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Effect of Ionic Strength on the Solubility of Neptunium(V) Hydroxide

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Abstract

The effect of ionic strength on the solubility of neptunium(V) hydroxide was studied under the oxidizing, CO₂-free argon atmosphere in the pH range of 7 to 13.5 at room temperature (20–25°C). The solubility was mainly approached from oversaturation direction. The ionic strength was adjusted by NaClO₄ to 0.012, 0.05, 0.10, 0.40 or 0.80. Estimated values for the solubility product (K_{sp}) and the first and the second hydrolysis constants (β_1 , β_2) were:

$$\log K_{sp} = -10.21 \pm 0.02, \log \beta_1 = 2.91 \pm 0.73, \\ \log \beta_2 = 5.50 \pm 0.06 \text{ at } I = 0.80,$$

$$\log K_{sp} = -9.61 \pm 0.04, \log \beta_1 = 3.49 \pm 0.25, \\ \log \beta_2 = 4.7 \pm 1.0 \text{ at } I = 0.40,$$

$$\log K_{sp} = -8.94 \pm 0.01, \log \beta_1 = 2.67 \pm 0.34, \\ \log \beta_2 = 5.74 \pm 0.07 \text{ at } I = 0.10,$$

$$\log K_{sp} = -8.91 \pm 0.05, \log \beta_1 = 3.31 \pm 0.30, \\ \log \beta_2 = 5.74 \pm 0.30 \text{ at } I = 0.05 \text{ and}$$

$$\log K_{sp} = -8.04 \pm 0.05, \log \beta_2 = 5.16 \pm 0.94 \\ \text{at } I = 0.012,$$

where I is the ionic strength in the molarity unit. By using these values, the specific-ion-interaction theory gives the constants at infinite dilution, $I = 0$: $\log K_{sp}^0 = -8.68 \pm 0.26$, $\log \beta_1^0 = 3.30 \pm 0.35$ and $\log \beta_2^0 = 5.58 \pm 0.31$.

Neptunium hydroxide precipitates showed no X-ray diffraction peaks from 1 day to 3 months after preparation. This result indicates that the precipitates remained non-crystalline for up to 3 months.

Introduction

Hydrolysis, as well as redox reaction and carbonate complexation, is one of critical reactions controlling the chemical behaviour of neptunium in near-neutral aqueous solutions [1]. Reliable data on the solubility and hydrolysis constants are, therefore, needed to predict the concentrations in natural waters.

The hydrolysis of neptunium(V) and the solubility of the hydroxide, NpO₂OH, have been studied by several researchers, and many sets of solubility prod-

uct and hydrolysis constants have been obtained as listed in Table 1 ([2–11]). However, the data have not yet systematically understood because of different experimental conditions employed such as ionic strength and temperature. Sometimes the data are doubtful due to large uncertainties arising from only a limited number of experimental points, and/or from poorly-controlled experimental conditions.

Speciation of the solubility-controlling solid is also essential to the solubility determination. Solubility depends strongly on the state of the solid phase. Strickert *et al.* [12] observed that crystallization changed the solubility of neptunium(IV) hydrous oxide, and Neck *et al.* [11] found the difference in the solubility between aged and fresh NpO₂OH precipitates.

In the present study, the hydrolysis of neptunium(V) was studied under the oxidizing condition in the pH range of 7 to 13.5. The objective is to obtain the dependence of the solubility product and the hydrolysis constants on the ionic strength of the solutions. Attempt was made to determine the state of the solubility-controlling solid phase.

Experimental

Reagents

A neptunium-237 (²³⁷Np) stock solution was prepared from neptunium dioxide powder (NpO₂, > 99 wt%, CEN, Fontenay aux Roses, France). The powder was dissolved in concentrated HNO₃, fumed to near dryness, and the residual was dissolved in 1 M HClO₄. The neptunium concentration of the final stock solution was 1×10^{-1} M.

Deionized water used in the experiments was deaerated by boiling. A 3 M NaOH solution for pH adjustment was prepared from reagent grade pellets of NaOH (Kanto Chemical Co., Inc., Tokyo) and the deaerated deionized water. The stock solution was placed under an inert atmosphere (> 99.995% Ar) in a glove box.

The NaOH pellets used contained 0.8% of Na₂CO₃. The carbonate was removed from the NaOH

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Table 1. Literature data on solubility product and hydrolysis constants of neptunium(V)

Method	Medium	$I^{(a)}$	$T^{(b)}$	$\log K_{sp}$	$\log \beta_1$	$\log \beta_2$	Ref.
Solubility		0.2	20	$-9.02 \pm 0.07^{(c)}$	$3.92^{(d)}$		[2]
Potentiometry	NaNO ₃	0.02		$-9.73 \pm 0.10^{(e)}$	$5.1 \pm 0.10^{(f)}$		[3]
Pulse radiolysis	NaClO ₄	0.001	25	$5.25 \pm 1.0^{(g)}$			[4]
Solubility	NaClO ₄ / NaHCO ₃	1.0	25		4.68 ± 0.06		[5]
Extraction	NaClO ₄ / NaHCO ₃	0.2	25		4.16		[6]
Solubility	NaClO ₄	1.0	25	-8.81 ± 0.05	2.33 ± 0.62	4.89 ± 0.05	[7]
Electromigration	NaClO ₄	0.1	25		$3.55^{(d)}$	$6.05^{(d)}$	[8]
Solubility	NaNO ₃	0.01	RT	-10.7	5.7	8.6	[9]
Electrophoresis		0.1	RT		6.0	9.9	[10]
		0.005			5.7	9.2	
Solubility	NaClO ₄	3.0	25	$-9.85 \pm 0.17^{(cr)}$	3.18 ± 0.33	5.15 ± 0.26	[11]
		1.0		$-9.30 \pm 0.06^{(am)}$	2.67 ± 0.20	4.41 ± 0.14	
		0.1		$-8.56 \pm 0.05^{(am)}$	2.44 ± 0.16	4.10 ± 0.12	

(a) I = ionic strength in the molar scale. (b) T = temperature ($^{\circ}\text{C}$), RT = room temperature. (c) Calculated from the published value of $K_{sp} = (9.5 \pm 1.5) \times 10^{-10}$. (d) Calculated from the published value for $[\text{NpO}_2\text{OH}][\text{H}^+]/[\text{NpO}_2^+]$ with $\log K_w^* = -14.0$. (e) Calculated from the published value of $K_{sp} = (1.85 \pm 0.42) \times 10^{-10}$. (f) Calculated from the published value of $[\text{NpO}_2\text{OH}][\text{H}^+]/[\text{NpO}_2^+] = (1.32 \pm 0.30) \times 10^{-10}$ with $\log K_w^* = 14.0$. (g) Calculated from the published value of $-\log \beta_1 = 8.75 \pm 0.5$ with $\log K_w^* = -14.0$.

solution by adding BaCl₂ through BaCO₃ precipitation [13] following filtration with 0.22 μm -pore size membrane filters. The NaOH stock solution was diluted before use for pH adjustment.

Both of barium and carbonate ion concentrations remained in neptunium sample solutions were too low to be directly measured. Because a small excess of BaCl₂ was added to the freshly prepared 3 M NaOH solution, the solution was considered to be saturated with BaCO₃(s). Considering the amount of BaCl₂ added and using the data on the solubility product ($\log[\text{Ba}^{2+}][\text{CO}_3^{2-}] = -8.3$ [14]), the hydrolysis constant for Ba(OH)⁻ ($\log K = 0.53$ [15]) and the carbonate complexation constant for BaCO₃ ($\log K = 2.8$ [14]), the total concentration of barium aqueous species in the NaOH solution was calculated to be about 5×10^{-4} M, and the maximum concentration in the neptunium sample solutions (pH ~ 13) was estimated to be about 5×10^{-8} M. Because smaller amounts of NaOH were introduced to lower-pH sample solutions, the barium concentrations are significantly lower than 5×10^{-8} M. These barium concentrations negligibly affect the hydrolysis behaviour of neptunium.

Carbonate ion concentration in the neptunium sample solutions were also calculated assuming that the high purity Ar gas used was not contaminated with CO₂ and that the concentrations in the NaOH stock solutions were kept constant during the experiments in the glove box. The total concentrations of neptunium carbonates were estimated with using the available carbonate complexation constants for NpO₂CO₃⁻ and NpO₂(CO₃)₂³⁻ [5, 6, 16] to be less than about 10^{-12} M in the pH range investigated.

Procedure

All experiments were conducted in a glove box under an Ar (> 99.995%) atmosphere at room temperature

(20–25 $^{\circ}\text{C}$). Temperature was not kept constant during our experiments. However, appreciable changes in the solubility and hydrolysis constants are not expected, according to the Nitsche's study [17] showing no clear change in solubility as the temperature changed from 25 $^{\circ}\text{C}$ to 60 $^{\circ}\text{C}$.

The Ar gas was passed through a BaCl₂ solution before introduction into the glove box to ensure the removal of CO₂. The BaCl₂ solution was also placed in the glove box. The inner pressure of the glove box was kept 5 to 10% higher than the outer pressure to prevent air intrusion.

Neptunium sample solutions were prepared in 20 ml glass vials. The initial concentrations were between 10^{-2} M and 10^{-3} M. The pH of the solutions were adjusted by HClO₄ and the above prepared CO₂-free NaOH. The solubility measurement was mainly approached from oversaturation direction. The oversaturation direction consisted of adding an excess amount of neptunium from the stock solution to NaClO₄ solution and monitoring the concentration of neptunium until equilibrium was reached. A few sample were approached from undersaturation direction. In the undersaturation direction, precipitates formed in the oversaturation direction were separated within one day after the preparation and dissolved in fresh NaClO₄ solution. The increasing neptunium concentration was measured until equilibrium was reached. The ionic strength (I) of the NaClO₄ solution was 0.012, 0.05, 0.10, 0.40 or 0.80.

Aliquots of the supernatant (usually 0.2 ml) were drawn from the sample solutions and filtered through a Millipore 10,000 molecular weight cutoff filter (pore size: ca. 3 nm) to separate solids from solutions. Loss of neptunium by sorbing on the filter is negligible [18]. Fifty microliters of the filtrate were dried on cleaned stainless steel planchettes. The α -radioactivity was measured with a 2π gas flow proportional counter. The filtrates from solutions of ionic strength of 0.40

Table 2. Ion products of water ($\log K'_w$), activity of water (a_w), mean activity coefficients of H^+ and OH^- ($\gamma_{\pm(H^+, OH^-)}$), and relations between pH and $[OH^-]$ in $NaClO_4$ at $25^\circ C$

$I^{(a)}$	$I_m^{(b)}$	$\log K'_w^{(c)}$	$a_w^{(d)}$	$\gamma_{\pm(H^+, OH^-)}$	$\log [OH^-] - pH$
0.012	0.012	-13.97	1.000	-0.015	-13.99
0.05	0.05	-13.88	0.998	-0.058	-13.94
0.10	0.10	-13.78	0.997	-0.111	-13.89
0.40	0.41	-13.75	0.987	-0.131	-13.88
0.80	0.83	-13.78	0.973	-0.116	-13.90

(a) Ionic strength in the molar scale. (b) Ionic strength in the molal scale. (c) Estimated values by linear interpolation with using literature values for $I = 0, 0.1, 0.5$ and 1.0 [15] in the molar scale. The value for $I = 0.1$ was directly cited from Ref. [15]. (d) The activity of water, a_w , is related to the osmotic coefficient, ϕ , as $\ln a_w = \frac{-W}{1000} (\sum_i m_i) \phi$, where W is the molecular weight of water (18.016), and m_i the molality of the solute species. The sum over i represents the sum over all solutes. For the case of $NaClO_4$, $\sum_i m_i$ is nearly equal to $2I_m$. The values of the osmotic coefficient, ϕ , of $NaClO_4$ solution at $25^\circ C$ are given in Ref. [19] as a function of I_m at intervals of 0.1 from 0.1 to 1.0. The values of ϕ for the present I_m 's were estimated through interpolation or extrapolation by fitting a three-order polynomial curve to the listed 10 points with the correlation coefficient of 0.96.

and 0.80 were diluted before drying to avoid the dried salts, which inhibits exact counting of α -radioactivity. Some of the separated solids were subject to X-ray diffractometry to examine the crystallization.

The pH was measured with a combination glass electrode (Horiba, Kyoto) with pH buffer standards (pH = 4.01, 6.86, 9.18, 12.00 and 13.00 at $25^\circ C$, Horiba, Kyoto). The observed pH, pH(obs), is shifted from the solution pH ($= -\log$ of H^+ ion activity) in $NaClO_4$ solutions because of the difference in liquid junction potential between standards and solutions. The difference was determined by measuring pH buffer solutions containing $NaClO_4$ as $\Delta pH = pH(obs) - pH = 0.49$ ($I = 0.80$), 0.40 ($I = 0.40$), 0.19 ($I = 0.10$), and 0.0 ($I = 0.05$ and 0.012).

The concentration of the OH^- ion is related to pH by the equation [11]

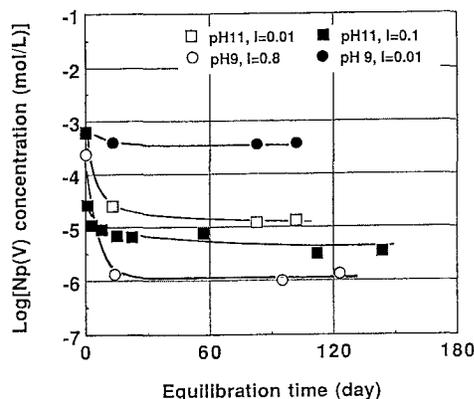
$$\log[OH^-] = \log K'_w + pH + \log \gamma_{H^+}, \quad (1)$$

$$\gamma_{H^+} = \gamma_{\pm(H^+, OH^-)} = \left(\frac{K'_w}{K_w} a_w \right)^{1/2}, \quad (2)$$

where γ_{H^+} is the activity coefficient of H^+ ion, $\gamma_{\pm(H^+, OH^-)}$ the mean activity coefficient of H^+ and OH^- ions, a_w the activity of water, K_w the ion product of water ($1.00 \times 10^{-14.00}$) and K'_w the apparent ion product of water. The values of K'_w , a_w , $\gamma_{\pm(H^+, OH^-)}$ and the resulting relation between $[OH^-]$ and pH for each ionic strength are listed in Table 2.

Results and discussion

Attainment of the solid-liquid equilibrium was confirmed for some selected sample solutions approached

**Fig. 1.** Equilibration of neptunium(V) concentrations in $NaClO_4$ solutions approached from oversaturation direction.

from oversaturation direction by measuring the concentrations of neptunium at intervals of time. The neptunium concentration measured in the course of equilibration are shown in Fig. 1. The concentrations in higher-pH solutions (pH 11) approach the steady-state values a little more slowly than those in lower-pH solutions (pH 9). Steady-state concentrations were found to be attained within between 1 day and 3 months for all values of pH and ionic strength.

X-ray diffractometric analysis was made for precipitated solids separated from several sample solutions. No X-rays peaks were observed in any of the precipitates stored for 1 day to 3 months after the sample preparation. This result indicates that the precipitated hydroxide remained non-crystalline for three months.

The obtained solubility values are plotted in Fig. 2 as a function of pH. Several samples (pH 7.80, 10.26 and 10.50 for $I = 0.10$, and pH 12.50 for $I = 0.80$) were approached from undersaturation direction. The measured concentrations of neptunium from over- and undersaturation directions converged into a single curve for each of the ionic strengths. We consider this result indicates the attainment of equilibrium from undersaturation direction as well as from oversaturation direction.

We found the solubility curves consisting of two parts. One is concave-type dependence observed at the higher pH region. The other is a pH-independent part appeared at the lower pH region. The first pH region, where the constant solubilities are observed, depends on the ionic strength such as 7.5 to 9 for $I = 0.012$ and 6 to 8.5 for $I = 0.10$. This constant solubility is the unexpected result which we did not predict from previous knowledge about the hydrolytic behaviour of neptunium(V) [7, 9, 11].

The concave-type pH dependence typically represents the hydrolysis behaviour of neptunium(V) [7, 9, 11]. We must be careful to interpret the increase in solubility at higher pH region because neptunium carbonates may contribute if the Ar atmosphere is contaminated with CO_2 . In the present experiments, we can neglect the contribution of the carbonates for

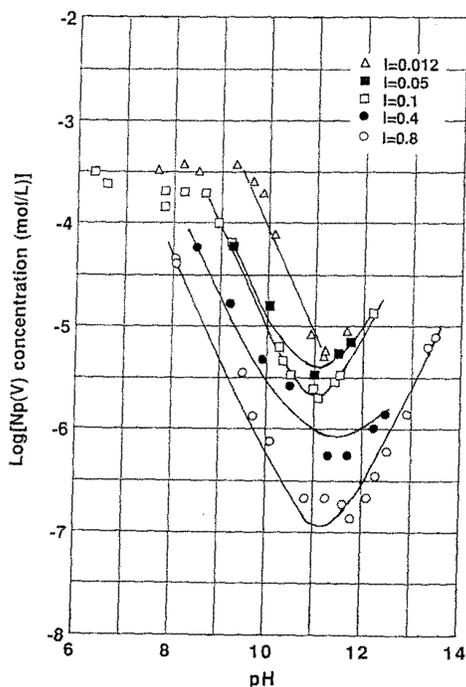
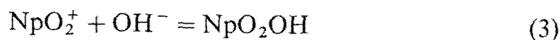


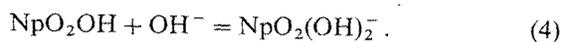
Fig. 2. Solubility of neptunium(V) hydroxide in NaClO_4 solutions. Samples for pHs 7.80, 10.26, and 10.50 at $I = 0.10$, and pH 12.50 at $I = 0.80$ were approached from undersaturation direction.

the two reasons: (1) estimated concentrations of neptunium carbonate complexes are extremely low as calculated above, and (2) the slopes of the measured concentrations vs. pH are 1, indicating the major contribution of an anionic hydroxide complex. Therefore, we interpret the pH-dependent, concave-type solubility curve composing of contributions from a dioxoion NpO_2^+ , an aqueous neutral hydroxide species $\text{NpO}_2\text{OH}(\text{aq})$, and an anionic hydroxide complex $\text{NpO}_2(\text{OH})_2^-$.

The hydrolysis reactions of neptunium(V) are expressed by



and



The total concentration of neptunium(V), $[\text{Np(V)}]_{\text{T}}$, in solutions is given by

$$[\text{Np(V)}]_{\text{T}} = [\text{NpO}_2^+] + [\text{NpO}_2\text{OH}] + [\text{NpO}_2(\text{OH})_2^-] \quad (5)$$

or

$$[\text{Np(V)}]_{\text{T}} = \frac{K_{\text{sp}}}{[\text{OH}^-]} (1 + \beta_1 [\text{OH}^-] + \beta_2 [\text{OH}^-]^2), \quad (6)$$

where K_{sp} denotes the solubility product ($= [\text{NpO}_2^+][\text{OH}^-]$), β_1 the first hydrolysis constant ($= [\text{NpO}_2(\text{OH})]/[\text{NpO}_2^+][\text{OH}^-]$), and β_2 the second hydrolysis constant ($= [\text{NpO}_2(\text{OH})_2^-]/[\text{NpO}_2^+][\text{OH}^-]^2$).

Table 3. Solubility product (K_{sp}), and first and second hydrolysis constants (β_1 , β_2) of neptunium(V) at room temperature (20–25°C)

Ionic strength (mol/l)	$\log K_{\text{sp}}$	$\log \beta_1$	$\log \beta_2$
0.0	$-8.68 \pm 0.26^{(a)}$	$3.30 \pm 0.35^{(b)}$	$5.58 \pm 0.31^{(c)}$
0.012	-8.04 ± 0.05	^(d)	5.16 ± 0.94
0.05	-8.91 ± 0.05	3.31 ± 0.30	5.74 ± 0.30
0.10	-8.94 ± 0.01	2.67 ± 0.34	5.74 ± 0.07
0.40	-9.61 ± 0.04	3.49 ± 0.25	4.7 ± 1.0
0.80	-10.21 ± 0.02	2.91 ± 0.73	5.50 ± 0.06

(a) $\log K_{\text{sp}}^0$. (b) $\log \beta_1^0$. (c) $\log \beta_2^0$. (d) Large error is associated.

Weighed nonlinear least-squares regressions of the experimental data to Eq. (6) give the values of K_{sp} , β_1 , and β_2 for each ionic strength. The obtained values are listed in Table 3 as well as the values at $I = 0$ obtained below. In the case of $I = 0.012$, β_1 is not listed because of the large uncertainty derived.

We use the specific ion interaction theory [20] to quantify the dependence of K_{sp} , β_1 , and β_2 on the ionic strength and to determine the values at infinite dilution ($I = 0$), K_{sp}^0 , β_1^0 , and β_2^0 , respectively. The Nuclear Energy Agency (NEA) of the Organization of Economic Cooperation and Development (OECD) uses this method for their Thermochemical Data Base project [21], and has published guidelines on the application of this method [22].

The specific ion interaction theory plots for neptunium(V) hydrolysis in NaClO_4 solutions are shown in Fig. 3. The following values of K_{sp}^0 , β_1^0 , and β_2^0 are derived from the non-weighted linear regressions and listed in Table 3:

$$\begin{aligned} \log K_{\text{sp}}^0 &= -8.68 \pm 0.26, \Delta\epsilon(\log K_{\text{sp}}^0) = 2.51 \pm 0.62, \\ \log \beta_1^0 &= 3.30 \pm 0.35, \Delta\epsilon(\log \beta_1^0) = -0.21 \pm 0.76 \text{ and} \\ \log \beta_2^0 &= 5.58 \pm 0.31, \Delta\epsilon(\log \beta_2^0) = -0.08 \pm 0.75, \end{aligned}$$

where

$$\begin{aligned} \Delta\epsilon(\log K_{\text{sp}}^0) &= \epsilon(\text{NpO}_2^+, \text{ClO}_4^-) + \epsilon(\text{OH}^-, \text{Na}^+) \\ \Delta\epsilon(\log \beta_1^0) &= -\epsilon(\text{NpO}_2^+, \text{ClO}_4^-) - \epsilon(\text{OH}^-, \text{Na}^+) \\ \Delta\epsilon(\log \beta_2^0) &= \epsilon(\text{NpO}_2(\text{OH})_2^-, \text{Na}^+) \\ &\quad - \epsilon(\text{NpO}_2^+, \text{ClO}_4^-) - 2\epsilon(\text{OH}^-, \text{Na}^+) \end{aligned}$$

and $\epsilon(i, j)$ denotes the interaction coefficient of i with j .

There is a clear discrepancy in the obtained values of $\Delta\epsilon$; the absolute value of $\Delta\epsilon(\log K_{\text{sp}}^0)$ and $\Delta\epsilon(\log \beta_1^0)$ should be equal but our values are not. Using reported values for $\epsilon(\text{NpO}_2^+, \text{ClO}_4^-) = 0.25 \pm 0.05$ [22, 23] and $\epsilon(\text{OH}^-, \text{Na}^+) = 0.04 \pm 0.01$ [22], the value of $\Delta\epsilon(\log K_{\text{sp}}^0) = -\Delta\epsilon(\log \beta_1^0) = 0.29$ is expected. The present value is considerably different from this expected value, and does not agree with the experimentally obtained value of 0.23 ± 0.04 [11]. As known from the above large uncertainties associated, the discrepancy between the expected and the present values were derived from large uncertainties for $\log K_{\text{sp}}^0$, $\log \beta_1^0$ and $\log \beta_2^0$ obtained and a limited number of experimental

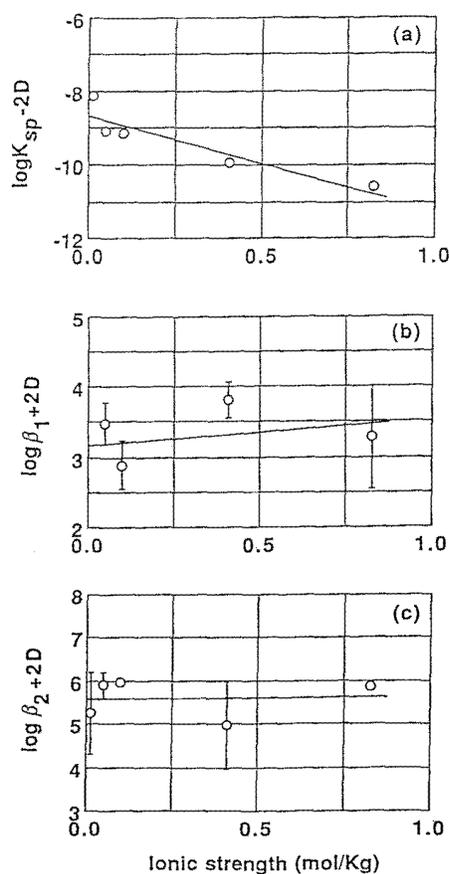


Fig. 3. The specific ion interaction theory plots for (a) the solubility products (K_{sp}), (b) the first hydrolysis constants (β_1), and (c) the second hydrolysis constants (β_2). $D = 0.51 \sqrt{I_m} / (1 + 1.5 \sqrt{I_m})$ denotes the Debye-Hückel term at 25°C, where I_m is the ionic strength in the molal scale. The straight lines show the results of the non-weighted linear regressions. The error bars represented 1σ determined by the weighed least-squares regressions of Eq. (6) to the solubility curves (Fig. 2). The error bars for K_{sp} are included in the circles.

points with respect to the ionic strength. It seems difficult to determine the $A\epsilon$ values from the experiments for low ionic strength solutions (< 1 M).

We have obtained pH-independent, constant solubilities. The phenomenon has not been reported previously. The initial concentrations of neptunium before pH adjustment were always high enough, and after pH adjustment the existence of precipitates were visually confirmed in the whole pH range investigated.

There are only a few researchers who showed the solubility curves as a function of pH [7, 9, 11]. Lierse *et al.* [7] measured the solubility in 1 M NaClO₄ solutions at pHs between 6.8 and 13. They did not observe the constant solubility values in this pH region. Nakayama *et al.* [9] studied at pHs of 7 to 13 in 0.01 M NaNO₃ solutions, and they also did not report such tendency. Solubility curves recently obtained by Neck *et al.* [11] for 0.1 M and 1.0 M NaClO₄ solutions also do not show the tendency. Their curve for 3.0 M NaClO₄ solution, however, represents some constant solubilities at pH between 7 and 8, though not so clear.

In the present results, the constant solubility region appears at lower pHs in solutions of higher ionic strength. The occurrence of the constant solubility seems related to the ionic strength of the solutions.

Analyses were made to identify the aqueous species and contacting precipitates under the above pH regions of the constant solubilities. First the solids were analyzed by X-ray diffractometry. No peaks were observed; accordingly it was concluded that no crystalline materials developed. A spectrophotometric analysis shows that neptunium in the strong brown solutions in contact with the precipitates was pentavalent. The filtration test with using 3 nm-pore size ultrafilters was also made for neptunium in solution. Concentrations of neptunium were not different between the unfiltered supernatant and the filtrate, meaning that no colloidal substances existed. At pH lower than 3, no precipitates were formed, i.e., the solubility at the low pHs probably much higher than those constant values. Although we have obtained these information at present, we have not yet found any reasonably explanations for the pH-independent solubility values.

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