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ORIGINAL PAPER

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Kenso FUJIWARA[1,*,†], Hajimu YAMANA[2], Toshiyuki FUJII[2], Keizo KAWAMOTO[2],
Takayuki SASAKI[1] and Hirotake MORIYAMA[1]

[1]*Department of Nuclear Engineering, Kyoto University, Yoshida, Sakyo-ku, Kyoto 606-8501*
[2]*Research Reactor Institute, Kyoto University, Kumatori-cho, Sennan-gun, Osaka 590-0494*

The solubility of U(VI) hydrous oxide was measured in the hydrogen ion concentration (pH_c) range from 4 to 6 at $25\pm1°C$ in a $NaClO_4$ solution. The experiment was carried out by oversaturation method at ionic strength $I=0.1$, 0.5 and 1.0 and by undersaturation method at $I=1.0$. The solid phase was found to be composed of a mixture of $UO_3 \cdot 2H_2O$ and $UO_2(OH)_2$ by XRD. The concentration of U(VI) was measured by inductively coupled plasma mass spectrometry (ICP-MS), and was analyzed to obtain the solubility products (K_{sp}), by taking into account the participation of the U(VI) hydrolysis species such as $(UO_2)_2(OH)_2^{2+}$. By using the literature values of the hydrolysis species and by using the specific interaction theory (SIT), the $\log K_{sp}°$ value at the standard state ($I=0$) was determined to be $\log K_{sp}° = -22.46 \pm 0.10$. Possible differences in the $\log K_{sp}°$ values due to different solid phases were recognized.

KEYWORDS: uranium, solubility, hexavalent uranium hydrous oxide, solubility product, ion interaction coefficient

I. Introduction

The solubility product of actinide oxides is one of the most important factors to be considered for safety assessment of radioactive waste disposal since it directly controls the concentration of soluble species. However, the reported values are often scattered, and in some cases there are very large differences of several orders of the magnitude between the lowest and the highest values. Since there are a number of experimental difficulties, it is likely that the differences in the reported solubility products are mostly due to experimental problems in the measurements.

In the report of Rai *et al.*,[1] extensive studies on the solubility products of tetravalent actinide hydrous oxides, they have found that the experimental $\log K_{sp}$ values of tetravalent actinide hydrous oxides (Th, Np and Pu) ($AnO_2 \cdot xH_2O$) show a linear relationship with the inverse square of the M^{4+} ionic radii. This means that the 5f-electrons of the actinides are well shielded from the environment similarly to the case of 4f-electrons of the lanthanides, and that the degree of covalency in these elements is relatively small compared to the covalency in d-group elements. Such a relationship is very useful to reliably estimate the $\log K_{sp}$ values for the other tetravalent actinide hydrous oxides, and it is interesting and important to confirm and establish this relationship. Thus, the solubility products of Pu(IV)[2] and U(IV)[3] hydrous oxides have been determined in our recent studies to confirm that the value of $\log K_{sp}°$ decreases with decreasing ionic radii.

For extension of our studies on An(IV) hydrous oxides to An(VI), the solubility product of Pu(VI)[4] hydrous oxides has also been determined to confirm that the $\log K_{sp}°$ value decreases with decreasing ionic radii. However the literature values of U(VI) and Np(VI) are still scattered, and no systematic difference has been recognized so far. In the present study, the K_{sp} value for U(VI) was determined by measuring the solubility of U(VI) hydrous oxides and the relationship of $\log K_{sp}°$ values *vs.* ionic radii was discussed.

II. Experiment

A stock solution of uranyl perchloride $UO_2(ClO_4)_2$ was prepared from natural uranyl nitrate hexahydrate of Merck Co., Ltd.[5] after the filtration by a $0.45\,\mu m$ membrane filter to remove any insoluble residue. The solubility of uranium was measured by oversaturation and undersaturation methods in a glovebox with a purified Ar atmosphere (below $0.5\,ppm$ of O_2). Each sample solution of 0.1, 0.5 and 1.0 mol/dm^3 (M) $NaClO_4$ was spiked by the U stock solution in a polypropylene tube. The pH_c value was adjusted with $HClO_4$ and/or NaOH, and the sample solution was stood at $25\pm1°C$ for aging. After aging, the pH_c value of the solution was measured by a pH meter (TOA Electronics Ltd.). Each sample solution was then filtered by using a filter of 3,000 NMWL (nominal molecular weight limit), and the concentration of U in the filtrate was measured by using UV/VIS spectrophotometer (Shimadzu Corp.) and Inductively Coupled Plasma Mass Spectrometer (ICP-MS) HP4500 (Hewlett Packard Co., Ltd.). The formed solid phase was analyzed by X-ray diffraction (RINT2000, RIGAKU).

The following cell[6] was used to measure the emf of the sample solutions with an error of 2 mV:

$$\text{Sample solution in } I\,\text{M NaClO}_4$$
$$| (0.9I\,\text{M NaClO}_4, 0.1I\,\text{M NaCl} | \text{AgCl, Ag.} \quad (1)$$
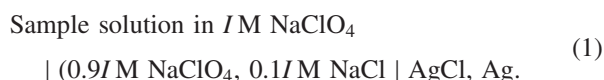
For each ionic strength experiment, the Ag/AgCl reference electrode compartment was filled with a new solution of the same ionic strength. The emf of the cell has a linear re-

*Corresponding author, Tel. +81-29-282-1111 (Ext. 3158), Fax. +81-29-282-9328, E-mail: fujiwara.kensou@jnc.go.jp
†Present address: *Japan Nuclear Cycle Development Institute., 4-33 Muramatsu, Tokai-mura, Naka-gun, Ibaraki 319-1194*

lationship with the logarithm of the hydrogen ion concentration as:

$$E = E_0 - RT/nF \ln a_{H^+} + E_j$$
$$= E_0^* - RT/nF \ln [H^+] + E_j, \tag{2}$$

where E_0 and E_0^* are constants, a_{H^+} is the activity of hydrogen ions, and E_j is the liquid junction potential. The electrode with I M NaClO$_4$ was calibrated within ± 1.0 mV by a Gran plot[7] in solutions with the same concentration of electrolyte.

III. Results and Discussion

1. Solubility of Uranium

Figure 1 shows the change of uranium concentrations with the standing time. In the oversaturation method, the uranium concentration decreased with increasing standing time and the steady state was almost attained in 10 days, and in the undersaturation method, increased with increasing standing time and the steady state was also attained in 10 days. The results for over 10 days are thus considered to represent the equilibrium uranium concentrations. The results of the solubility measurement are summarized in **Table 1** and
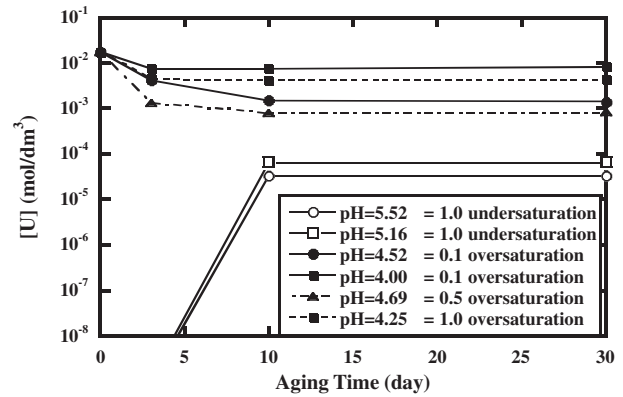

Fig. 1 Time dependence of U(VI) concentrations

Fig. 2.

Figure 3 shows a typical X-ray diffraction pattern of the solid phase precipitated in the experiments together with the reference data[8] of UO$_3 \cdot$2H$_2$O and UO$_2$(OH)$_2$. It can be seen that although there are some amorphous phases with broad peaks at around 24° and 26°, most of the observed peaks are attributed to these two compounds. It concludes

Table 1 Experimental data from the solubility measurement of hexavalent uranium hydrous oxide[a]

I=0.1 M Oversaturation Period: 10 days		30 days		I=0.5 M Oversaturation Period: 10 days		30 days	
pH$_c$	[U(VI)] (M)	pH$_c$	[U(VI)] (M)	pH$_c$	[U(VI)] (M)	pH$_c$	[U(VI)] (M)
3.98	7.63×10^{-3}	4.00	8.62×10^{-3}	4.22	4.65×10^{-3}	4.22	4.64×10^{-3}
4.08	7.03×10^{-3}	4.17	6.86×10^{-3}	4.40	2.18×10^{-3}	4.40	2.16×10^{-3}
4.18	6.45×10^{-3}	4.17	5.26×10^{-3}	4.60	7.57×10^{-4}	4.60	6.94×10^{-4}
4.45	1.52×10^{-3}	4.45	2.55×10^{-3}	4.67	8.06×10^{-4}	4.69	8.26×10^{-4}
4.50	1.90×10^{-3}	4.52	1.36×10^{-4}	4.93	1.46×10^{-4}	4.93	1.37×10^{-4}
4.76	3.23×10^{-4}	4.62	3.66×10^{-4}	5.15	8.83×10^{-5}	5.11	8.04×10^{-5}
4.82	3.00×10^{-4}	4.86	5.20×10^{-4}	5.28	4.13×10^{-5}	5.25	3.49×10^{-5}
5.03	1.21×10^{-4}	5.08	2.33×10^{-4}	5.35	3.17×10^{-5}	5.30	2.95×10^{-5}
5.16	7.91×10^{-5}	5.13	4.51×10^{-5}	5.52	1.17×10^{-5}	5.50	1.15×10^{-5}
5.37	2.14×10^{-5}	5.35	1.69×10^{-5}	5.77	6.14×10^{-6}	5.75	7.10×10^{-6}

I=1.0 M Oversaturation Period: 10 days		30 days		Undersaturation 30 days	
pH$_c$	[U(VI)] (M)	pH$_c$	[U(VI)] (M)	pH$_c$	[U(VI)] (M)
4.25	4.22×10^{-3}	4.25	4.25×10^{-3}	4.57	2.53×10^{-3}
4.37	2.47×10^{-3}	4.37	2.55×10^{-3}	4.63	2.44×10^{-3}
4.60	1.02×10^{-3}	4.60	9.87×10^{-4}	5.00	3.20×10^{-4}
4.67	7.28×10^{-4}	4.66	8.37×10^{-4}	5.02	2.44×10^{-4}
4.84	3.04×10^{-4}	4.84	3.32×10^{-4}	5.05	2.51×10^{-4}
5.10	7.19×10^{-5}	5.10	5.93×10^{-5}	5.08	1.76×10^{-4}
5.40	2.71×10^{-5}	5.33	2.43×10^{-5}	5.24	8.43×10^{-5}
5.62	1.30×10^{-5}	5.57	1.13×10^{-5}	5.27	6.56×10^{-5}
5.72	1.16×10^{-5}	5.70	9.65×10^{-6}	5.48	2.19×10^{-5}
5.92	5.22×10^{-6}	5.92	4.75×10^{-6}	5.48	2.76×10^{-5}
				5.49	3.50×10^{-5}
				5.51	1.90×10^{-5}
				5.52	1.99×10^{-5}
				5.52	3.34×10^{-5}
				5.57	2.14×10^{-5}
				5.62	1.88×10^{-5}

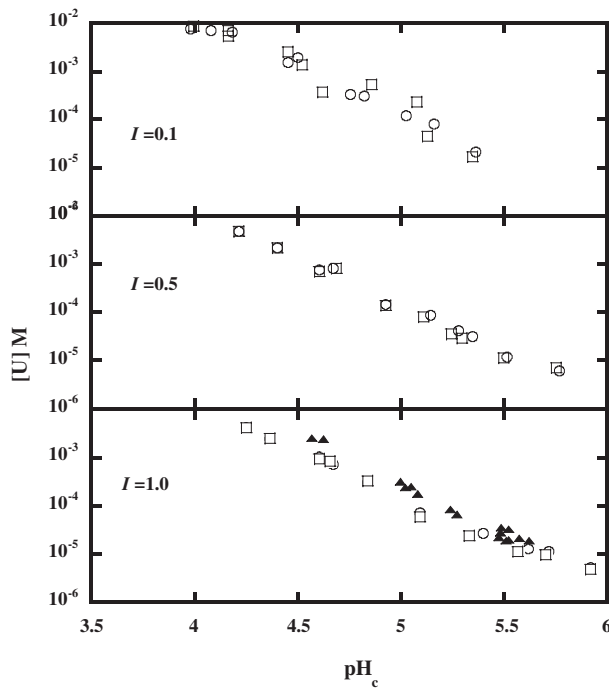[a] pH$_c$ is within ± 2 mV and [U] is $\pm 3\%$.

Fig. 2 Results of solubility measurement of hexavalent uranium hydrous oxide

The solubility data are taken in the present study from over-saturation in 10 days (open circles), oversaturation in 30 days (open squares) and undersaturation in 30 days (filled triangles).
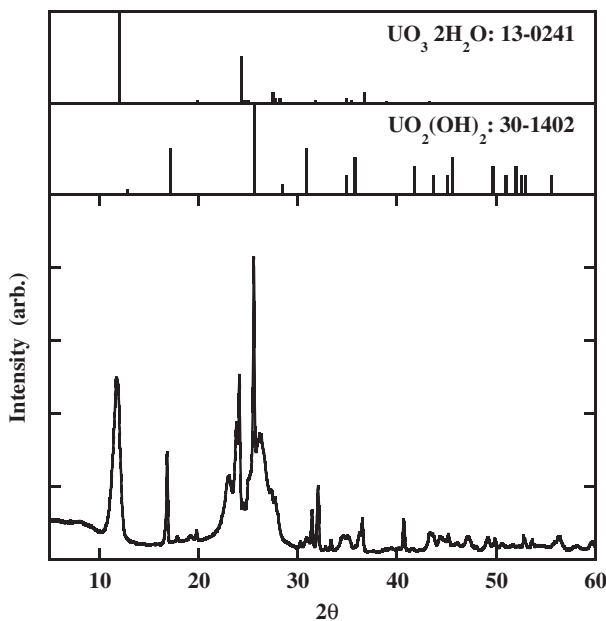

Fig. 3 Typical X-ray diffraction pattern of the solid phase precipitated in the experiments and the reference data[8] of $UO_3 \cdot 2H_2O$ and $UO_2(OH)_2$

that the present solid phase is mostly composed of a mixture of $UO_3 \cdot 2H_2O$ and $UO_2(OH)_2$.
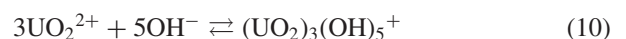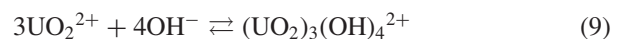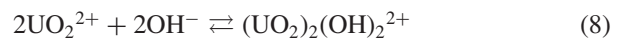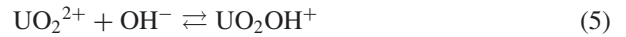
2. Solubility Product of U(VI) Hydrous Oxide

Under the present conditions, the presence of the UO_2^{2+}

species was observed in solution by using UV/VIS spectro-photometer, while the solid phase was found to be mainly of $UO_3 \cdot 2H_2O$ and $UO_2(OH)_2$. Then the dissolution equilibrium of the present system can be expressed as:

$$UO_3 \cdot 2H_2O \rightleftarrows UO_2^{2+} + 2OH^- + H_2O \qquad (3)$$

$$UO_2(OH)_2 \rightleftarrows UO_2^{2+} + 2OH^-. \qquad (4)$$

By considering the pH_c values of the present system, however, it is important to check possible presence of the U(VI) species other than UO_2^{2+}, for example, as

$$UO_2^{2+} + OH^- \rightleftarrows UO_2OH^+ \qquad (5)$$

$$UO_2^{2+} + 2OH^- \rightleftarrows UO_2(OH)_2(aq) \qquad (6)$$

$$2UO_2^{2+} + OH^- \rightleftarrows (UO_2)_2OH^{3+} \qquad (7)$$

$$2UO_2^{2+} + 2OH^- \rightleftarrows (UO_2)_2(OH)_2^{2+} \qquad (8)$$

$$3UO_2^{2+} + 4OH^- \rightleftarrows (UO_2)_3(OH)_4^{2+} \qquad (9)$$

$$3UO_2^{2+} + 5OH^- \rightleftarrows (UO_2)_3(OH)_5^+ \qquad (10)$$

$$4UO_2^{2+} + 7OH^- \rightleftarrows (UO_2)_4(OH)_7^{3+}. \qquad (11)$$
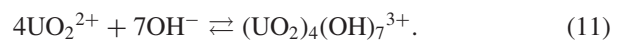
The literature values are available for the equilibrium constants of these reactions and the ion interaction coefficients of the relevant species.[9] By taking these values, it is found that such hydrolysis species as $(UO_2)_2(OH)_2^{2+}$ are formed at $pH_c < 5$ while $(UO_2)_3(OH)_5^+$ is predominantly formed at $pH_c > 5$ as shown in **Fig. 4**. This is consistent with the results of our previous study,[10] in which the formation of $(UO_2)_2(OH)_2^{2+}$ was observed in a lower pH region by laser Raman spectrometry. Thus reactions (3) to (11) are taken into consideration in the present analysis to evaluate the solubility product of U(VI) hydrous oxide.

By taking reactions (3) to (11), the concentration of U(VI) is given by

$$
\begin{aligned}
[U(VI)] &= [UO_2^{2+}] + [UO_2OH^+] + [UO_2(OH)_2(aq)] \\
&\quad + [(UO_2)_2OH^{3+}] + [(UO_2)_2(OH)_2^{2+}] \\
&\quad + [(UO_2)_3(OH)_4^{2+}] + [(UO_2)_3(OH)_5^+] \\
&\quad + [(UO_2)_4(OH)_7^+] \\
&= K_{sp}[OH^-]^{-2} + \beta_{11}K_{sp}[OH^-]^{-1} \\
&\quad + \beta_{12}K_{sp}[OH^-]^{-2} + \beta_{21}K_{sp}^2[OH^-]^{-1} \\
&\quad + \beta_{22}K_{sp}^2[OH^-]^{-2} + \beta_{34}K_{sp}^3[OH^-]^{-4} \\
&\quad + \beta_{35}K_{sp}^3[OH^-]^{-5} + \beta_{47}K_{sp}^4[OH^-]^{-7}, \quad (12)
\end{aligned}
$$

where K_{sp} denotes the solubility product of $UO_3 \cdot 2H_2O$ and/or $UO_2(OH)_2$, that is $K_{sp} = [UO_2^{2+}][OH^-]^2$, and β_{nm} the formation constant of reactions (5) to (11). It is rather hard to determine the fractions of $UO_3 \cdot 2H_2O$ and $UO_2(OH)_2$ especially on the surface of the solid phase, the K_{sp} value is for a mixture of the two compounds. According to the SIT method,[9] the K_{sp} and β_{nm} are given by

$$
\begin{aligned}
\log K_{sp} &= \log K_{sp}^\circ + 6D - [\varepsilon(UO_2^{2+}, ClO_4^-) \\
&\quad + 2\varepsilon(OH^-, Na^+)]I_m, \qquad (13)
\end{aligned}
$$

$$
\begin{aligned}
\log \beta_{nm} &= \log \beta_{nm}^\circ - [n \times 2^2 + m - (2n-m)^2]D \\
&\quad - [(2n-m)\varepsilon((UO_2)_n(OH)_m^{(2n-m)+}, ClO_4^-) \\
&\quad - n\varepsilon(UO_2^{2+}, ClO_4^-) - m\varepsilon(OH^-, Na^+)]I_m,
\end{aligned}
$$
$$(14)$$

Table 2 Solubility products of An(VI) hydrous oxides

	Media	$\log K_{sp}$	$\log K_{sp}°$ at $I=0$	Refs.
U	0.1 M NaNO$_3$	-23.5	-24.10[a]	Kraus[12]
	NH$_4$NO$_3$	-21.9 ± 0.3		Milkey[13]
	NaClO$_4$	-21.96		Gayer *et al.*[14]
	0.2 M NH$_4$NO$_3$	-21.74	-22.45[a]	Babko *et al.*[15]
	0.5 M NaClO$_4$	-20.93 ± 0.01	-21.71 ± 0.04[a]	Bruno *et al.*[16]
	0.1 M NaClO$_4$	-22.21 ± 0.01	-22.81 ± 0.04[a]	Kramer-Schnabel *et al.*[17]
	0.1 M NaClO$_4$	-22.34 ± 0.23	-22.94 ± 0.23[a]	Meinrath *et al.*[18]
		-22.20 ± 0.12	-22.80 ± 0.13[a]	
	0.1 M NaClO$_4$	-22.15 ± 0.06	-22.75 ± 0.07[a]	Kato *et al.*[19]
			-23.191 ± 0.428	NEA-TDB[9]
	0.1 to 1.0 M NaClO$_4$		-22.46 ± 0.10	This work
Np	0.1 M NaNO$_3$	-21.6	-22.20[a]	Kraus[12]
		-22.7		Moskvin[20]
	$I=0$		-21.4	Baes *et al.*[11]
	0.1 M NaClO$_4$	-21.72 ± 0.13	-22.32 ± 0.14[a]	Kato *et al.*[19]
		-21.74 ± 0.22	-22.34 ± 0.22[a]	
			-22.530 ± 0.400	NEA-TDB[9]
Pu	0.1 M NaNO$_3$	-20.5	-21.10[a]	Kraus[12]
		-22.74		Moskvin *et al.*[21]
	0.186 mM HNO$_3$	-24.52 ± 0.18	-24.56[a]	Gel'man *et al.*[22]
	0.1 M NaClO$_4$	-24.05 ± 0.25	-24.65 ± 0.26[a]	Musante *et al.*[23]
	0.1 M NaClO$_4$	-23.0	-23.6[a]	Lierse *et al.*[24]
	0.1 M NaClO$_4$	-21.1 ± 0.1	-21.7 ± 0.11[a]	Pashalidis *et al.*[25]
			-22.500 ± 1.000	NEA-TDB[9]
	0.1 to 1.0 M NaClO$_4$		-22.88 ± 0.39	Fujiwara *et al.*[4]

[a]Recalculated from the experimental data by using the SIT corrections.[9]

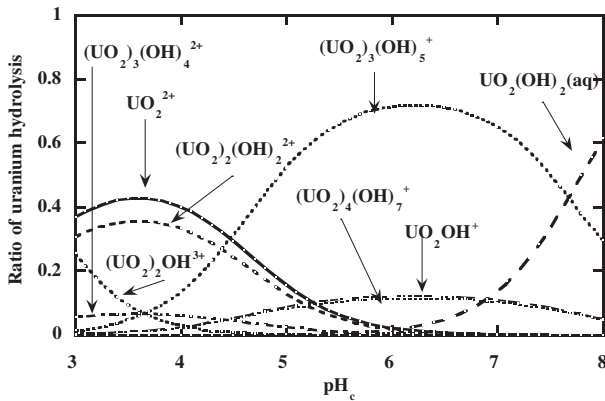**Fig. 4** Fractional abundance of U(VI) hydrolysis species at $I=0$
Curves are calculated with $\log K_{sp}°=-22.46$ and the formation constants of reactions (4) to (10).[9]

where $\varepsilon(OH^-, Na^+)$, $\varepsilon(UO_2^{2+}, ClO_4^-)$ and $\varepsilon((UO_2)_n$-$(OH)_m^{(2n-m)+}, ClO_4^-)$ are the ion interaction coefficients, D the Debye–Hückel term at 25°C and I_m the molal ionic strength. Together with the ion product (pK_w) values,[11] in the analysis, the literature values are used for $\log \beta_{11}°=$ 8.75 ± 0.24, $\log \beta_{12}°=15.85\pm0.07$, $\log \beta_{21}°=11.3\pm0.41$, $\log \beta_{22}°=22.38\pm0.04$, $\log \beta_{34}°=44.1\pm0.3$, $\log \beta_{35}°=$ 54.45 ± 0.12, $\log \beta_{47}°=76.1\pm1.0$, $\varepsilon(UO_2^{2+}, ClO_4^-)=0.46\pm$ 0.03, $\varepsilon(OH^-, Na^+)=0.04\pm0.01$, $\varepsilon(UO_2OH^+, ClO_4^-)=$ -0.06 ± 0.40, $\varepsilon((UO_2)_2OH^{3+}, ClO_4^-)=0.48\pm0.08$, $\varepsilon((UO_2)_2$-

$(OH)_2^{2+}, ClO_4^-)=0.57\pm0.07$, $\varepsilon((UO_2)_3(OH)_4^{2+}, ClO_4^-)=$ 0.89 ± 0.23, $\varepsilon((UO_2)_3(OH)_5^+, ClO_4^-)=0.45\pm0.15$, $\varepsilon((UO_2)_4$-$(OH)_7^+, ClO_4^-)=0.48\pm0.08$.[9] The $\log K_{sp}°$ value is treated as a free parameter. In order to minimize the effect of uncertainties in the $\log \beta_{nm}°$ values on the $\log K_{sp}°$ value, the solubility data in a limited pH_c region are subjected to the analysis, where the contribution of the $(UO_2)_n(OH)_m^{(2n-m)+}$ species is not so predominant compared with that of UO_2^{2+}. Using Eqs. (12) to (14), the solubility data at $pH_c<5$ are then analyzed by the least-squares method to evaluate the $\log K_{sp}°$ value. The value is determined to be $\log K_{sp}°=$ -22.46 ± 0.10. In the present case, the least-squares method was applied to the logarithmic values and the obtained uncertainties were of standard deviations.

3. Comparison of $K_{sp}°$ Values of U(VI) Hydrous Oxide

In **Table 2**, the K_{sp} values reported for U(VI) are summarized together with the values for Np(VI) and Pu(VI). The $K_{sp}°$ values at $I=0$ which are calculated by the SIT corrections[9] are also given for comparison. The values are compared and discussed here in some details.

Kraus[12] reported a very low $\log K_{sp}$ value at 0.1 M NaNO$_3$. In his case, however, the value was obtained from the results of an acid/base titration experiment in which the value was likely to be underestimated. In his analysis, in fact, only reaction (3) was considered, and no correction was made for the formation of such species as the $(UO_2)_2(OH)_2^{2+}$ which consumes the OH$^-$ in the titration. This problem may be more complicated since the titration

curves are often affected by the rate with which equilibrium is reached. Similar problems are also found in the solubility measurements of Milkey,[13] Gayer and Leider[14] and Babko and Kodenskaya,[15] in which no consideration was made of the formation of such polymeric species.

In their solubility measurement, on the other hand, Bruno and Sandino[16] considered the formation of some hydrolysis species including $(UO_2)_3(OH)_5^+$. Unfortunately, however, the pH region was rather limited to pH 7–8 where the solubility equilibrium was often hard to be reached. Any details are given for the time dependence of the solubility data in their report and it is not clear whether the solubility equilibrium has been reached or not.

Kramer-Schnabel et al.[17] reported the $\log K_{sp}$ value of -22.21 at $0.1\,M$ $NaClO_4$ which would be extrapolated to $\log K_{sp}°$ value of -22.81 by the SIT correction.[9] They took into consideration the formation of a number of hydrolysis species including the $(UO_2)_2(OH)_2^{2+}$ in the pH range 4.5–5.5. Although their value is a little lower than the present value of -22.46 ± 0.10, this difference may be attributed to different ion product (pK_w) values used in the analysis. In fact, their value may be corrected to the $\log K_{sp}°$ value of -22.36 by using the pK_w value of $13.77^{[10]}$ at $I=0.1$.

The lower values were reported by Meinrath and Kimura[18] and Kato et al.[19] in their solubility measurements. In their cases, the measurements were done under 100, 0.98 and 0.03% CO_2 partial pressures to observe the relevant solid phases under conditions of natural aquatic systems and to obtain the solubility products of these solid phases. UO_2CO_3 (rutherfordine) was observed to be in equilibrium with 100% CO_2, and $UO_3\cdot2H_2O$ (schoepite) was in equilibrium with 0.98 and 0.03% CO_2. The solubility product values of these solid phases were obtained by taking into account the hydrolysis and carbonate complexation of U(VI). The obtained values are a little lower than the present value, as shown in Table 2. This difference may be due to different solid phases. Their results are for $UO_3\cdot2H_2O$ while the present results are for a mixture of $UO_3\cdot2H_2O$ and $UO_2(OH)_2$.

It is interesting to compare the $K_{sp}°$ values for U(VI) with the values for Np(VI) and Pu(VI) and to see some systematic trends in these values. In **Fig. 5**, the $K_{sp}°$ values for U(VI), Np(VI) and Pu(VI) are plotted as a function of inverse ionic radii of hexavalent actinide ions. Here the ionic radii are of the effective ones in the equatorial plane which are estimated from the experimental values for the distance between the actinide atoms and the coordinated water molecules.[26] As shown in this figure, the reported values are much scattering not only for U(VI) but also for Np(VI) and Pu(VI). However, most of the scatters may be due to experimental problems or due to different solid phases as discussed above for U(VI). More careful measurements with well defined solid phases are needed to observe such systematic trends in the $K_{sp}°$ value for U(VI), Np(VI) and Pu(VI).

IV. Conclusions

The solubility product of U(VI) hydrous oxide was measured by controlling the condition to reach a steady state between U(VI) hydrous oxide and aqueous species in the pH
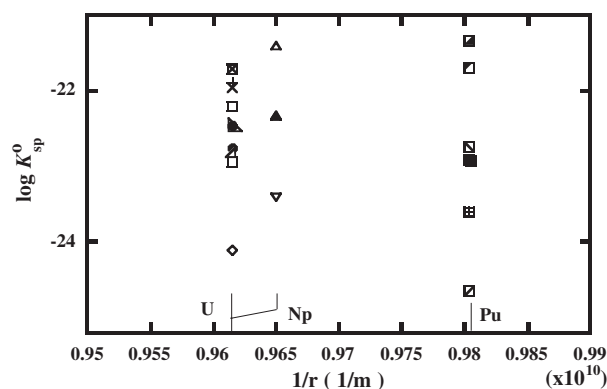
Fig. 5 Variation of solubility product values of hexavalent actinide hydroxides

Marks are the $\log K_{sp}°$ values in Table 2, which are of Kato et al. (○), Meinrath et al. (□), Bruno et al. (⊠), Gayer et al. (×), Kramer-Schonabel et al. (⬗), Babko et al. (◹), Milkey et al. (+), Kraus et al. (◇), Kato et al. (▲), Baes et al. (△), Moskvin et al. (▽), Lierse et al. (⊞), Musante et al. (⬕), Moskvin (◰), Kraus et al. (◪), Pashalidis et al. (◩), Fujiwara et al. (■), this work (●), respectively.

range low enough to identify the hydrolysis species. The result of $\log K_{sp}°=-22.46\pm0.10$ was obtained. By comparing the present result with the literature values, the differences in the $K_{sp}°$ values were discussed and a slight difference was found to be due to different solid phases of $UO_2(OH)_2$ and $UO_3\cdot2H_2O$.

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