

Solubility of Np(IV) under Carbonate Conditions

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Solubility of Np(IV) under Carbonate Conditions

Akira Kitamura*, Yukitoshi Kohara**

Abstract

Solubility of Np(IV) in carbonate media under reducing conditions was studied. The concentration of dissolved Np(IV) was measured with ionic strengths of 0.5 M ($M \equiv \text{mol} \cdot \text{dm}^{-3}$) and 1.0 M, hydrogen-ion concentration exponent ($\text{pH}_c = -\log [\text{H}^+]$) from 8.5 to 13 and with the total carbonate concentration (C_T) from 0.005 M to 0.1 M by the oversaturation method. The reducing agent used was sodium dithionite. It was found that the solubility of Np(IV) decreased with increasing pH_c and increased with increasing C_T and the ionic strength. On the basis of analysis of the solubility data, the dominant aqueous species of Np(IV) were expected to be $\text{Np}(\text{CO}_3)_2(\text{OH})_2^{2-}$ and $\text{Np}(\text{CO}_3)_2(\text{OH})_4^{4-}$ in the present study. The apparent equilibrium constants of the carbonatohydroxo complexes were obtained in the respective ionic strength of 0.5 M and 1.0 M, and the thermodynamic equilibrium constants at the zero ionic strength, were extrapolated by a model called "specific ion interaction theory (SIT)". Comparing with the literature data of thermodynamic equilibrium constants, the reasonableness of the present data was discussed.

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炭酸共存下における Np(IV)の溶解度測定

(研究報告)

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要 旨

炭酸共存下における Np(IV)の溶解度を測定した。過飽和法を用い、イオン強度を 0.5 M ($M \equiv \text{mol} \cdot \text{dm}^{-3}$)および 1.0 M に、水素イオン濃度指数($\text{pH}_c = -\log [\text{H}^+]$)を 8.5~13 に、全炭酸濃度を 0.005~0.1 M に調整した水溶液中の Np(IV)溶解成分の濃度を測定した。還元剤には、亜二チオン酸ナトリウムを用いた。得られた Np(IV)の溶解度は、 pH_c の増加により減少し、また全炭酸濃度およびイオン強度の増加により増大することが明らかになった。得られた溶解度曲線の pH_c および全炭酸濃度依存性を考慮することにより、本実験条件においては $\text{Np}(\text{CO}_3)_2(\text{OH})_2^{2-}$ および $\text{Np}(\text{CO}_3)_2(\text{OH})_4^{4-}$ の 2 種の溶存種の存在が予想された。また、各イオン強度におけるこれらのヒドロキソ炭酸錯体の見かけの平衡定数を取得した。さらに、見かけの平衡定数のイオン強度依存性を特別なイオン相互作用が考慮されたモデル(SIT)を用いて解析することにより、標準状態すなわちイオン強度 $0 \text{ mol} \cdot \text{kg}^{-1}$ における熱力学的な平衡定数値を取得した。得られた熱力学データを既報の文献値と比較することにより、その妥当性を論じた。

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1. INTRODUCTION

Reliable thermodynamic data for the migration analysis of radionuclides in the engineered barrier system and in the geosphere are required to assess the safety of the geological disposal of high-level radioactive waste (HLW). The thermodynamic data for solubility of actinide elements, which contain the solubility product of actinide compounds and the formation constants of the aqueous actinide complexes, are parts of the most important data for the safety assessment of HLW disposal. Especially, Np-237, which is an α -emitter and has the long half-life of 2.14×10^6 years, is regarded as one of the most hazardous elements for HLW disposal. In deep geological environment which is expected to be under reducing conditions, a tetravalent neptunium will be a dominant redox state, while a pentavalent neptunium is a dominant redox state in the near-neutral solutions contact with air. Thus, it is important to understand the migration behavior of Np(IV).

A thermodynamic database developed by Japan Nuclear Cycle Development Institute (JNC-TDB) [1] has been used to the safety assessment of the geological disposal of HLW in the report of "H12: Project to Establish the Scientific and Technical Basis for HLW Disposal in Japan." [2] The thermodynamic data for the solubility of Np(IV) are of the literature data by Rai et al. [3-5], and the hydrolysis species of $\text{Np}(\text{OH})_4(\text{aq})$ and the carbonatohydroxo complexes of $\text{Np}(\text{CO}_3)_2(\text{OH})_2^{2-}$ are assumed as dominant aqueous Np(IV) species in near-neutral and weak alkaline groundwaters. However, the solubility of tetravalent actinide ions are usually much lower than that of other oxidation states (trivalent, pentavalent and hexavalent). There are only a few literatures of the thermodynamic data for the solubility of Np(IV), and these literature data are scattering. Thus, the reliability of the thermodynamic data of Np(IV) for JNC-TDB will have to be confirmed.

In the present study, the reliability of the thermodynamic data for the aqueous carbonatohydroxo complexes of $\text{Np}(\text{CO}_3)_2(\text{OH})_2^{2-}$ was investigated. The solubility of Np(IV) was determined by oversaturation method. The obtained solubility curves as a function of pH_c ($= -\log [\text{H}^+]$) and total carbonate concentration (C_T) were analyzed and the aqueous species under the present experimental condition were predicted. The apparent equilibrium constants of the species were obtained from the analysis. The thermodynamic equilibrium constants at standard state, i.e., zero ionic strength were evaluated by a model called "specific ion interaction theory (SIT)". Comparing with

the literature values, the reliability of obtained thermodynamic data was discussed. Part of the results of the present study has been already published [6]. In the present paper, the experimental data were revised and the obtained solubility curves were reanalyzed.

2. EXPERIMENTAL

An oversaturation method was applied to the solubility measurement of Np(IV). A stock solution of pentavalent neptunyl perchlorate was prepared from either diluting a hydrochloric acid solution of Np-237 (Amersham Co.) or dissolving of neptunyl (Np-237) nitrate (AEA Technology Co.) with perchloric acid. Sample solutions were prepared in sealed polypropylene tubes. The stock solution of neptunyl perchlorate was added so as to adjust the neptunium concentration from 1.2×10^{-5} M (M: mol-dm⁻³) to 1.0×10^{-3} M, i.e. larger than the Np(IV) solubility in the region of interests. Reagents of analytical grade of NaOH, NaHCO₃ and NaClO₄ (Wako Pure Chemical Industries Ltd.) were used to adjust the hydrogen ion concentration, total carbonate ion concentration and ionic strength, respectively, without further purification. The logarithm of hydrogen ion concentration ($\text{pH}_c = -\log [\text{H}^+]$) was varied from 8.5 to 12.5 at the total carbonate concentration of 0.1 M, and the total carbonate concentration was varied from 5×10^{-3} M to 0.1 M at the pH_c from 8.5 to 10.5. The ionic strength standing for molarity (I) was adjusted either 0.5 M or 1.0 M. A reagent of Na₂S₂O₄ (Wako Pure Chemical Industries Ltd.) was used as the reducing agent. The sample solutions were shaken at 22 ± 3 °C for a certain period to attain equilibrium.

The pH_c values of the test solutions with two different ionic strengths (I = 0.5, 1.0 M) were determined using a cell with a combination glass electrode:



The electrode with the ionic strength I M was calibrated against a solution with I M NaClO₄, and was used in the test solution with the same electrolyte concentration. The oxidation-reduction potential (ORP) and the total carbonate concentration (C_T) were measured using the ORP electrode and CO₂ electrode CE-235 (TOA Electronics Ltd.) with the pH/ion meter IM-55G (TOA Electronics Ltd.), respectively. The concentration of dissolved neptunium was defined as the concentration of neptunium contained in the solution filtrated through the ultrafilter (Toyo Roshi Kaisha Ltd., molecular weight cut-off (MWCO) of 10^4). Neptunium(IV) concentrations in the filtrate were determined using 0.5 M thenoyltrifluoroacetone (TTA) in xylene extractions from nearly equal volumes of filtrate solutions containing 0.5 M HNO₃, from which only monomeric Np(IV) can be extracted [7,8]. The total and solvent-

extracted neptunium concentrations were determined by counting a specific α -ray radioactivity of Np-237 with the alpha spectrometer Octete PCTM (EG&G ORTEC Co.).

All treatments except α -ray radioactivity counting were conducted under an inert argon gas atmosphere to exclude contamination by O₂ and CO₂ contained in air.

3. RESULTS AND DISCUSSION

3.1 Experimental Results

The obtained aqueous Np(IV) concentrations at shaking times of 2 and 4 weeks are shown in Figs. 1, 2, 3, and 4. The concentrations of Np(IV) as a function of pH_c are shown in Figs. 1 ($I = 0.5 \text{ M}$) and 3 ($I = 1.0 \text{ M}$), and those as a function of C_T are shown in Figs. 2 ($I = 0.5 \text{ M}$) and 4 ($I = 1.0 \text{ M}$). Little difference in the concentrations of Np(IV) between the shaking time of 2 weeks and that of 4 weeks is found. Thus, the equilibrium between the Np(IV) in solution and Np(IV) precipitate seems to be attained. Aqueous Np(IV) concentrations, approximately constant in pH_c from 8.5 to 10 and from 12 to 13 at a constant C_T , increase with decreasing pH_c from 10 to 12 and increase with increasing C_T . These solubility values are higher than the literature data by Rai et al. [3], especially in pH_c from 9 to 10. The initial neptunium concentrations are 10^{-5} M and 10^{-4} M for $I = 0.5 \text{ M}$ and 1.0 M , respectively. Thus, the solubility values in pH_c from 8.5 to 10 at $C_T = 0.1 \text{ M}$ are considered to be less reliable than other values.

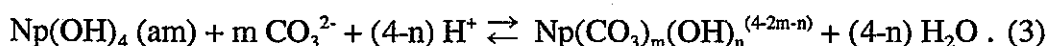
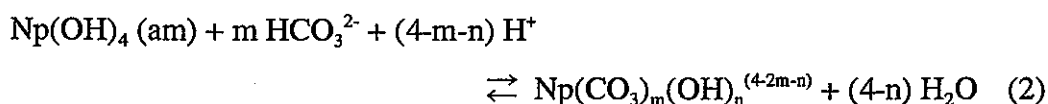
The measured C_T values as a function of initial C_T (C_{int}) are shown in Fig. 5. Despite of large deviations, the experimental values seem to be similar to C_{int} . However, these experimental values are often scattering and to be less reliable, especially for $C_T > 0.05 \text{ M}$. Thus, the C_{int} values are adopted to be the final C_T values for the following analysis. The measured standard redox potential (E_h) shows that all samples are found to maintain under reducing conditions, though the measured E_h values are scattered from 2×10^{-2} to $6.4 \times 10^{-1} \text{ V}$ vs. SHE. The ratios between the concentration of tetravalent neptunium ($[\text{Np(IV)}]$) which is obtained by TTA-extraction method and the total neptunium concentration ($[\text{Np}]_T$) are extremely scattered from 10^{-3} to 1. However, the obtained $[\text{Np}]_T$ values are much lower than the solubility of Np(V), of which the solubility is much higher than that of Np(IV), thus the equilibrium between the Np(IV) precipitate and Np(IV) solution is considered to be valid. It is observed that part of the experimental samples at the initial neptunium concentration of 10^{-3} M contains the brown solubility limiting solid.

The list of the experimental values of pH_c , C_T and $[\text{Np(IV)}]$ at $I = 0.5 \text{ M}$ and 1.0 M are shown in Tables 1 and 2, respectively.

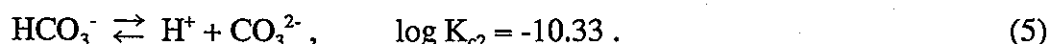
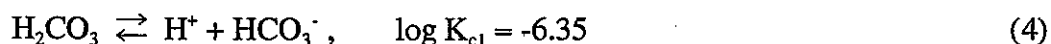
3.2 Determination of the Apparent Equilibrium Constants

Identification of the solubility limiting solid phase is required for the determination of thermodynamic equilibrium constant. In the hydrolysis reactions, the solubility limiting solid phase of tetravalent actinide (An(IV)) is considered to be $\text{AnO}_2 \cdot x\text{H}_2\text{O}$ (am) [9]. In carbonate solution, the formation of solid phase of $\text{AnCO}_3(\text{OH})_2$ (s), which is identified for Pu(IV) by Lierse and Kim [10], may be inferred. Pratopo et al. evaluated the possibility of the solubility limiting solid phase of $\text{NpCO}_3(\text{OH})_2$ (am) in carbonate solution, and concluded that the dominant solid phase is considered to be $\text{Np}(\text{OH})_4$ (am) (which is chemically equivalent to $\text{NpO}_2 \cdot x\text{H}_2\text{O}$ (am)) [11]. Rai et al. carried out the solubility measurement in highly carbonate solutions by both oversaturation and undersaturation methods, showing that the obtained solubility values by oversaturation method were consistent with that by undersaturation method [5]. Thus, the solubility limiting solid phase of Np(IV) in carbonate solution is considered to be $\text{Np}(\text{OH})_4$ (am) (or $\text{NpO}_2 \cdot x\text{H}_2\text{O}$ (am)).

Formation of the Np(IV) carbonatohydroxo complexes $(\text{Np}(\text{CO}_3)_m(\text{OH})_n^{(4-2m-n)})$ is characterized by apparent equilibrium constant $K_{1,m,n}$ for the following reactions in bicarbonate solution (reaction (2)) and in carbonate solution (reaction (3)) assuming the solubility limiting solid phase to be $\text{Np}(\text{OH})_4$ (am):



The equilibrium reactions and their equilibrium constants among carbonic acid, carbonate ion and bicarbonate ion [12] are



Using these equilibrium constants and the total carbonate concentration (C_T), the concentration of aqueous neptunium(IV) species is determined as a function of pH_c and C_T . The apparent equilibrium constant $K_{1,m,n}$ is treated as a free parameter in the calculation.

In the basic solutions, the hydrolysis species of Np(IV) are expected to be Np(OH)_4 (aq). However, the solubility of Np(OH)_4 (aq) are measured to be below 10^{-8} M by several researchers [3,13,14], which is much lower than the present result. Thus, carbonato and/or carbonatohydroxo complexes of Np(IV) are expected to be dominant species in the present study. The carbonato and/or carbonatohydroxo complexes of Np(IV) of which the formation constants are determined in the literatures are $\text{Np(CO}_3)_3^{2-}$ [15], $\text{Np(CO}_3)_5^{6-}$ [5], $\text{Np(CO}_3)_2(\text{OH})_2^{2-}$ [5,11], $\text{NpCO}_3(\text{OH})_3^-$ [13], $\text{NpCO}_3(\text{OH})_4^{2-}$ [13,16] and $\text{Np(CO}_3)_2(\text{OH})_4^{4-}$ [11]. Some of the carbonato and carbonatohydroxo complexes of tetravalent actinides, e.g., $\text{An(CO}_3)_5^{6-}$ (An = Th, U and Pu) [17-20], $\text{ThCO}_3(\text{OH})_3^-$ [17], $\text{U(CO}_3)_2(\text{OH})_2^{2-}$ [19], $\text{Pu(CO}_3)_2(\text{OH})_2^{2-}$ [20,21] and $\text{Pu(CO}_3)_2(\text{OH})_4^{4-}$ [21] have been already reported. Considering the dependencies of the solubility on both pH_c and C_T , the carbonatohydroxo complex of $\text{Np(CO}_3)_2(\text{OH})_2^{2-}$ is expected to be one of the dominant species, mainly in pH_c from 8.5 to 10.5. The dominant species above pH_c 10.5, the dominant species is expected to have the 4 hydroxo ions because no dependence of the solubility on pH_c (see reaction (3)). The carbonatohydroxo complex of $\text{NpCO}_3(\text{OH})_4^{2-}$ or $\text{Np(CO}_3)_2(\text{OH})_4^{4-}$ is expected to be the other dominant species. However, we were not able to determine the dominant species from the present solubility data because the dependency of the solubility on the C_T had been not able to be observed. Eriksen et al. measured the solubility of Np(IV) as a function of carbonate concentration at pH 11.2, and determined the dominant species as $\text{NpCO}_3(\text{OH})_4^{2-}$ due to the proportionality of the logarithm of solubility to that of the carbonate concentrations [13]. However, the measured solubility data are only 3 points which are insufficient to be reliable. Yamaguchi et al. measured the solubility of Pu(IV) as a function of carbonate concentration at pH 12 and 13, and determined the dominant species as $\text{Pu(CO}_3)_2(\text{OH})_4^{4-}$ due to the proportionality of the logarithm solubility to that of the carbonate concentrations [21]. The number of measured solubility data are more than that by Eriksen et al., thus the result by Yamaguchi et al. is considered to be more reliable than that by Eriksen et al. Thus, the other dominant species in the present work is assumed to be $\text{Np(CO}_3)_2(\text{OH})_4^{4-}$.

Considering the dominant species of Np(IV), the concentration of Np(IV) in the present solubility measurement is written as follows:

$$[\text{Np(IV)}] = [\text{Np(CO}_3)_2(\text{OH})_2^{2-}] + [\text{Np(CO}_3)_2(\text{OH})_4^{4-}]. \quad (6)$$

The apparent equilibrium constants of $K_{1,2,2}'$ and $K_{1,2,4}'$ are defined from reaction (2) or (3) as

$$\log K_{1,2,2}' = \log [\text{Np}(\text{CO}_3)_2(\text{OH})_2^{2-}] - 2 \log [\text{HCO}_3^-] \quad (7)$$

$$\log K_{1,2,4}' = \log [\text{Np}(\text{CO}_3)_2(\text{OH})_4^{4-}] - 2 \log [\text{CO}_3^{2-}] \quad (8)$$

Using the equations (6), (7) and (8), the $[\text{Np(IV)}]$ value can be written as

$$\begin{aligned} [\text{Np(IV)}] &= K_{1,2,2}' [\text{CO}_3^{2-}]^2 [\text{H}^+]^2 / K_{c2}^2 + K_{1,2,4}' [\text{CO}_3^{2-}]^2 \\ &= \left(\frac{K_{1,2,2}' \cdot 10^{-2\text{pH}_c}}{K_{c2}^2} + K_{1,2,4}' \right) \left(C_T \frac{K_{c1} K_{c2} \cdot 10^{2\text{pH}_c}}{1 + K_{c1} \cdot 10^{\text{pH}_c} + K_{c1} K_{c2} \cdot 10^{2\text{pH}_c}} \right)^2 \quad (9) \end{aligned}$$

Thus the $[\text{Np(IV)}]$ value can be calculated by giving pH_c and C_T with the free parameters of $K_{1,2,2}'$ and $K_{1,2,4}'$.

The experimental data listed in Tables 1 and 2 were used to compute the apparent equilibrium constants $K_{1,2,2}'$ and $K_{1,2,4}'$. The numerical computations of $K_{1,2,2}'$ and $K_{1,2,4}'$ were performed by the non-linear least-squares fitting to minimize the sum of the squared deviations $\sum (\log [\text{Np(IV)}]_{\text{cal}} - \log [\text{Np(IV)}]_{\text{exp}})^2$, dealing with both dependencies of pH_c and C_T simultaneously for a given ionic strength. The analytical solubility curves obtained from the present study are shown in Figs. 6, 7, 8 and 9, and the determined apparent equilibrium constants of $\log K_{1,2,2}'$ and $\log K_{1,2,4}'$ are listed in Table 3. The error of the parameter means 95 % confidence level, i.e., 1.96 times as much as the standard deviation.

3.3 Determination of the Thermodynamic Equilibrium Constants

The ionic strength corrections were made before the comparison of the present results with the literature data. The apparent equilibrium constants extrapolated to the condition at zero ionic strength ($K_{1,m,n}^0$) are determined by using a model called "The Specific Ion Interaction Theory (SIT)". This model is usually used by adding terms to the Debye-Hückel expression as outlined by Brønsted [22] and elaborated by Guggenheim [23] and Scatchard [24]. It has an equation representing the activity coefficient dependence of ionic strength standing for molality (I_m) valid for up to $I_m = 3.5 \text{ mol}\cdot\text{kg}^{-1}$ [25]. In the model, the activity coefficient γ_i of an ion of charge z_i in a solution of ionic strength at 298.15 K is equal to:

$$\log \gamma_i = -z_i^2 D + \sum_k \epsilon(i,k) m_k \quad (10)$$

$$D = \frac{0.5091 \sqrt{I_m}}{1 + 1.5 \sqrt{I_m}} \quad (11)$$

where D , $\epsilon(i,k)$ and m_k mean a particular form of Debye-Hückel term, an ion interaction coefficient between the ion i and k , and molality of an electrolyte ion k used in the SIT model, respectively [26]. The value of m_k becomes equal to I_m for simple electrolyte solution, e.g., NaClO_4 . Using equations (10) and (11), equations (7) and (8) can be written as follows:

$$\log K_{1,2,2}' - 2 D = \log K_{1,2,2}^0 - \Delta \epsilon_1 I_m \quad (12)$$

$$\log K_{1,2,4}' - 8 D = \log K_{1,2,4}^0 - \Delta \epsilon_2 I_m \quad (13)$$

$$\Delta \epsilon_1 = \epsilon(\text{Na}^+, \text{Np}(\text{CO}_3)_2(\text{OH})_2^{2-}) - 2 \epsilon(\text{Na}^+, \text{HCO}_3^-) \quad (14)$$

$$\Delta \epsilon_2 = \epsilon(\text{Na}^+, \text{Np}(\text{CO}_3)_2(\text{OH})_4^{4-}) - 2 \epsilon(\text{Na}^+, \text{CO}_3^{2-}) \quad (15)$$

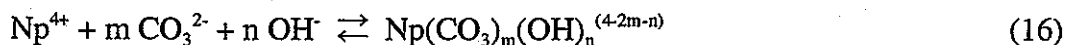
Thus, the linear relationship between $(\log K_{1,2,2}' - 2 D)$ and I_m and that between $(\log K_{1,2,4}' - 8 D)$ and I_m are found from the equations (12) and (13), respectively.

A least-squares fitting analysis was applied to the apparent equilibrium constants. The logarithm of thermodynamic equilibrium constant of $\log K_{1,2,2}^0$ and that of $\log K_{1,2,4}^0$ are estimated in Figs. 10 and 11, respectively, and listed in Table 3. In the analysis, the ion interaction coefficients of $\epsilon(\text{Na}^+, \text{HCO}_3^-)$, $\epsilon(\text{Na}^+, \text{CO}_3^{2-})$, $\epsilon(\text{Na}^+, \text{Np}(\text{CO}_3)_2(\text{OH})_2^{2-})$ and $\epsilon(\text{Na}^+, \text{Np}(\text{CO}_3)_2(\text{OH})_4^{4-})$ are assumed as 0.00, -0.08, -0.10 and -0.09, respectively. The former two values are of the literature [26], and the latter two values are of the average of the ϵ values between Na^+ and anions with the charge of -2 [26] and the ϵ values of $\text{U}(\text{CO}_3)_4^{4-}$ [26], respectively. Despite of large standard deviations, the assumed ion interaction coefficients describe a good agreement for the dependency of $(\log K' - z^2 D)$ on I_m as shown in Figs. 10 and 11. Thus, the assumed ion interaction coefficients are considered to be reasonable.

3.4 Comparison of the Obtained Thermodynamic Equilibrium Constants with the Literature Data

It is convenient to compare the present thermodynamic equilibrium constants with the literature data in terms of the formation constants β^0 at zero ionic strength.

The β^0 is defined for the equilibrium constant of the following reaction and given as follows:



$$\beta_{1,m,n}^0 = \frac{[\text{Np}(\text{CO}_3)_m(\text{OH})_n^{(4-2m-n)}]}{[\text{Np}^{4+}][\text{CO}_3^{2-}]^m[\text{OH}^-]^n} \quad (17)$$

Thus the β^0 values can be evaluated by combining the solubility product of the solubility limiting solid phase $\text{Np}(\text{OH})_4$ (am). The solubility product at zero ionic strength (K_{sp}^0) is given for $\text{Np}(\text{OH})_4$ (am) as:

$$K_{sp}^0 = [\text{Np}^{4+}][\text{OH}^-]^4 \quad (18)$$

Using equations (7), (8), (17) and (18), the formation constants of $\beta_{1,2,2}^0$ and $\beta_{1,2,4}^0$ are given as follows:

$$\log \beta_{1,2,2}^0 = \log K_{1,2,2}^0 - \log K_{sp}^0 - 2 \log K_{c2}^0 - 2 \log K_w^0 \quad (19)$$

$$\log \beta_{1,2,4}^0 = \log K_{1,2,4}^0 - \log K_{sp}^0, \quad (20)$$

where K_w^0 is the ion product of water at zero ionic strength ($= 10^{-14}$).

The K_{sp}^0 value is not available at present. There are several researches for the determination of K_{sp}^0 or the apparent solubility products K_{sp}' [4,15,16,27]. Considering of these experimental conditions and discussions, the most reliable K_{sp}^0 value seems to be of that by Rai et al. as $\log K_{sp}^0 = -54.5 \pm 0.3$ [4]. Thus, the $\log K_{sp}^0$ of -54.5 ± 0.3 is assumed in the present study.

Values for $\log \beta_{1,2,2}^0$ and $\log \beta_{1,2,4}^0$ obtained from the present study and reported in literatures which are not only for $\text{Np}(\text{IV})$ but also $\text{U}(\text{IV})$ and $\text{Pu}(\text{IV})$ are listed in Tables 4 and 5, respectively. In Table 4, it is found that the $\log \beta_{1,2,2}^0$ of 43.35 ± 0.35 obtained in the present study is in good agreement with that of 43.17 by Rai et al. [5] which has been adopted in JNC-TDB [1]. Thus, the present study supports the thermodynamic formation constant of $\text{Np}(\text{CO}_3)_2(\text{OH})_2^{2-}$ in JNC-TDB. The ionic strength of the solubility data by Rai et al. [5] is varied, and the ionic strength corrections are made by using Pitzer equations [28] for each experimental value. In the present study, on the other hand, the apparent equilibrium constants are determined and the ionic strength

corrections are carried out by using SIT. Comparing the present study with the study by Rai et al. [5], the ionic strength dependency of the solubility in the present study is considered to be more understandable and more reliable than that by Rai. et al. The $\log \beta_{1,2,2}^0$ of 45.69 ± 0.44 by Pratopo et al. [11] is found to be larger than that in the present study. However, their experimental data of the solubility measurement are scattering and seem to be less reliable than the present data.

On the other hand, there are only a few literature values of the formation constant of $\text{Np}(\text{CO}_3)_2(\text{OH})_4^{4-}$ listed in Table 5. Only the apparent formation constants have been obtained in the previous studies. Thus, the present study is the first determination of the thermodynamic formation constant of $\text{Np}(\text{CO}_3)_2(\text{OH})_4^{4-}$, as well as the study of ionic strength dependency for the solubility of $\text{Np}(\text{CO}_3)_2(\text{OH})_4^{4-}$. However, the obtained $\log \beta_{1,2,4}^0$ in the present study has a large standard deviation, thus further solubility measurements are required to confirm the reliability of the formation constant. For comparison, the apparent formation constant of $\text{NpCO}_3(\text{OH})_4^{2-}$ are also listed in Table 5. It is found that the formation constant of $\text{NpCO}_3(\text{OH})_4^{2-}$ are similar to that of $\text{Np}(\text{CO}_3)_2(\text{OH})_4^{4-}$.

For the calculations of the formation constants from the equilibrium constants listed in Tables 4 and 5, the solubility products of $\text{An}(\text{OH})_4$ (am) (An: U, Np or Pu) by Rai et al. have been applied to the many literatures [5,11,19-21] as well as the present study. However, Neck and Kim evaluated K_{sp} value for $\text{Np}(\text{OH})_4$ (am) as $10^{-56.7 \pm 0.4}$, which is much smaller than that by Rai et al. [4], by using the same experimental values [4] and considering the contribution of hydrolysis species of NpOH^{3+} and $\text{Np}(\text{OH})_2^{2+}$ [31]. Thus, the solubility product of $\text{Np}(\text{OH})_4$ (am) will have to be reevaluated.

4. CONCLUSIONS

Solubility of Np(IV) was measured in carbonate media under reducing conditions in basic solutions at ionic strength of 0.5 M and 1.0 M by oversaturation method. The obtained dependencies of the solubility on hydrogen ion concentration and carbonate ion concentration were interpreted by considering the two carbonatohydroxo complexes of Np(IV) which were $\text{Np}(\text{CO}_3)_2(\text{OH})_2^{2-}$ and $\text{Np}(\text{CO}_3)_2(\text{OH})_4^{4-}$. The apparent equilibrium constants of these complexes were determined as a function of ionic strength. The ionic strength correction was carried out for the determination of the thermodynamic equilibrium constants of the complexes, and the logarithm of the equilibrium constants of $\text{Np}(\text{CO}_3)_2(\text{OH})_2^{2-}$ and $\text{Np}(\text{CO}_3)_2(\text{OH})_4^{4-}$ were determined as -3.81 ± 0.35 and -6.82 ± 1.03 , respectively. The former value was similar to the recent literature value and the latter value was first determined. However, for the improvement of the reliability of the formation constants, the solubility product of the amorphous Np(IV) hydroxide should be reevaluated.

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Table 1 Experimental data for the system $\text{Np(IV)}/\text{CO}_3^{2-}/\text{OH}^-$ at $I = 0.5 \text{ M}$ The initial neptunium concentration was set at $1.2 \times 10^{-5} \text{ M}$.

run: p01					4 weeks			
period: 2 weeks								
	pH_c	$C_{\text{int}} (\text{M})$	$C_T (\text{M})$	$[\text{Np(IV)}] (\text{M})$	pH_c	$C_{\text{int}} (\text{M})$	$C_T (\text{M})$	$[\text{Np(IV)}] (\text{M})$
	8.77	1.00×10^{-1}	8.42×10^{-2}	7.79×10^{-6}				
	9.01	1.00×10^{-1}	5.26×10^{-2}	8.84×10^{-6}				
	9.38	1.00×10^{-1}	1.13×10^{-1}	4.98×10^{-6}	9.38	1.00×10^{-1}	1.38×10^{-1}	4.96×10^{-6}
	9.34	1.00×10^{-1}	1.08×10^{-1}	9.24×10^{-6}				
	9.77	1.00×10^{-1}	6.13×10^{-2}	6.17×10^{-6}	9.74	1.00×10^{-1}	7.50×10^{-2}	6.14×10^{-6}
	10.02	1.00×10^{-1}	8.57×10^{-2}	6.18×10^{-6}	9.99	1.00×10^{-1}	9.69×10^{-2}	4.82×10^{-6}
	10.20	1.00×10^{-1}	8.69×10^{-2}	4.53×10^{-6}	10.18	1.00×10^{-1}	1.07×10^{-1}	3.69×10^{-6}
	10.52	1.00×10^{-1}	8.77×10^{-2}	9.59×10^{-7}	10.49	1.00×10^{-1}	9.74×10^{-2}	9.41×10^{-7}
	10.67	1.00×10^{-1}	9.59×10^{-2}	2.82×10^{-7}	10.63	1.00×10^{-1}	8.20×10^{-2}	1.01×10^{-7}
	10.96	1.00×10^{-1}	6.75×10^{-2}	6.30×10^{-8}	10.90	1.00×10^{-1}	8.89×10^{-2}	1.33×10^{-7}
	11.18	1.00×10^{-1}	6.99×10^{-2}	7.21×10^{-8}	11.12	1.00×10^{-1}	8.91×10^{-2}	1.88×10^{-8}
	11.41	1.00×10^{-1}	9.50×10^{-2}	5.35×10^{-8}	11.33	1.00×10^{-1}	1.13×10^{-1}	3.03×10^{-8}
	11.65	1.00×10^{-1}	7.00×10^{-2}	6.43×10^{-8}				
	11.92	1.00×10^{-1}	6.68×10^{-2}	7.85×10^{-8}				

run: c01					4 weeks			
period: 2 weeks								
	pH_c	$C_{\text{int}} (\text{M})$	$C_T (\text{M})$	$[\text{Np(IV)}] (\text{M})$	pH_c	$C_{\text{int}} (\text{M})$	$C_T (\text{M})$	$[\text{Np(IV)}] (\text{M})$
	9.81	6.19×10^{-3}	2.25×10^{-4}	1.31×10^{-8}	8.57	6.19×10^{-3}	2.39×10^{-4}	3.14×10^{-7}
	10.09	7.67×10^{-3}	1.66×10^{-4}	3.50×10^{-8}	9.73	7.67×10^{-3}	1.42×10^{-3}	1.20×10^{-7}
	10.14	9.50×10^{-3}	2.26×10^{-4}	2.15×10^{-8}	9.54	9.50×10^{-3}	3.73×10^{-4}	1.26×10^{-7}
	10.31	1.18×10^{-2}	1.55×10^{-4}	1.54×10^{-8}		1.18×10^{-2}		
	10.26	1.46×10^{-2}	1.10×10^{-2}	8.10×10^{-8}	10.01	1.46×10^{-2}	6.31×10^{-3}	7.74×10^{-7}
	10.35	1.81×10^{-2}	8.33×10^{-3}	4.10×10^{-8}	10.12	1.81×10^{-2}	1.10×10^{-2}	8.75×10^{-9}
	10.39	2.24×10^{-2}	1.41×10^{-2}	4.38×10^{-8}	10.20	2.24×10^{-2}	1.23×10^{-2}	6.83×10^{-9}
	10.37	2.77×10^{-2}	1.99×10^{-2}	5.97×10^{-8}	10.23	2.77×10^{-2}	1.74×10^{-2}	3.21×10^{-8}
	10.58	3.43×10^{-2}	2.01×10^{-2}	8.24×10^{-8}	10.43	3.43×10^{-2}	2.19×10^{-2}	1.65×10^{-6}
	10.51	4.25×10^{-2}	3.36×10^{-2}	5.54×10^{-8}	10.41	4.25×10^{-2}	3.48×10^{-2}	1.69×10^{-7}
	10.61	5.26×10^{-2}	4.46×10^{-2}	1.06×10^{-7}	10.32	5.26×10^{-2}	4.48×10^{-2}	3.35×10^{-7}
	10.65	6.52×10^{-2}	6.05×10^{-2}	7.99×10^{-8}	10.59	6.52×10^{-2}	6.04×10^{-2}	1.24×10^{-7}
	10.63	8.07×10^{-2}	6.32×10^{-2}	6.49×10^{-8}	10.60	8.07×10^{-2}	8.66×10^{-2}	1.02×10^{-7}
	10.65	1.00×10^{-1}	9.76×10^{-2}	4.27×10^{-7}	10.62	1.00×10^{-1}	8.77×10^{-2}	2.18×10^{-7}

Table 2 Experimental data for the system $\text{Np(IV)/CO}_3^{2-}/\text{OH}^-$ at $I = 1.0 \text{ M}$ The initial neptunium concentration was set at $1 \times 10^{-4} \text{ M}$ or $1 \times 10^{-3} \text{ M}$.

run: p02						4 weeks			
period:	2 weeks	pH_c	$C_{\text{int}} (\text{M})$	$C_T (\text{M})$	$[\text{Np(IV)}] (\text{M})$	pH_c	$C_{\text{int}} (\text{M})$	$C_T (\text{M})$	$[\text{Np(IV)}] (\text{M})$
		8.53	1.00×10^{-1}	8.74×10^{-2}	2.28×10^{-5}	8.73	1.00×10^{-1}	7.21×10^{-2}	2.45×10^{-5}
		8.71	1.00×10^{-1}	1.09×10^{-1}	5.33×10^{-5}	8.82	1.00×10^{-1}	1.03×10^{-1}	3.35×10^{-5}
		8.88	1.00×10^{-1}	8.99×10^{-2}	3.46×10^{-5}	8.91	1.00×10^{-1}	1.15×10^{-1}	2.96×10^{-5}
		9.63	1.00×10^{-1}	9.08×10^{-2}	3.48×10^{-5}	9.55	1.00×10^{-1}	8.70×10^{-2}	2.63×10^{-5}
		10.08	1.00×10^{-1}	7.50×10^{-2}	2.67×10^{-5}	10.18	1.00×10^{-1}	1.16×10^{-1}	3.92×10^{-5}
		10.48	1.00×10^{-1}	8.41×10^{-2}	8.35×10^{-6}	10.38	1.00×10^{-1}	1.12×10^{-1}	7.35×10^{-6}
		10.65	1.00×10^{-1}	8.88×10^{-2}	2.39×10^{-6}	10.50	1.00×10^{-1}	1.53×10^{-1}	1.63×10^{-6}
		11.01	1.00×10^{-1}	1.03×10^{-1}	1.43×10^{-7}	10.90	1.00×10^{-1}	1.76×10^{-1}	2.95×10^{-7}
		11.52	1.00×10^{-1}	1.02×10^{-1}	2.48×10^{-7}	11.46	1.00×10^{-1}	1.58×10^{-1}	4.52×10^{-7}

run: c02						4 weeks			
period:	2 weeks	pH_c	$C_{\text{int}} (\text{M})$	$C_T (\text{M})$	$[\text{Np(IV)}] (\text{M})$	pH_c	$C_{\text{int}} (\text{M})$	$C_T (\text{M})$	$[\text{Np(IV)}] (\text{M})$
		10.03	6.19×10^{-3}	5.98×10^{-3}	1.06×10^{-8}	9.88	6.19×10^{-3}	3.98×10^{-3}	2.52×10^{-8}
		10.10	7.67×10^{-3}	8.52×10^{-3}	1.16×10^{-8}	9.96	7.67×10^{-3}	8.97×10^{-3}	2.83×10^{-8}
		10.14	9.50×10^{-3}	9.15×10^{-3}	1.20×10^{-8}	10.01	9.50×10^{-3}	8.79×10^{-3}	2.13×10^{-8}
		10.20	1.18×10^{-2}	1.33×10^{-2}	6.84×10^{-9}	10.08	1.18×10^{-2}	1.55×10^{-2}	2.95×10^{-8}
		10.26	1.46×10^{-2}	1.99×10^{-2}	1.88×10^{-8}	10.12	1.46×10^{-2}	2.05×10^{-2}	4.07×10^{-8}
		10.25	1.81×10^{-2}	2.01×10^{-2}	2.45×10^{-8}	10.15	1.81×10^{-2}	2.54×10^{-2}	9.16×10^{-8}
		10.29	2.24×10^{-2}	2.29×10^{-2}	4.09×10^{-8}	10.19	2.24×10^{-2}	3.41×10^{-2}	1.23×10^{-7}
		10.30	2.77×10^{-2}	4.22×10^{-2}	5.52×10^{-8}	10.20	2.77×10^{-2}	2.13×10^{-2}	7.33×10^{-8}
		10.32	3.43×10^{-2}	6.08×10^{-2}	4.35×10^{-7}	10.22	3.43×10^{-2}	5.45×10^{-2}	2.49×10^{-7}
		10.42	4.25×10^{-2}	7.24×10^{-2}	1.39×10^{-7}	10.32	4.25×10^{-2}	6.95×10^{-2}	2.02×10^{-7}
		10.41	5.26×10^{-2}	9.41×10^{-2}	3.95×10^{-7}	10.31	5.26×10^{-2}	7.66×10^{-2}	5.76×10^{-7}
		10.37	6.52×10^{-2}	1.08×10^{-1}	7.87×10^{-7}	10.28	6.52×10^{-2}	1.00×10^{-1}	5.62×10^{-7}
		10.40	8.07×10^{-2}	1.27×10^{-1}	6.91×10^{-7}	10.28	8.07×10^{-2}	1.26×10^{-1}	1.12×10^{-6}
		10.39	1.00×10^{-1}	1.36×10^{-1}	1.45×10^{-6}	10.30	1.00×10^{-1}	1.55×10^{-1}	2.02×10^{-6}

run: p03						4 weeks			
period:	2 weeks	pH_c	$C_{\text{int}} (\text{M})$	$C_T (\text{M})$	$[\text{Np(IV)}] (\text{M})$	pH_c	$C_{\text{int}} (\text{M})$	$C_T (\text{M})$	$[\text{Np(IV)}] (\text{M})$
		8.55	1.00×10^{-1}	1.32×10^{-1}	6.22×10^{-5}	8.52	1.00×10^{-1}	8.58×10^{-2}	7.15×10^{-5}
		8.79	1.00×10^{-1}	1.16×10^{-1}	3.74×10^{-5}	8.67	1.00×10^{-1}	8.19×10^{-2}	5.00×10^{-5}
		9.01	1.00×10^{-1}	1.25×10^{-1}	3.14×10^{-5}	8.86	1.00×10^{-1}	1.07×10^{-1}	3.43×10^{-5}
		9.27	1.00×10^{-1}	1.09×10^{-1}	1.43×10^{-5}	9.09	1.00×10^{-1}	1.11×10^{-1}	1.98×10^{-5}
		9.54	1.00×10^{-1}	1.06×10^{-1}	9.23×10^{-7}	9.37	1.00×10^{-1}	1.16×10^{-1}	5.16×10^{-7}
		10.54	1.00×10^{-1}	1.30×10^{-1}	4.21×10^{-7}	10.36	1.00×10^{-1}	1.19×10^{-1}	8.25×10^{-7}
		10.77	1.00×10^{-1}	1.36×10^{-1}	3.64×10^{-7}	10.57	1.00×10^{-1}	1.20×10^{-1}	6.35×10^{-7}
		11.03	1.00×10^{-1}	1.07×10^{-1}	9.78×10^{-8}	10.82	1.00×10^{-1}	1.35×10^{-1}	1.21×10^{-7}
		11.28	1.00×10^{-1}	9.19×10^{-2}	4.78×10^{-8}	11.04	1.00×10^{-1}	1.17×10^{-1}	9.04×10^{-8}
		11.52	1.00×10^{-1}	1.25×10^{-1}	5.62×10^{-8}	11.29	1.00×10^{-1}	1.03×10^{-1}	4.34×10^{-8}
		11.76	1.00×10^{-1}	1.34×10^{-1}	1.96×10^{-9}	11.61	1.00×10^{-1}	1.19×10^{-1}	3.69×10^{-8}
		12.12	1.00×10^{-1}	1.52×10^{-1}	1.98×10^{-8}	12.05	1.00×10^{-1}	1.36×10^{-1}	1.67×10^{-8}

run: c03						4 weeks			
period:	2 weeks	pH_c	$C_{\text{int}} (\text{M})$	$C_T (\text{M})$	$[\text{Np(IV)}] (\text{M})$	pH_c	$C_{\text{int}} (\text{M})$	$C_T (\text{M})$	$[\text{Np(IV)}] (\text{M})$
		8.00	1.06×10^{-2}	9.10×10^{-4}	3.56×10^{-8}				
		8.30	2.24×10^{-2}	3.57×10^{-3}	1.20×10^{-7}	7.75	2.24×10^{-2}	2.29×10^{-3}	6.98×10^{-8}
		8.72	4.73×10^{-2}	2.18×10^{-2}	1.09×10^{-6}	7.98	4.73×10^{-2}	1.67×10^{-2}	2.79×10^{-7}

Table 3 Summary for the logarithm of apparent equilibrium constants ($\log K'$) and the equilibrium constants extrapolated to $I_m = 0 \text{ mol}\cdot\text{kg}^{-1}$ ($\log K^0$) for the Np(IV) carbonatohydroxo complexes at $22 \pm 3^\circ\text{C}$ based on the reactions (7) and (8). The errors indicate the 95 % confidence level.

Species	$\log K'$		$\log K^0$
	$I = 0.5 \text{ M}$	$I = 1.0 \text{ M}$	
$\text{Np}(\text{CO}_3)_2(\text{OH})_2^{2-}$	-3.30 ± 0.08	-3.31 ± 0.12	-3.81 ± 0.35
$\text{Np}(\text{CO}_3)_2(\text{OH})_4^{4-}$	-5.41 ± 0.26	-5.43 ± 0.37	-6.82 ± 1.03

Table 4 Comparison of the logarithm of equilibrium constant ($\log K_{1,2,2}$) and the logarithm of formation constant ($\log \beta_{1,2,2}$) for $\text{An}(\text{CO}_3)_2(\text{OH})_2^{2-}$ (An: U, Np or Pu) with the reported values at 22 ± 3 °C

The errors indicate the 95 % confidence level.

Element	I (M)	$\log K_{1,2,2}$	$\log \beta_{1,2,2}$	reference
Np	0	-3.81 ± 0.35	$43.35 \pm 0.35^*$	present
	0	-4.44	43.17	[5]
	0.3	-0.35 ± 0.33	45.69 ± 0.44	[11]
U	0	-4.8	41.33	[19]
	Varied	> -2.44	> 41.7	[11]
Pu	0	-4.76	44.76	[20]
	0.1	-2.7 ± 0.5	44.2 ± 0.6	[21]

*For the calculation of $\log \beta_{1,2,2}^0$, the solubility product $K_{sp} = 10^{-54.5 \pm 0.3}$ [4] was used.

Table 5 Comparison of the logarithm of equilibrium constant ($\log K_{1,2,4}$) and the logarithm of formation constant ($\log \beta_{1,p,4}$) ($p = 1$ or 2) for $\text{An}(\text{CO}_3)_p(\text{OH})_4^{2p-}$ (An: Np or Pu) with the reported values at 22 ± 3 °C

The errors indicate the 95 % confidence level.

species	I (M)	$\log K_{1,2,4}$	$\log \beta_{1,p,4}$	reference
$\text{Np}(\text{CO}_3)_2(\text{OH})_4^{4-}$	0	-6.82 ± 1.03	$47.48 \pm 1.07^*$	present
	0.3	-1.43 ± 0.33	53.07 ± 0.44	[11]
$\text{Pu}(\text{CO}_3)_2(\text{OH})_4^{4-}$	0.1	-4.98 ± 0.31	49.72 ± 0.48	[21]
$\text{NpCO}_3(\text{OH})_4^{2-}$	var.		53.08 ± 0.01	[16]
	0.5		49.20 ± 0.50	[13]

*For the calculation of $\log \beta_{1,2,4}^0$, the solubility product $K_{sp} = 10^{-54.5 \pm 0.3}$ [4] was used.

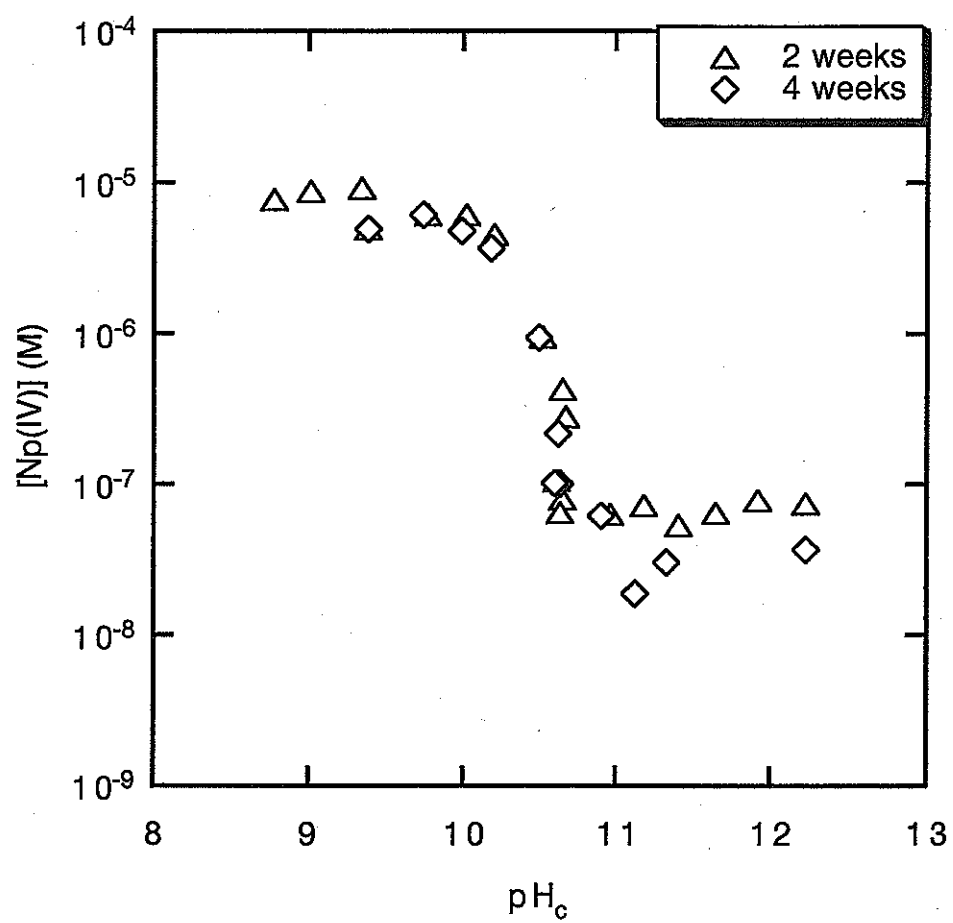


Fig. 1 Solubility of Np(IV) as a function of pH_c ($I = 0.5 \text{ M}$, $C_T = 0.1 \text{ M}$)

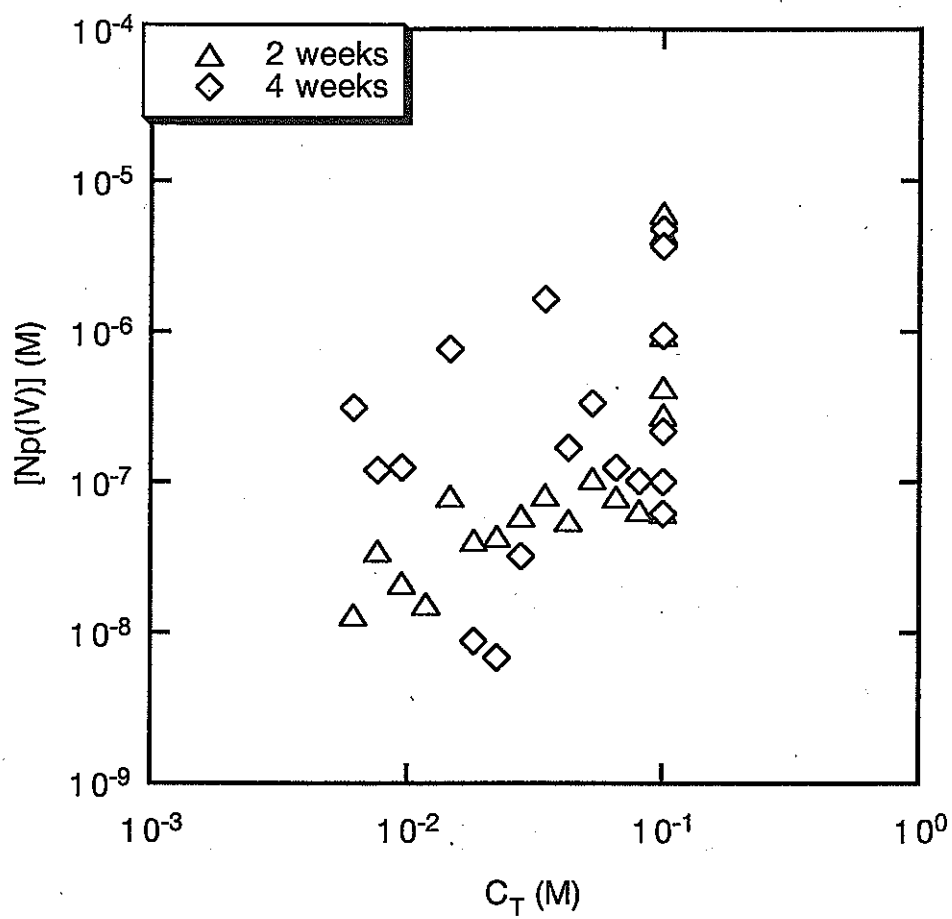


Fig. 2 Solubility of Np(IV) as a function of C_T ($I = 0.5$ M, $pH_c: 10 - 11$)

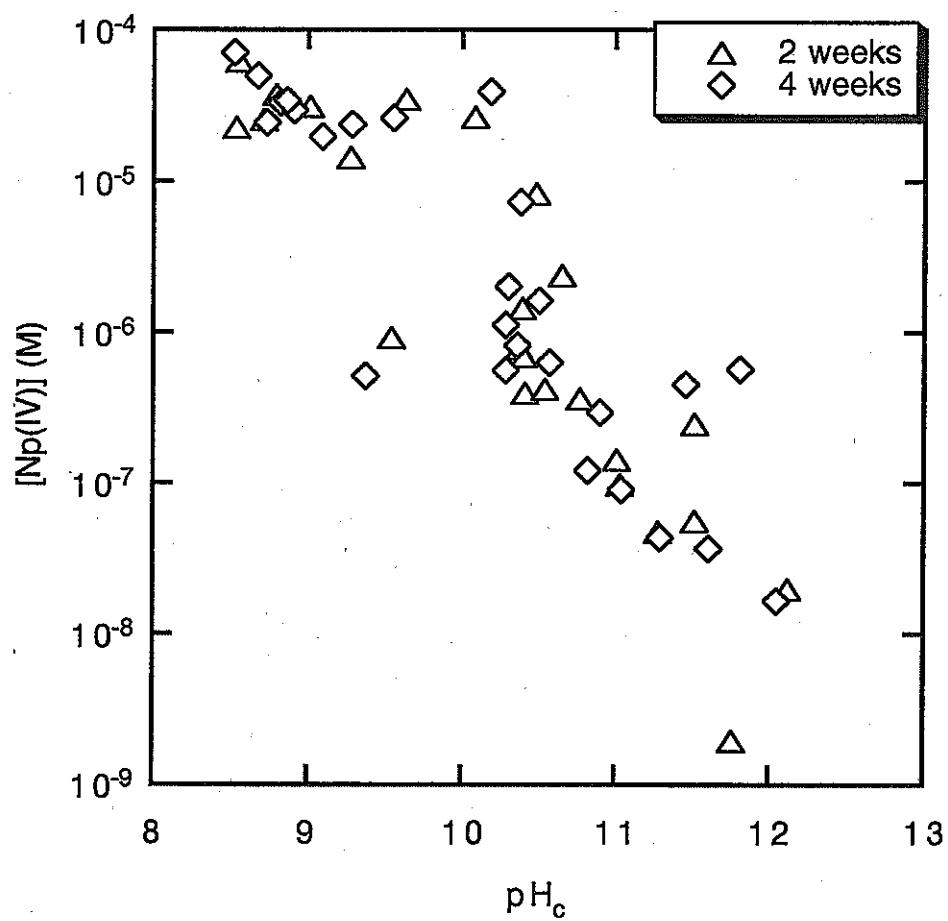


Fig. 3 Solubility of Np(IV) as a function of pH_c ($I = 1.0 \text{ M}$, $C_T = 0.1 \text{ M}$)

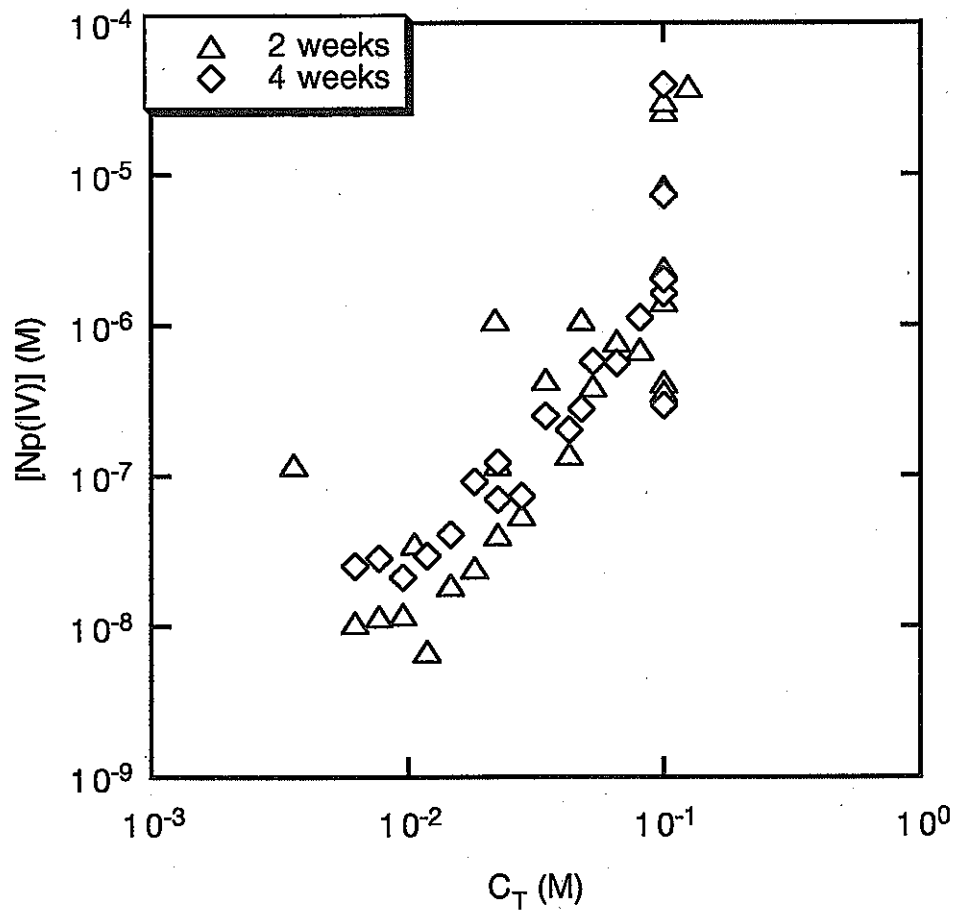


Fig. 4 Solubility of Np(IV) as a function of C_T ($I = 1.0$ M, pH_c : 10 - 11)

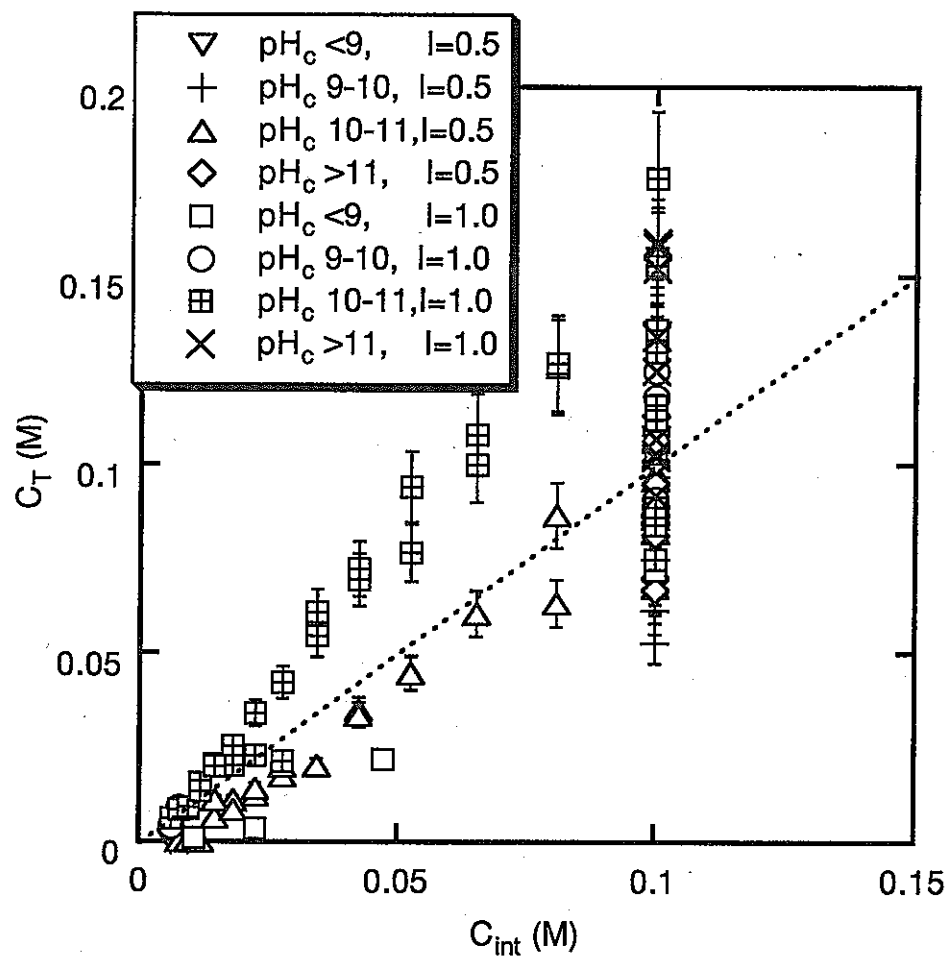


Fig. 5 Measured total carbonate concentration (C_T) as a function of initial carbonate concentration (C_{int})

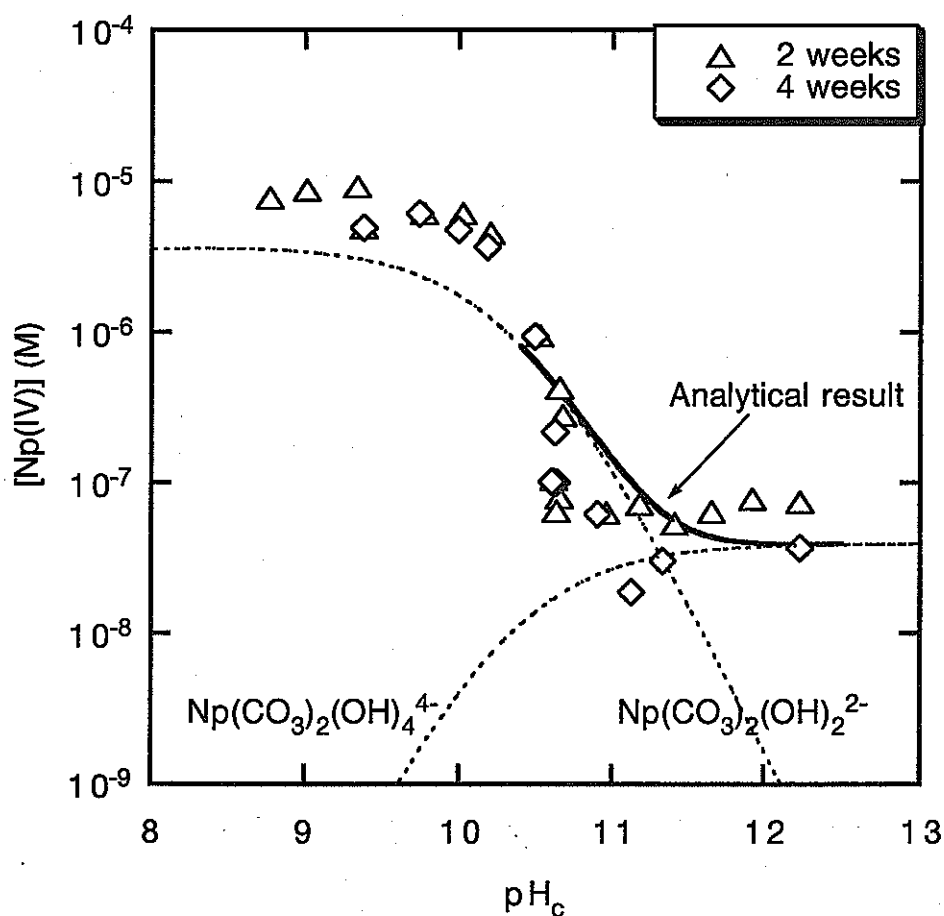


Fig. 6 Solubility of Np(IV) as a function of pH_c ($I = 0.5 \text{ M}$, $C_T = 0.1 \text{ M}$) and the analytical result

Marks are the experimental data, a solid line shows the least-squares fitting result based on equation (8), and dashed lines are the extrapolations. See text for details.

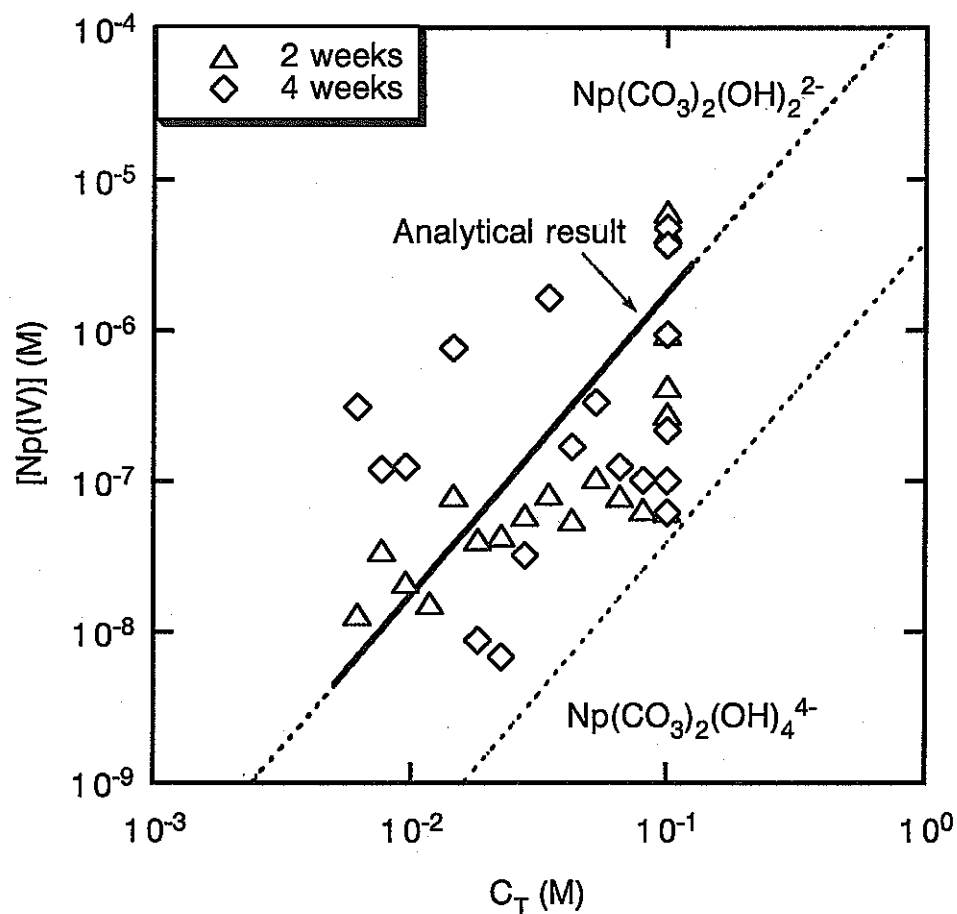


Fig. 7 Solubility of Np(IV) as a function of C_T ($I = 0.5 \text{ M}$, $pH_c: 10 - 11$) and the analytical result

Marks are the experimental data, a solid line shows the least-squares fitting result based on equation (8), and dashed lines are the extrapolations. See text for details.

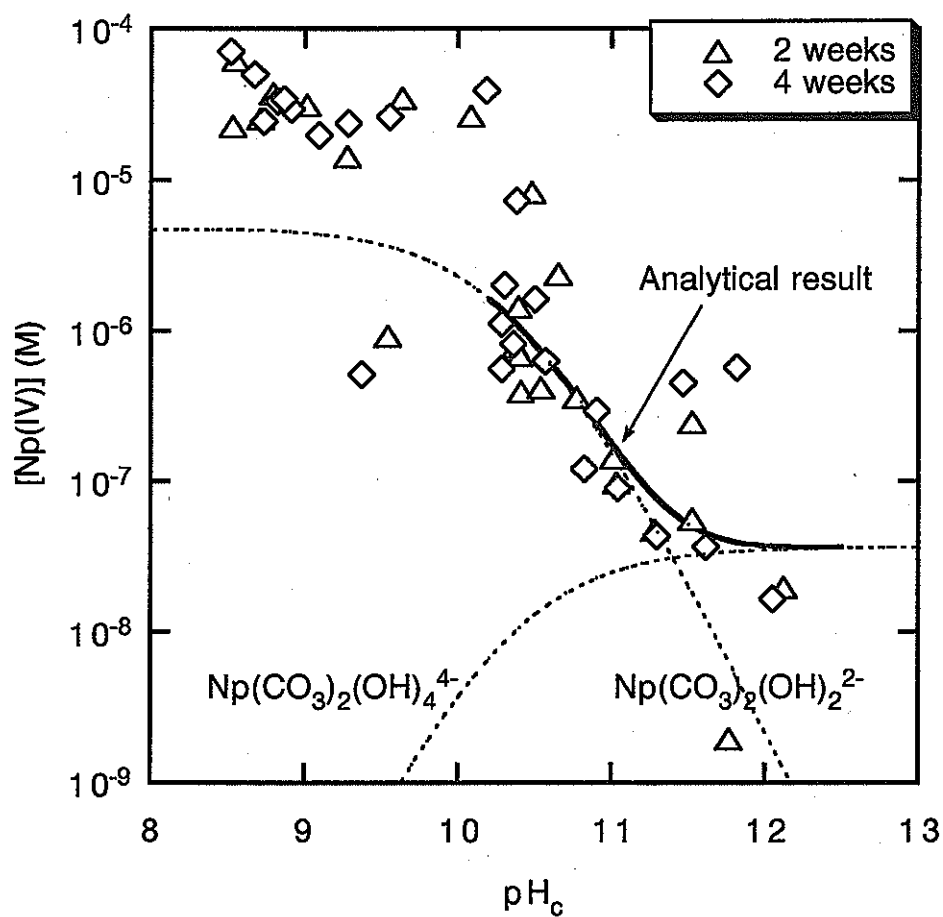


Fig. 8 Solubility of Np(IV) as a function of pH_c ($I = 1.0 \text{ M}$, $C_T = 0.1 \text{ M}$) and the analytical result

Marks are the experimental data, a solid line shows the least-squares fitting result based on equation (8), and dashed lines are the extrapolations. See text for details.

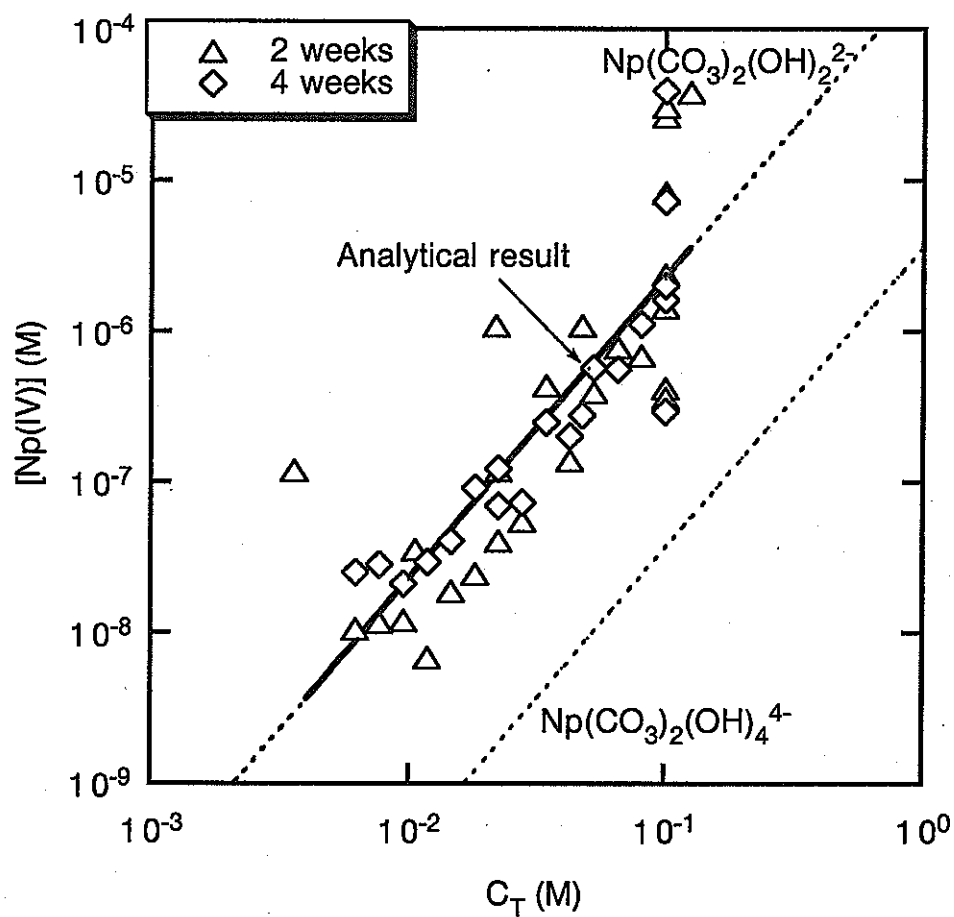


Fig. 9 Solubility of Np(IV) as a function of C_T ($I = 1.0 \text{ M}$, $pH_c: 10 - 11$) and the analytical result

Marks are the experimental data, a solid line shows the least-squares fitting result based on equation (8), and dashed lines are the extrapolations. See text for details.

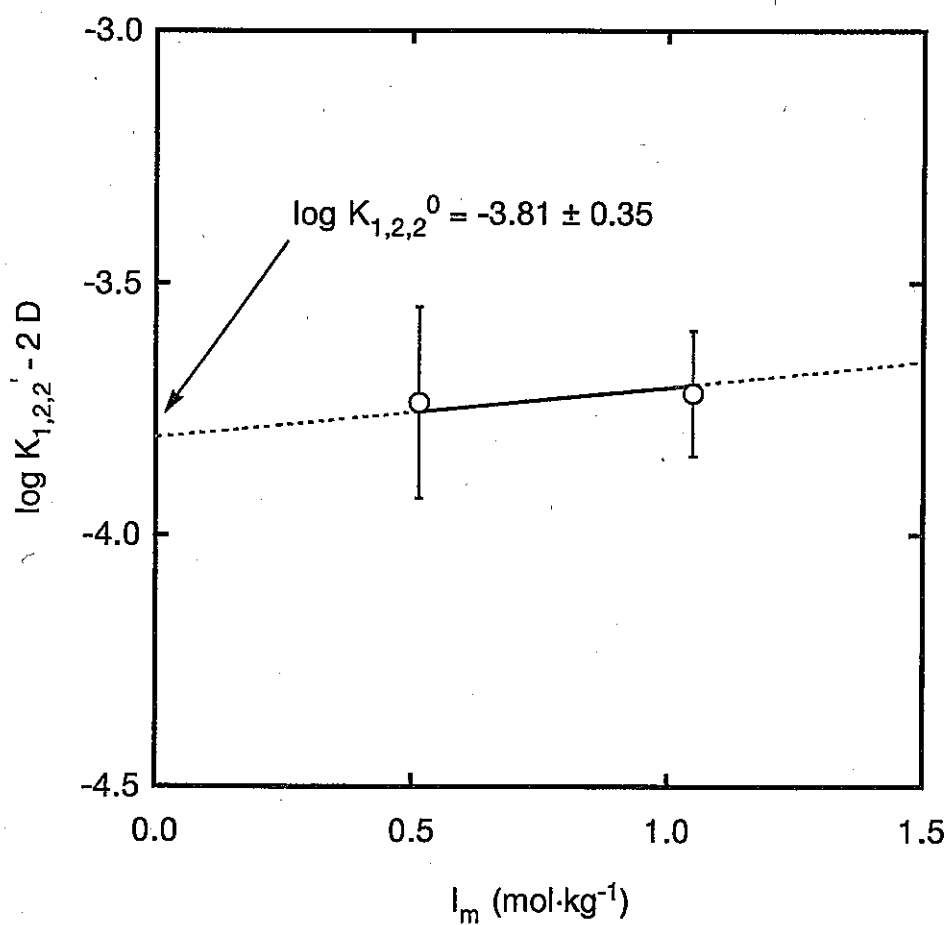


Fig. 10 Calculation of the equilibrium constant of $\text{Np}(\text{CO}_3)_2(\text{OH})_2^{2-}$ extrapolated to $I_m = 0 \text{ mol.kg}^{-1}$ according to SIT

The open circle shows the apparent equilibrium constant, a solid line is the least-squares fitting result based on equation (11), and a dashed line is the extrapolations. See text for detail.

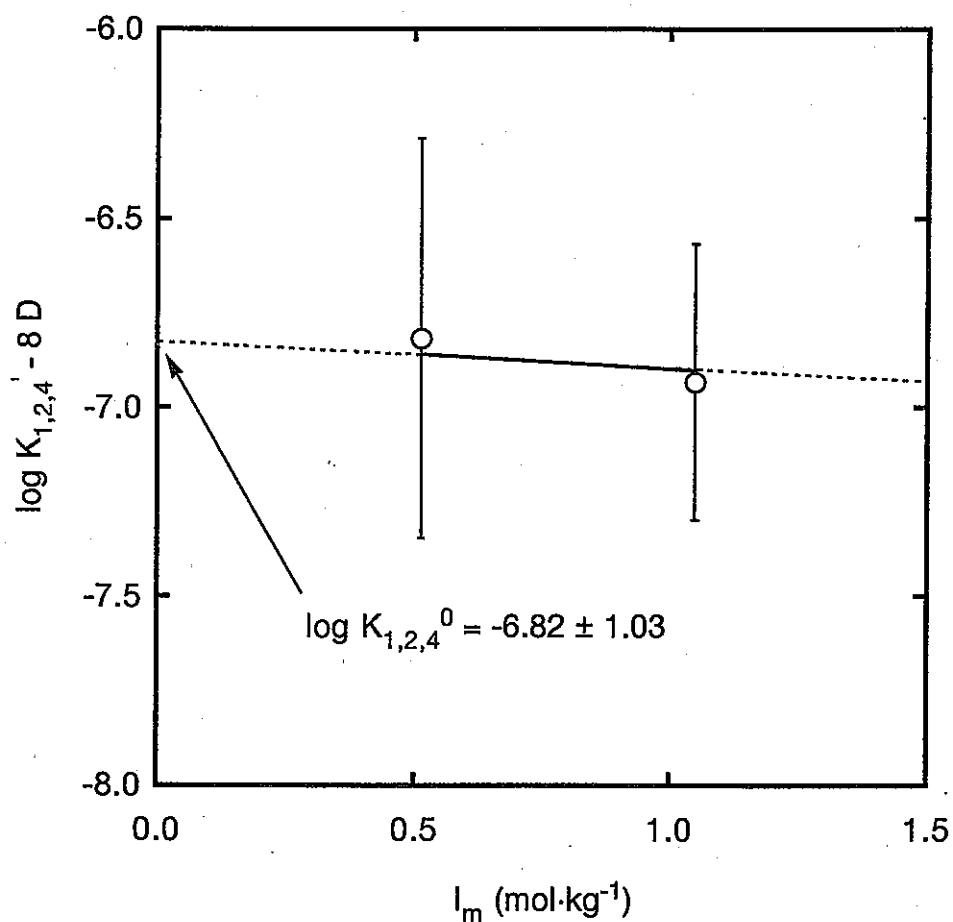


Fig. 11 Calculation of the equilibrium constant of $\text{Np}(\text{CO}_3)_2(\text{OH})_4^{4-}$ extrapolated to $I_m = 0 \text{ mol}\cdot\text{kg}^{-1}$ according to SIT

The open circle shows the apparent equilibrium constant, a solid line is the least-squares fitting result based on equation (12), and a dashed line is the extrapolations. See text for detail.