Solubility product of plutonium hydrous oxide

Kenso Fujiwara* Hajimu Yamana Toshiyuki Fujii** Hirotake Moriyama****

The solubility of $PuO_2\bullet xH_2O$ was measured in the pH range from 4 to 9 at 25 °C in 1.0 M $NaClO_4$ solution containing $Na_2S_2O_4$ as a reductant. The concentration of Pu^{3+} was measured by α-spectrometry and UV/Visible spectrophotometry, and the equilibrium constant of the reaction, $PuO_2\bullet xH_2O + e^- = Pu^{3+} + 4\,OH^- + (x\text{-}2)\,H_2O$, was obtained to be $\log K = -38.39 \pm 0.19$ at I=1.0. From the obtained results, the solubility product of $PuO_2\bullet xH_2O$ at I=0 was calculated to be $\log K_{sp}^0 = -58.08 \pm 0.25$ by using the known Pu^{4+}/Pu^{3+} formal potential and the specific ion interaction theory for ionic strength corrections. The hydrolysis constant for $Pu(OH)_4$ was evaluated from the measured solubility data by the help of a polymer model to be $\log\ \beta_4^0 \geq 47.50$ at $I = 0$.

Keywords : actinide, solubility, hydrolysis, $PuO_2\bullet xH_2O$, solubility product, hydrolysis constant

1 Introduction

The solubility product of actinide oxides is one of the most important factors to be considered for the safety assessment of geological disposal since it directly controls the actinide solubility. However, the reported values are often scattered and, especially for tetravalent actinide oxides, 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 their measurements. In the case of tetravalent actinide ions, for example, the concentrations of the solution species are very low and are not so easily determined by direct means. This is one of the main reasons for such large differences, in addition to the effect of aging of the solid phase.

In their extensive studies on the solubility products of tetravalent actinide hydrous oxides, Rai et al.[1] have found that the experimental $\log K_{sp}^0$ values of tetravalent actinide hydrous oxides 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 the 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 much useful to reliably estimate the $\log K_{sp}^0$ values for other tetravalent actinide hydrous oxides as well, and the values are estimated to be -50.6 for Pa(IV), -52.6 for U(IV), -58.0 for Am(IV), -59.1 for Cm(IV), -60.7 for Bk(IV), and -61.4 for Cf(IV). However, the reported experimental values are still scattered in the case of Pu(IV)[2-4]; in comparison of the value (-56.85±0.36) of Rai [2] which was used to obtain this linear relationship, lower $\log K_{sp}^0$ values of -60.73±0.05 and -58.3±0.5 were reported by Kim and Kanellakopulos[3] and Capdevila and Vitorge[4], respectively. It is thus interesting and important to confirm and establish this relationship.

For its importance, in the present study, the K_{sp} value for Pu(IV) was determined by measuring the solubility of $PuO_2\bullet xH_2O$, and compared with the literature data. The solubility of $PuO_2\bullet xH_2O$ was measured in the pH range from 4 to 9 at 25 °C in 1.0 M $NaClO_4$ solution containing $Na_2S_2O_4$ as a reductant. In order to determine the very low Pu^{4+} concentration, following the manner of Capdevila and Vitorge[4], the condition was carefully controlled to reach a steady state between $PuO_2\bullet xH_2O$ and Pu^{3+} aqueous species in a concentration range high enough to be directly measured by spectrophotometry. In order to eliminate the uncertainties, the redox potential was measured by a direct means in the present study, while it was calculated from the measured $[PuO_2^{2+}]/[PuO_2^{+}]$ ratio in the case of Capdevila and Vitorge[4]. The concentration of Pu^{3+} was measured by α-spectrometry and UV/Visible spectrophotometry, and the solubility product of $PuO_2\bullet xH_2O$ at I=0 was calculated by using the known Pu^{4+}/Pu^{3+} formal potential and the specific ion interaction theory (SIT) for ionic strength corrections. The hydrolysis constant for $Pu(OH)_4$ was also evaluated from the measured solubility data by the help of a polymer model.

2 Experimental

2.1 Preparations

Plutonium stock solution (10^{-3} M) was prepared from $Pu(NO_3)_4$ in which the isotopic abundance of ^{239}Pu was >99%. For its purification from possible contaminants of Am and Cm, the following manner was applied. Plutonium solid was dissolved in 8N HNO_3 and the insoluble residue was filtered out. The plutonium solution was then purified by anion exchange (Dowex 1X8) in 8N HNO_3. The plutonium was eluted with a NH_2OH solution, and was oxidized to Pu^{4+} with $NaNO_2$ for subsequent cation exchange (Dowex 50W-X8) in 0.5N HNO_3. The $Pu(NO_3)_6^{2-}$ was eluted from the cation exchanger with 8N HNO_3. The obtained Pu solution was thermally evaporated to incipient denitration. The residue was dissolved in 1 M $HClO_4$ and was again evaporated, and this step was repeated three or more times to thoroughly removes nitrates.

2.2 Solubility measurement

The solubility of plutonium was measured by oversaturation method in a glovebox with a purified Ar atmosphere (below 0.5ppm of O_2). Each sample solution of 1 M $NaClO_4$ containing $Na_2S_2O_4$ was spiked by the Pu stock solution in a polypropylene

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tube. The pH value was adjusted with $HClO_4$ and/or NaOH, and the sample solution was shaken at 25 ± 1 °C for aging.

After aging, the pH value of the solution was measured by a pH meter (TOA Electronics Ltd.), and the Eh was measured by a redox combination electrode (Pt-electrode vs. Ag/AgCl: TOA Electronics Ltd.). Each sample solution was then filtered by using a filter of 3000 NMWL (nominal molecular weight limit), and the concentration of Pu in the filtrate was measured using α-spectrometer (SEIKO EG&G Co Ltd.) and UV/VIS/NIR spectrophotometer (Shimadzu Co Ltd.).

The hydrogen ion concentration, $[H^+] = 10^{-pH_c}$, of the sample solutions was measured within ± 0.01 using the following cell [5]:

Sample solution in 1M $NaClO_4$ | 0.9 M $NaClO_4$, 0.1 M NaCl | AgCl, Ag. (1)

The emf of the cell has a linear relationship with the logarithm of the hydrogen ion concentration as:

$$E = E_0 + \ln a_{H^+} + E_j = E_0^* + \ln [H^+] + E_j \qquad (2)$$

where E_0 and E_0^* are constants, a_{H^+} is the activity of the hydrogen ion, and E_j is the liquid junction potential. The electrode with 1.0 M $NaClO_4$ was calibrated within ± 1.0mV by the Gran plot [6] in the same concentration of electrolyte.

For α-counting, 10 μl of the filtrate was evaporated on a sample holder. The detection limit was found in the order of 10^{-9} M in this case, and another method of fluoride coprecipitation was also applied for lower detection limit [7]. A 200 μl portion of the filtrate was added in 20 ml of 1N HNO_3 containing a Sm carrier, and SmF_3 was precipitated by adding HF. The SmF_3 was filtered for α-counting with the detection limit in the order of 10^{-11} M.

3 Results and discussion

3.1 Solubility of plutonium

Figure 1 shows a typical absorption spectrum of the solution species observed at pH 4.04, in which the absorption bands at 560, 569, 600 and 665 nm are all of Pu^{3+} species[8]. Similarly, only the presence of Pu^{3+} species was observed in the sample solution below pH 6. On the other hand, above pH 6, no meaningful absorption bands were observed possibly because of very low solubility of Pu [9]. From its olive-green color [10], the solid phase was considered to be Pu(IV) hydrous oxide ($PuO_2 \cdot xH_2O$), although the amount of the solid phase was too small for X-ray diffraction measurement.

The results of the solubility measurement are summarized in Table 1 and shown in Fig. 2. It can be seen that the Pu concentration decreases with increasing standing time from 1 week to 1 month and that the steady state is almost attained in 1 month. The results for 1 month to 3 months are thus considered to represent the equilibrium Pu concentrations.

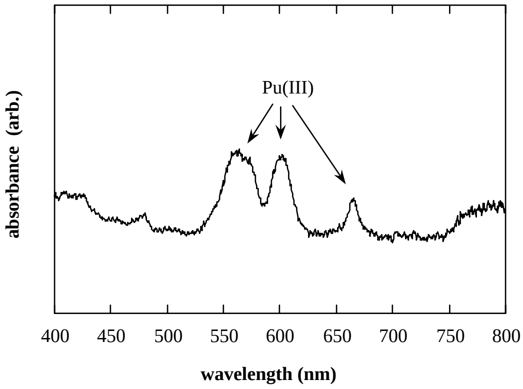

Fig. 1. Typical absorption spectrum of Pu solution species at pH 4.04.

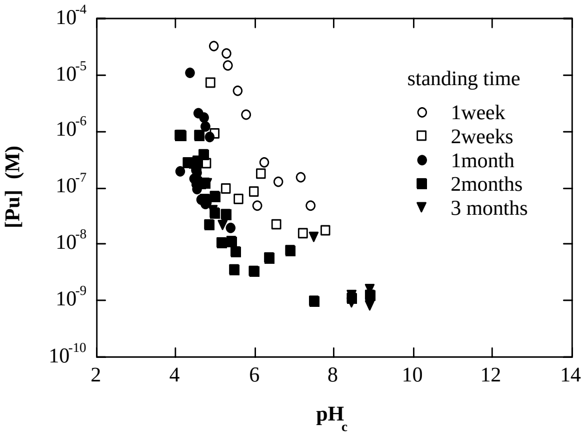

Fig. 2. Results of solubility measurement of $PuO_2 \cdot xH_2O$.

3.2 Solubility Product of $PuO_2 \cdot xH_2O$

Under the present reducing conditions, the presence of Pu(III) species was observed in solution by absorption spectroscopy while the solid phase was considered to be Pu(IV) hydrous oxide, $PuO_2 \cdot xH_2O$. Then the dissolution equilibrium can be expressed as:

$$PuO_2 \cdot xH_2O + e^- = Pu^{3+} + 4\,OH^- + (x\text{-}2)\,H_2O \qquad (3)$$

From the obtained solubility and redox potential data and the ion product (pK_w = 13.76)[11], the equilibrium constant (K_3) of reaction (3) was calculated to be $\log K_3 = -38.39 \pm 0.19$ at $I = 1.0$ by least-squares method. In the present case, the least-squares method was applied to the logarithmic values and the obtained uncertainties were of standard deviations. The standard state equilibrium constant (K_3^0) was also calculated to be $\log K_3^0 = -40.44 \pm 0.19$ by using the SIT corrections [12], in which the values of $\varepsilon(Pu^{3+}, ClO_4^-) = 0.46$ and $\varepsilon(OH^-, Na^+) = 0.04 \pm 0.01$ were taken for specific interaction coefficients.

Table 1. Experimental data from the solubility measurement of $PuO_2 \cdot xH_2O$

Period :	1 week			2weeks	
pH_c	Eh (mV)	[Pu] (M)	pH_c	Eh (mV)	[Pu] (M)
4.94	216.1	3.26E-5	4.77	191.2	2.66E-7
5.26	167.9	2.48E-5	4.87	198.4	7.46E-6
5.29	173.1	1.53E-5	4.99	193.2	9.22E-7
5.54	154.9	5.40E-6	5.27	177.1	9.75E-8
5.75	136.9	2.05E-6	5.59	168.0	6.35E-8
6.03	122.8	5.09E-8	5.95	147.9	8.80E-8
6.22	60.8	3.00E-7	6.15	133.0	1.75E-7
6.56	9.7	1.31E-7	6.54	110.9	2.23E-8
7.13	-58.1	1.55E-7	7.20	88.0	1.54E-8
7.37	-45.2	4.92E-8	7.76	42.0	1.75E-8

Period :	1 month			2months	
pH_c	Eh (mV)	[Pu] (M)	pH_c	Eh (mV)	[Pu] (M)
4.09	324.8	2.05E-7	4.09	332.6	8.78E-7
4.34	155.7	1.11E-5	4.11	328.7	8.75E-7
4.46	317.7	1.51E-7	4.51	334.8	1.30E-7
4.51	316.7	9.79E-8	4.60	309.6	8.75E-7
4.53	292.6	1.88E-7	4.68	310.8	3.93E-7
4.56	138.4	2.12E-6	4.72	324.7	6.44E-8
4.63	315.8	6.27E-8	4.73	305.6	1.21E-7
4.68	142.9	1.81E-6	4.83	292.7	2.27E-8
4.71	147.4	1.25E-6	4.97	283.6	3.65E-8
4.73	302.6	5.28E-8	4.99	292.8	7.08E-8
4.78	308.8	5.53E-8	5.15	283.6	1.11E-8
4.83	143.9	8.17E-7			
5.37	316.6	2.01E-8			

Period :		3 months			
pH_c	Eh (mV)	[Pu] (M)	pH_c	Eh (mV)	[Pu] (M)
4.32	229.9	2.90E-7	5.51	204.7	7.68E-9
4.44	213.8	2.95E-7	5.95	192.7	3.34E-9
4.51	219.9	2.49E-7	6.35	184.9	6.08E-9
4.56	241.2	3.10E-7	6.88	173.9	7.85E-9
4.63	227.0	1.27E-7	7.50	159.9	1.37E-8
4.81	342.5	1.21E-7	7.50	159.9	9.89E-10
4.93	343.5	4.20E-8	8.43	131.8	1.18E-9
4.97	283.6	3.67E-8	8.43	131.8	1.33E-9
5.19	322.3	2.32E-8	8.43	131.8	9.68E-10
5.25	214.9	3.36E-8	8.92	137.9	1.26E-9
5.39	213.6	1.17E-8	8.92	137.9	1.70E-9
5.47	212.6	3.57E-9	8.92	137.9	8.45E-10

* pH is within ± 0.01, Eh is ± 1.0 and [Pu] is ± 3%.

Table 2. Solubility products of $PuO_2 \cdot xH_2O$

Media	log K_{sp}	log K_{sp}^0 at $I = 0$	Refs.
Nitric acid		-56.85 ± 0.36	Rai [2]
1.0 M $HClO_4$		-60.73 ± 0.05*	Kim [3]
0.1 to 3.0 M $NaClO_4$		-58.3 ± 0.5	Capdevila [4]
0.062 M HCl	-55.1		Kasha [14]
1.0 M $HClO_4$	-55.2		Kasha [14]
	-47.3 to -56.3		Perez-Bustanmante [10]
1.0M $NaClO_4$	-54.92 ± 0.21	-58.08 ± 0.25	This work

*Recalculated from the experimental data by using the SIT corrections[12].

Considering the contribution of Pu^{4+} in the reaction scheme, reaction (3) is divided into two reactions as:

$$Pu^{3+} = Pu^{4+} + e^- \qquad (4)$$

$$PuO_2 \cdot xH_2O = Pu^{4+} + 4\,OH^- + (x\text{-}2)\,H_2O \qquad (5)$$

From the standard potential (1.044 ± 0.010 (V) [13]) for the redox couple of Pu^{4+}/Pu^{3+}, the logarithm of the equilibrium constant K_4 of reaction (4) is obtained to be -17.64 ± 0.17 at I = 0. The solubility product of $PuO_2 \cdot xH_2O$ at I=0 is thus calculated to be log K_{sp}^0 = -58.08 ± 0.25 by combining the obtained results. Similarly, the log K_4 and log K_{sp} values at I = 1.0 are obtained to be -16.53 ± 0.08 and -54.92 ± 0.21, respectively, from the formal potential (0.978 ± 0.005 (V) [13]).

3.3 Comparison of K_{sp}^0 values

As shown in Fig. 3, Rai et al.[1] have found that the experimental log K_{sp} values of tetravalent actinide hydrous oxides show a linear relationship with the inverse square of the M^{4+} ionic radii. Such a relationship is very useful to reliably estimate the log K_{sp} values for other tetravalent actinide hydrous oxides, and so it is important to establish this relationship by comparing the estimated log K_{sp} values with the experimental ones.

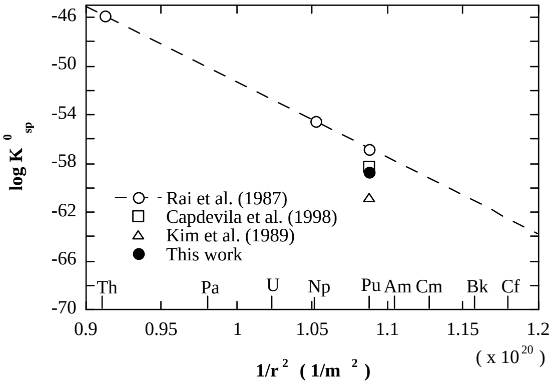

Fig. 3. Variation of solubility product values of tetravalent actinide hydrous oxides

Table 2 summarizes the reported K_{sp} values for Pu(IV) together with the standard state values calculated by the SIT corrections[12]. Similarly to the present study, the aqueous speciation was controlled and taken into account in the interpretation in three works of Rai[2], Kim and Kanellakopulas[3], and Capdevila and Vitorge[4]. In the other works, plutonium in solution was assumed to be in the 4+ oxidation state, the Pu(IV) disproportionation was then neglected, and thus the solubility product were considered to be overestimated[10,14]. The results of the three works and the present work are compared and discussed here.

Rai[2] reported the log K_{sp}^0 value of -56.85±0.36 which was used to obtain the linear relationship in Fig. 3. His experiment was carried out in nitrate medium and a correction for nitrate complexation was made. However the reported stability constants of nitrate complex are scattered and the K_{sp} value may vary with the value of the stability constant. On the other hand, a lower log K_{sp}^0 value of -58.3 ± 0.5 was obtained in perchloric medium by Capdevila and Vitorge[4]. In the study of Capdevila and Vitorge[4], equilibrium concentrations of PuO_2^{2+}, PuO_2^{+} and Pu^{3+} were directly determined by spectrophotometry. In order to keep their concentrations sufficiently high for the detection by spectrophotometry, the redox condition and pH of the solution were carefully controlled. The redox potential of the solution was calculated from the measured $[PuO_2^{2+}]/[PuO_2^{+}]$ ratio and the known potential of this couple, and then the Pu^{4+} concentration was deduced from the calculated redox potential, the measured $[Pu^{3+}]$ and the known Pu^{4+}/Pu^{3+} potential.

As shown in Table 2, the present result of log K_{sp}^0 = -58.08 ± 0.25 is rather close to that of Capdevila and Vitorge[4]. Since the direct Eh measurement has been performed more directly in the present study, the reliability of the value is considered to be much improved. Compared with these two

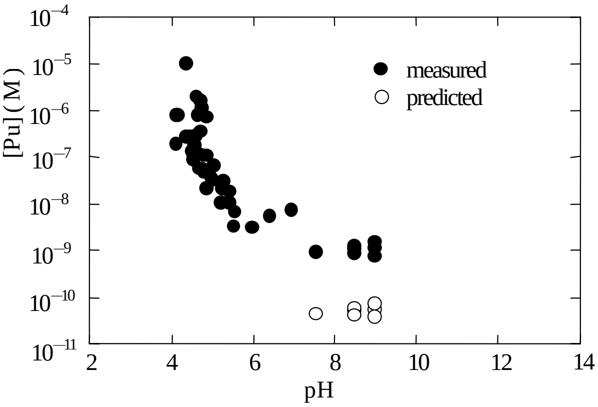

Fig. 4. Steady state Pu concentration in solution in contact with $PuO_2 \cdot xH_2O$.

values, Kim and Kanellakopulos[3] reported a much lower value by their direct measurement of the Pu^{4+} concentration by a spectrophotometry. Although their calculations were not sufficiently documented for evaluating the Pu^{4+} activity coefficient, a very low value of -60.73±0.05 would be obtained from their results by taking the SIT corrections[12]. In this case, however, it should be pointed out that the spectrophotometric measurement was not very precise because of the interference with the Pu(IV) polymer[4].

3.4 Hydrolysis constant for $Pu(OH)_4$

Considering the present reducing conditions, Pu solubility is expected to be as low as detection limit in the region above pH 6[9]. As shown in Fig. 4, however, the Pu concentrations in this region are found be constantly about 10^{-9} M, which is much higher than the detection limit of 10^{-11} M, and this suggests the presence of colloidal species of Pu(IV). The formation of colloidal species was thus checked and confirmed by using filters of different pore sizes. It is well known that Pu(IV) forms colloidal species [15], and the formation of the colloidal $Pu(OH)_4$ is inferred from the relevant thermodynamic data[16] in the present case. The concentration of monomeric $Pu(OH)_4$ is evaluated here by applying a simple model to the observed concentration of colloidal $Pu(OH)_4$, giving the hydrolysis constant β_4.

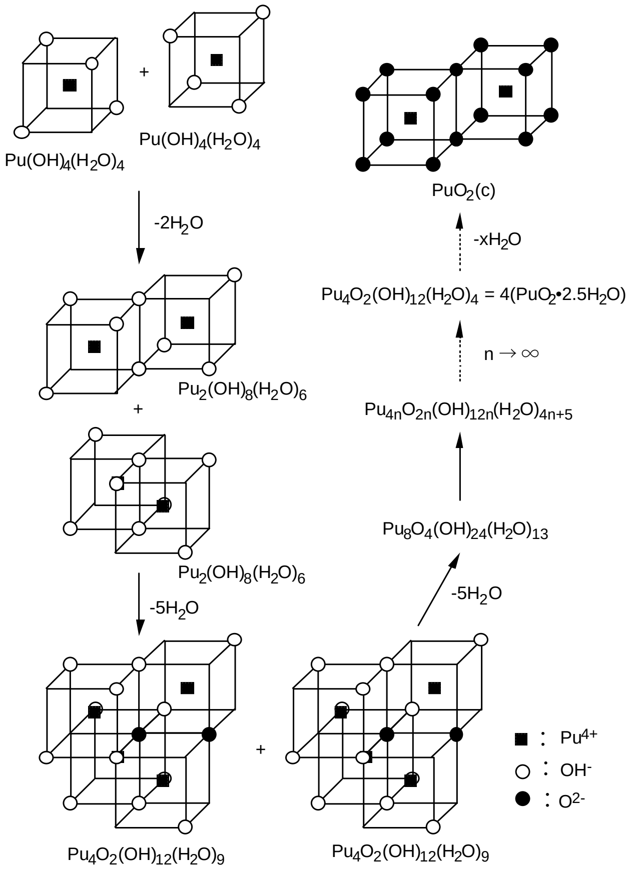

Fig. 5. Formation of polymeric Pu(IV) species.

It has been reported that a classical polymer model of Flory[17], in which a chain-type polymer is assumed, has successfully been applied to describe the size distribution of a colloidal FeOOH[18]. Thus it is possible to calculate the concentration of monomeric species by applying this model to the measured size distribution. In the present case of $Pu(OH)_4$, however, no information on its size distribution has been obtained, and then only the lower limit concentration of monomeric $Pu(OH)_4$ may be obtained from the measured concentration of colloidal species in the filtrate by assuming the formation of the chain-type polymers of $Pu(OH)_4$.

Johnson and Toth [15] have considered the bridging structure of hydroxyl- and oxygen-bridged groups for the polymerization of Pu(IV). Following them, the formation of chain-type polymers may be given as shown in Fig. 5. By

Table 3. Pu concentrations predicted by polymer model.

pH_c	Eh (mV)	[Pu] (M)	*p* value	[Pu]* (M)	log $\beta_4^{\#}$
7.50	159.9	9.89E-10	0.9998227	4.71E-11	44.59
8.43	131.8	1.18E-9	0.9998064	5.62E-11	44.70
8.43	131.8	1.33E-9	0.9997944	6.34E-11	44.67
8.43	131.8	9.68E-10	0.9998246	4.61E-11	44.85
8.92	137.9	1.26E-9	0.9997999	6.00E-11	44.72
8.92	137.9	1.70E-9	0.9997676	8.10E-11	44.52
8.92	137.9	8.45E-10	0.9998362	4.03E-11	44.58
				ave.	44.66 ± 0.08
					(≥44.58)

* predicted by polymer model.

[#] $\log \beta_4 = \log [Pu]^* - \log K_{sp} = \log [Pu]^* + (54.92 \pm 0.21)$

successive dehydration, the monomeric $Pu(OH)_4(H_2O)_4$ will be transformed to $Pu_2(OH)_8(H_2O)_6$, $Pu_4O_2(OH)_{12}(H_2O)_9$, ・・・ $Pu_{4n}O_{2n}(OH)_{12n}(H_2O)_{4n+5}$, ・・・. The chain-type polymers thus formed are expressed by a general form of $\{–Pu_4O_2(OH)_{12}(H_2O)_4–\}_n$ which are equal to $PuO_2•2.5H_2O$ and different from PuO_2 in composition. In this case, the total number, $N(l_1, l_2)$, of unit molecules comprising chain molecules in the range l_1 to l_2 in size is given by:

$$N(l_1, l_2)/N_0 = 1/p\,[(1\text{-}p)/\ln p]^2\,[p^{l_2/l_0}\,(\,l_2/l_0 \ln p - 1\,) - p^{l_1/l_0}\,(\,l_1/l_0 \ln p - 1\,)] \qquad (6)$$

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 is the length of the unit molecule. The value of $N(l_0, l_{cut})/N_0$ is obtained from the measured Pu concentration and substituted into eq. (6) to obtain the p value, which allows to calculate the concentration of monomeric species. By taking values of 5.4 Å for l_0 from ionic radii[19,20] and of 2 nm for l_{cut} from the nominal filter pore size of 3000 NMWL, the p value is obtained to be 0.99977 to 0.99984 as shown in Table 3. It is noted that the value of 2 nm for l_{cut} is only temporal one considering a possible distribution of the actual filter pore size. According to Flory [17], the fractional ratio of monomeric species N_1 to N_0 is given by

$$N_1 / N_0 = (1\text{-}p)^2 \qquad (7)$$

By substituting the above obtained p value to eq.(7), the concentration of monomeric species is calculated, as shown in Fig. 4. The value of the hydrolysis constant β_4 is thus obtained to be $\log \beta_4 = 44.66 \pm 0.08$ at $I = 1.0$ by using the K_{sp} value of $\log K_{sp} = -54.92 \pm 0.21$ in the present study. Because of the assumed type of polymer, however, the obtained value may be considered to be $\log \beta_4 \geq 44.58$ as a lower limit one. The standard state constant is also obtained to be $\log \beta_4^0 \geq 47.50$ by using the SIT corrections, which is consistent with the literature values of 48.68 ± 2.78[16].

4 Conclusions

The solubility product of $PuO_2•xH_2O$ was measured by controlling the condition to reach a steady state between $PuO_2•xH_2O$ and Pu^{3+} aqueous species in a concentration range high enough to be directly measured by spectrophotometry. Although the redox potential was measured by more direct means in the present study, the obtained result of $\log K_{sp}^0 = -58.08 \pm 0.25$ was found to be rather close to that (-58.30 ± 0.50) of Capdevila and Vitorge. It is important to note that these values are much lower than that (-56.85±0.36) of Rai which has been used to obtain a linear relationship between the experimental $\log K_{sp}$ values of tetravalent actinide hydrous oxides and the inverse square of the M^{4+} ionic radii. It is thus important to confirm the $\log K_{sp}^0$ values of other tetravalent actinide hydrous oxides.

The hydrolysis constant for $Pu(OH)_4$ was also evaluated from the measured solubility data by the help of a polymer model to be $\log \beta_4^0 \geq 47.50$ at $I = 0$. Because of the assumed type of polymers, the obtained value is the lower limit one, and the measurement of the size distribution of colloidal species is needed for confirmation.

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