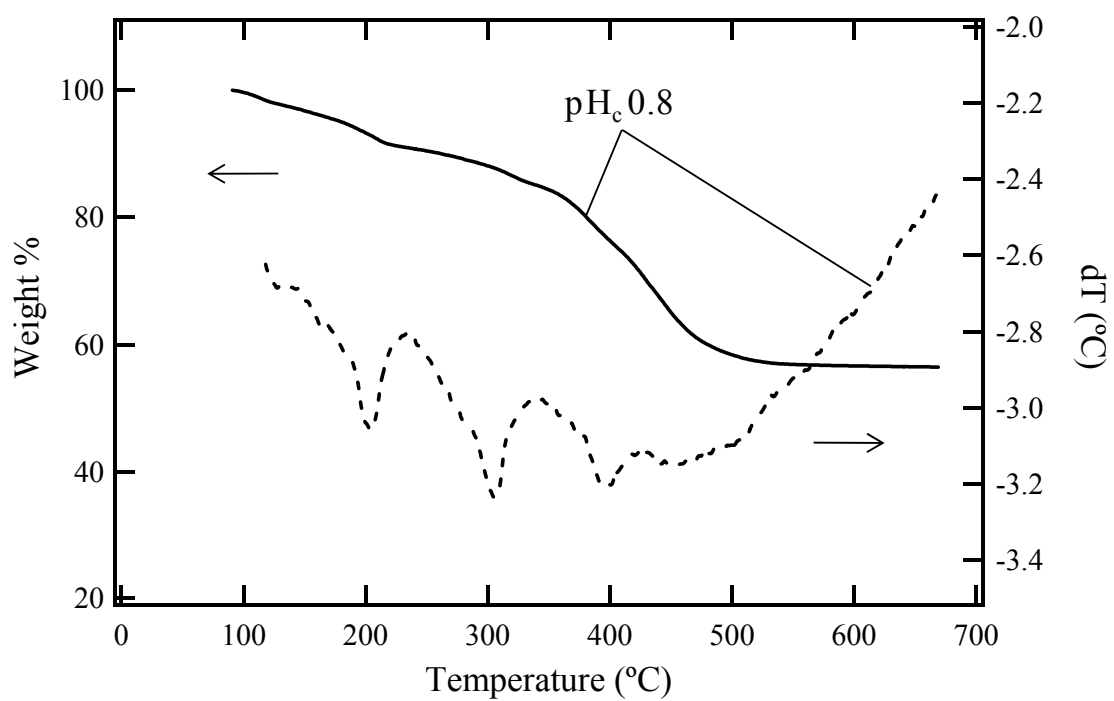


Fig. 4.14 TGA and DTA curves of the thorium solid phase precipitated in the presence of oxalic acid.

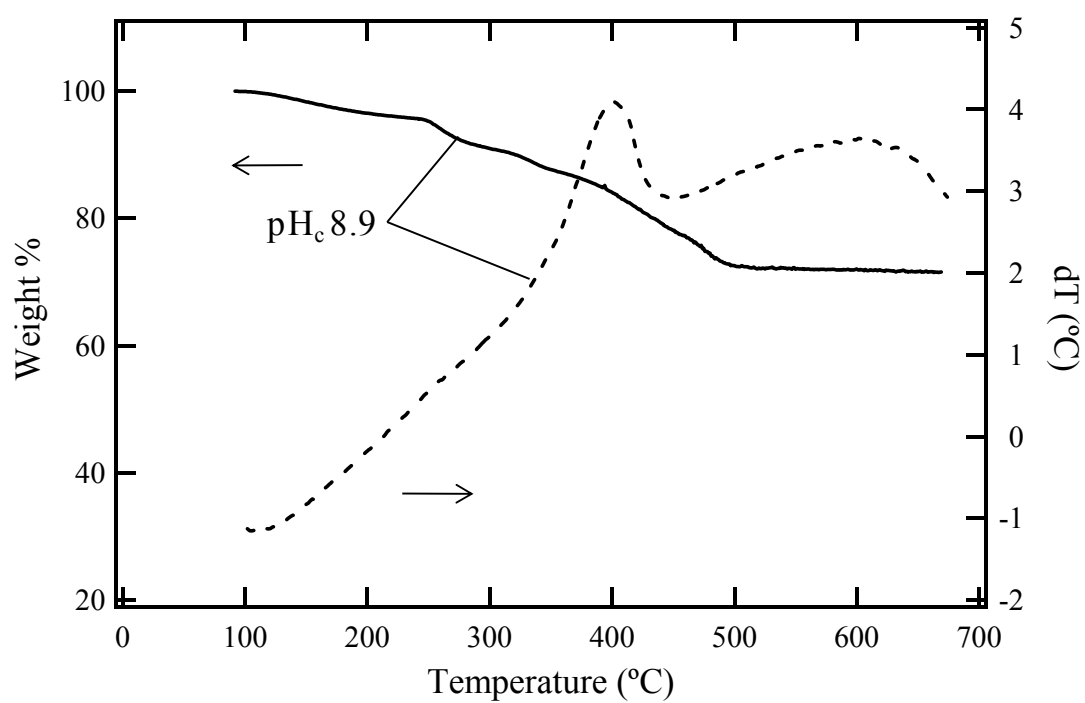


Fig. 4.15 TGA and DTA curves of the thorium solid phase precipitated in the presence of malonic acid.

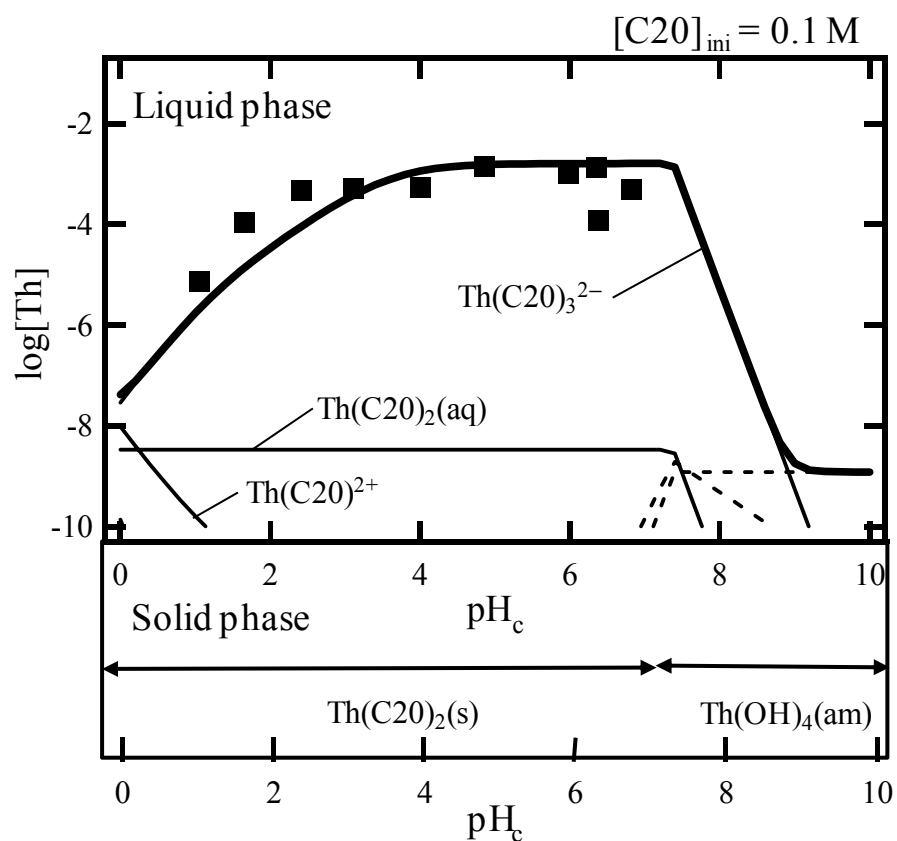


Fig. 4.16 Solubility curve, soluble species and solubility-limiting solid phase in the presence of 0.1 M oxalic acid ($I = 0.5$). Data points represent the experimental values and the broken, solid, and bold curves represent the hydrolytic species, oxalate complexes, and the solubility calculated from the constants in Table 4.3, respectively.

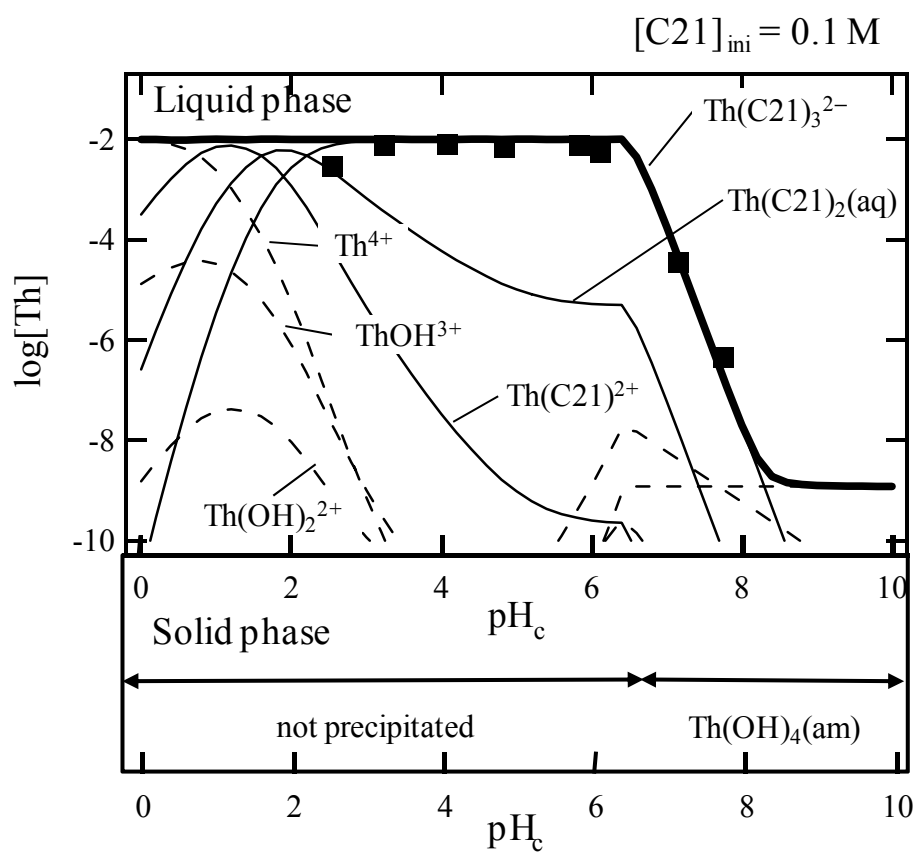


Fig. 4.17 Solubility curve, soluble species and solubility-limiting solid phase in the presence of 0.1 M malonic acid ($I = 0.5$). See also Fig. 4.16 caption.

Chapter 5 General Conclusion

In this thesis, the interactions of oxalic (C20) and malonic acid (C21) to form a soluble species and a solid phase with tetravalent Zr and Th were investigated under the condition of competitive hydrolysis reaction. Because of the strong tendency of the tetravalent ions to hydrolyze in an aqueous solution, special emphasis was placed on the formation of polynuclear species, colloidal species, and a solubility-limiting solid phase. Although the tetravalent ions can be easily hydrolyzed, stable oxalate and malonate complexes were considered to exist in a wide range of pH_c under the presence of excess oxalic and malonic acids. No significant indication of the formation of colloidal species was observed contrary to the case in the absence of carboxylic acids. The formation of the colloidal species may be suppressed by the competing reactions to form stable carboxylate complexes. On the other hand, some indications of Zr and Th carboxylate solid phases were observed in the acidic pH region. The composition of the Zr solid phase was determined to be ternary $\text{Zr(OH)}_2(\text{C2x})$ ($x = 0,1$) from both an analysis of the solid phase and the apparent solubility, whereas Th forms a binary Th(C20)_2 solid phase and no precipitate was observed with malonic acid. The difference between the solid phase compositions may be caused by the different balance of hydrolysis and complexation reactions between Zr and Th. The solubility products of $\text{Zr(OH)}_2(\text{C20})$ and $\text{Zr(OH)}_2(\text{C21})$ were found to be very similar to each other, contrary to their binary complex formation constants. Using thermodynamic constants such as the solubility product, hydrolysis constant, and complexation constant, the solubility can be explained quantitatively. The prediction of the solubility based on the thermodynamic data is important for the reliable safety assessment of geological disposal.

As a preliminary investigation of the fate of these carboxylic acids, the formation of polynuclear hydrolysis species, colloidal species, and a solid phase in the absence of ligands was examined and discussed in Chapters 2 and 3. The apparent solubility of amorphous zirconium hydroxide and thorium hydroxide in the absence of the carboxylic acids was investigated from an oversaturation direction. The size distributions of the soluble species were examined by sequential filtration. The solubility of zirconium and thorium increased with an increase in the filter pore size, indicating the possible presence of large soluble

species. These species having sizes of the order of a few nanometers were considered as colloidal species and assumed to be different from well-ordered polynuclear species. A simple polymer model was introduced to analyze the size distributions of the colloidal species. By considering the mononuclear hydrolysis species as a “monomeric unit” in the concept of the model, the size distributions were well reproduced and the concentrations of the mononuclear species were estimated. The solubility product of amorphous hydroxide was determined by excluding any colloidal contributions.

In Chapter 3, systematic trends of the mononuclear and polynuclear hydrolysis constants of zirconium and thorium were investigated assuming an antiprismatic structure for Zr and a cubic one for Th hydrolysis species. The central metal ions, coordinated hydroxyl ions, and water molecules were treated as hard spheres and electrostatic interactions between the hard spheres were calculated to estimate the hydrolysis constants. Although the parameter values depend on the selected structures, ionic radii, and selected hydrolysis constants, the present model provides a basis not only for checking abnormal experimental data but also for predicting unknown values from a systematic viewpoint. With regard to the solubility of $\text{Zr(OH)}_4(\text{am})$, the contributions of polynuclear species were considered to be dominant under acidic conditions, whereas those of mononuclear species were considered to be dominant in the near neutral pH region. In the case of thorium, the contributions of polynuclear species were not significant, possibly due to the low hydrolysis constants.

In Chapter 4, the effect of oxalic and malonic acids on the formation of soluble species and a solid phase were investigated under the competitive hydrolysis reaction. In the presence of the acids, no significant solubility dependence on filter pore size was observed, contrary to the case in the absence of the acids. The solid phases were observed in a wide range of pH, even in the acidic region, indicating the formation of insoluble carboxylate compounds. The solid phases precipitated at various pH were examined, and it was found that Zr forms $\text{Zr(OH)}_2(\text{C}_2\text{x})$ ternary solid phase. On the other hand, there was no significant indication of the Th ternary solid phase, whereas binary $\text{Th(C}_2\text{O)}_2(\text{s})$ was confirmed by thermal analysis. As mentioned above, such differences may be due to the different balance of hydrolysis and complexation reactions between Zr and Th, which possibly arose from the difference between the ionic radii of Zr and Th.

The solubility product values of $\text{Zr(OH)}_2(\text{C}_2\text{x})$ were similar to each other whereas the complex formation constants were not. No significant dependence of the alkyl chain

length on the solubility product values was observed. This may indicate that the carboxylate in these ternary solid phases may bridge two Zr ions with a monodentate configuration. Structural studies on the solid phase will provide more information to understand the formation mechanism of the solid phase. Although this thesis dealt with the solubility and solubility-limiting solid phase in the presence of oxalic and malonic acids, the method to consider and discuss the solubility-limiting solid phase and apparent solubility will be applicable not only to other organic acids but also to inorganic ligands, especially under high salt concentration conditions in groundwater near the disposal site.

Acknowledgement

I would like to first express my deep gratitude to Professor Hirotake Moriyama at Research Reactor Institute, Kyoto University for his encouragement, suggestions, guidance and many discussions throughout this study.

I am greatly indebted to Associate Professor Takayuki Sasaki, Department of Nuclear Engineering, Kyoto University. This study could not have been completed without his invaluable encouragement, guidance and discussions.

The works of this thesis was carried out at Department of Nuclear Engineering and Research Reactor Institute, Kyoto University. I would like to acknowledge a number of people in both divisions: Professor Ikuji Takagi, Assistant Professors Kimikazu Moritani and Masafumi Akiyoshi and technical personnel Mr. Masahiro Naito at Nuclear Engineering Department and Professor Hajimu Yamana, Associate Professor Toshiyuki Fujii and Assistant Professor Akihiro Uehara at Research Reactor Institute. They have generously given me a lot of knowledge in their respective fields.

²³²Th used in this study is a radioactive element with a 14.1×10^9 years and is in radioactive equilibrium with its daughters. The experiments were performed in a glove box and fume hood in the Hot Laboratory at Research Reactor Institute, Kyoto University. I would like to express my great appreciation for all members in the laboratory. Thanks to their kind support, I could complete my work.

I am grateful to each member of my laboratory for their cooperation and many discussions over the past several years since I joined the laboratory. I had an enjoyable and quality time with them.

Finally, I would like to appreciate my family and friends for their warm encouragement, understanding and support, which enabled me to carry and keep on my study forward.

This research was partly supported by Japan Society for the Promotion of Science (JSPS), Grant-in-Aid for JSPS Fellows.

List of Publications

- Chapter 2 **T. Kobayashi**, T. Sasaki, I. Takagi, H. Moriyama,
"Solubility of Zirconium(IV) Hydrated Oxides," Journal of Nuclear Science
and Technology, Atomic Energy Society of Japan, Vol.44, 90-94 (2007).
- T. Sasaki, **T. Kobayashi**, I. Takagi, H. Moriyama,
"Solubility measurement of zirconium(IV) hydrated oxide," Radiochimica
Acta, Oldenbourg Wissenschaftsverlag, Vol.94, 489-494 (2006).
- Chapter 3 T. Sasaki, **T. Kobayashi**, I. Takagi, H. Moriyama,
"Hydrolysis Constant and Coordination Geometry of Zirconium(IV),"
Journal of Nuclear Science and Technology, Atomic Energy Society of
Japan, Vol.45, 735-739 (2008).
- H. Moriyama, T. Sasaki, **T. Kobayashi**, I. Takagi,
"Systematics of Hydrolysis Constants of Tetravalent Actinide Ions,"
Journal of Nuclear Science and Technology, Atomic Energy Society of
Japan, Vol.42, 626-635 (2005).
- Chapter 4 **T. Kobayashi**, T. Sasaki, I. Takagi, H. Moriyama,
"Solubility of Thorium(IV) in the Presence of Oxalic and Malonic Acids,"
Journal of Nuclear Science and Technology, Atomic Energy Society of
Japan, Vol.46, 1085-1090 (2009).
- T. Kobayashi**, T. Sasaki, I. Takagi, H. Moriyama,
"Solid phase precipitates in (Zr, Th)-OH-(oxalate, malonate) ternary
aqueous system," Radiochimica Acta, Oldenbourg Wissenschaftsverlag,
Vol.97, 237-241 (2009).
- T. Kobayashi**, T. Sasaki, I. Takagi, H. Moriyama,

"Zirconium Solubility in Ternary Aqueous System of Zr(IV)-OH-carboxylates," Journal of Nuclear Science and Technology, Atomic Energy Society of Japan, Vol.46, 142-148 (2009).

Others

T. Sasaki, **T. Kobayashi**, I. Takagi, H. Moriyama, A. Fujiwara, Y.M. Kulyako, S.A. Perevalov, B.F. Myasoedov,
"Complex formation and solubility of Pu(IV) with malonic and succinic acids," Radiochimica Acta, Oldenbourg Wissenschaftsverlag, Vol.97, 193-197 (2009).

T. Sasaki, Y. Takaoka, **T. Kobayashi**, T. Fujii, I. Takagi, H. Moriyama,
"Hydrolysis constants and complexation of Th(IV) with carboxylates," Radiochimica Acta, Oldenbourg Wissenschaftsverlag, Vol.96, 799-803 (2008).

T. Sasaki, **T. Kobayashi**, I. Takagi, H. Moriyama,
"Discrete Fragment Model for Complex Formation of Europium(III) with Humic Acid," Journal of Nuclear Science and Technology, Atomic Energy Society of Japan, Vol.45, 718-724 (2008).

T. Sasaki, Y. Terakado, **T. Kobayashi**, I. Takagi, H. Moriyama,
"Analysis of sorption behavior of cesium ion on mineral components of granite," Journal of Nuclear Science and Technology, Atomic Energy Society of Japan, Vol.44, 641-648 (2007).

T. Sasaki, S. Kubo, **T. Kobayashi**, I. Takagi, H. Moriyama,
"Measurement and Analysis of Formation Constants of Europium with Carboxylates," Journal of Nuclear Science and Technology, Atomic Energy Society of Japan Vol.42, 724-731 (2005).

H. Moriyama, T. Sasaki, **T. Kobayashi**, I. Takagi,
"Systematics of polymeric hydrolysis constants of actinide ions," Journal of Alloys and Compounds, Elsevier, Vol.408, 1302-1304 (2005).