Comprehensive Thermodynamic Model Applicable to Highly Acidic to Basic Conditions for Isosaccharinate Reactions with Ca(II) and Np(IV)

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Isosaccharinate (ISA^-), a degradation product of cellulose codisposed in low-level nuclear wastes, is expected to be one of the dominant complexing ligands for radionuclides, especially tetravalent actinides. This paper presents a comprehensive thermodynamic model for isosaccharinate reactions with Ca(II) and Np(IV). The model is valid for a wide range of pH values (~ 2 – 14), ISA^- concentrations (ranging up to $0.1\text{ }m$), and ionic strengths (ranging up to $6.54\text{ }m$), and is based on (1) NMR investigations of HISA(aq) (α -D-isosaccharinic acid) and ISL(aq) [dehydration product of HISA(aq)], and the solubility of $\text{Ca}(\text{ISA})_2(\text{c})$ as a function of pH and concentrations of Ca and ISA^- ; (2) $\text{NpO}_2(\text{am})$ solubility in a wide range of pH values (~ 2 – 14) and total ISA concentrations of 0.0016 and $0.008\text{ }m$ and at fixed pH values of approximately 5 and 12 with total ISA concentrations ranging from 0.0001 to $0.1\text{ }m$; and (3) solvent extraction of Np-ISA solutions, containing fixed NaClO_4 concentrations ranging from 0.103 to $6.54\text{ }m$ and at fixed pC_{H^+} values ranging from 1.5 to 1.9 , with dibenzoylmethane. Pitzer's ion-interaction approach was used to interpret the data. The different aqueous species required to explain these data included $\text{HISA}(\text{aq})$, $\text{ISL}(\text{aq})$, $\text{Ca}(\text{ISA})^+$, $\text{Np}(\text{OH})_3(\text{ISA})(\text{aq})$, $\text{Np}(\text{OH})_3(\text{ISA})_2^-$, $\text{Np}(\text{OH})_4(\text{ISA})^-$, and $\text{Np}(\text{OH})_4(\text{ISA})_2^{2-}$. The values of equilibrium constants for reactions involving these species and determined from these data provided close agreements between the observed and predicted concentrations in all of the systems investigated in this study and those reported previously.

KEY WORDS: Isosaccharinate; isosaccharinic acid; thermodynamics; ion-interaction parameters; solubility; $\text{NpO}_2(\text{am})$; solvent extraction; equilibrium constants; α -D-isosaccharinic acid; α -D-isosaccharino-1,4-lactone.

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1. INTRODUCTION

Low- and intermediate-level nuclear wastes contain significant quantities of organic materials such as cotton, wood, and paper that have high cellulose content. The degradation products of these organic materials have been reported^(1–12) to contain soluble, low-molecular weight acids that have a high affinity for tetravalent actinides, making the tetravalent actinides, which otherwise form fairly insoluble hydrous oxides, more soluble. In particular, α -D-isosaccharinic acid [HISA(aq)] (Fig. 1), a degradation product of cellulose, has been reported as the dominant complexing agent for tetravalent actinides under highly alkaline conditions.^(1,2,4,5,10) However, no comprehensive thermodynamic model applicable to a wide range in pH and isosaccharinate concentrations is currently available for any of the tetravalent actinides. Such models and data are needed to reliably predict tetravalent actinide behavior in low- and intermediate-level nuclear waste repositories. It is known that isosaccharinate under acidic conditions transforms into HISA(aq) and ISL(aq) [α -D-isosaccharino-1,4-lactone; a dehydration product of HISA(aq), Fig. 1].⁽¹³⁾ However, reliable values are not known for the acid dissociation constant of HISA(aq) or the hydrolysis constant of ISL(aq). Therefore, fundamental data on the following aspects are necessary to determine the complexation effects of ISA^- in a wide range of conditions: (1) data for protonation/deprotonation constant of HISA(aq) and equilibrium constant of hydrolysis reaction of ISL(aq), and (2) complexation constants of ISA^- with tetravalent actinides applicable to a wide range in pH and ISA^- concentrations.

In an earlier study, Rai *et al.*⁽¹⁴⁾ determined the protonation/deprotonation constants of HISA(aq) through the measurement of $\text{Ca}(\text{ISA})_2(\text{c})$ solubility as a

Fig. 1. Structures of organic ligands discussed in the paper: HISA(aq) (α -D-isosaccharinic acid), ISL(aq) [α -D-isosaccharino-1,4-lactone, a product of dehydration of HISA(aq)], and ISA^- (α -D-isosaccharinate).

function of pH. From this study they also determined the solubility product of $\text{Ca(ISA)}_2(\text{c})$ and Ca-ISA complexes. These values were then used⁽¹⁵⁾ to interpret $\text{NpO}_2(\text{am})$ solubility data in the presence of Ca isosaccharinate solutions in a relatively acidic and neutral region ($\text{pH} < 6.5$). Since these publications,^(15,14) our, yet unpublished, data based on NMR studies [Cho *et al.*⁽¹⁶⁾] indicate that the deprotonation constant value for $\text{HISA}(\text{aq})$, estimated in Rai *et al.*,⁽¹⁴⁾ is about 1.2 orders of magnitude too low, and $\text{ISL}(\text{aq})$ species, hitherto ignored, play a dominant role in the acidic conditions. Although Cho *et al.*⁽¹⁶⁾ were able to determine the equilibrium constant for hydrolysis reaction of $\text{ISL}(\text{aq})$ [$\text{ISL}(\text{aq}) + \text{H}_2\text{O} \rightleftharpoons \text{ISA}^- + \text{H}^+$], the value they obtained contained a large uncertainty due to the fundamental difficulty of measuring ISA^- at low pH. In addition, recent data have also become available^(17,18) indicating that CaISA^+ is an important complexed species at pH values > 5 in the Ca-ISA system. This discussion indicates that reliable values are not available for equilibrium constants applicable to the Ca-ISA system, including those for reactions involving ISA^- in equilibrium with $\text{HISA}(\text{aq})$ or $\text{ISL}(\text{aq})$.

The main objectives of this study are to develop comprehensive models for the solubility of $\text{NpO}_2(\text{am})$ in the $\text{Np(IV)}\text{-H}^+\text{-Na}^+\text{-Ca}^{2+}\text{-HISA}(\text{aq})\text{-ISA}^-\text{-ISL}(\text{aq})\text{-OH}^-\text{-H}_2\text{O}$ and for the solubility of $\text{Ca(ISA)}_2(\text{c})$ in the $\text{Ca}^{2+}\text{-H}^+\text{-HISA}(\text{aq})\text{-ISA}^-\text{-ISL}(\text{aq})\text{-OH}^-\text{-H}_2\text{O}$ systems. To accomplish this goal, we (1) conducted experiments on the solubility of $\text{NpO}_2(\text{am})$ as a function of time and in a range of pH values from 5 to 14 and at a fixed isosaccharinate concentration of 0.0016 *M*, and in a range of isosaccharinate concentrations varying from 0.0001 to 0.1 *M* at a fixed pH value of 12, (2) conducted experiments on the solubility of $\text{Ca(ISA)}_2(\text{c})$ at a fixed pH value of about 8.3 as a function of isosaccharinate concentrations ranging up to 0.2 *M* and interpreted these data with data previously reported for $\text{Ca(ISA)}_2(\text{c})$ solubility⁽¹⁴⁾ to obtain/validate equilibrium constant values for reactions involving $\text{HISA}(\text{aq})$ and $\text{ISL}(\text{aq})$ and for Ca-ISA complexes and for use in interpreting Np data, and (3) used Pitzer's ion-interaction model to develop thermodynamic models based on the $\text{NpO}_2(\text{am})$ and $\text{Ca(ISA)}_2(\text{c})$ solubilities reported in this study and those reported previously for this system.^(15,14) Thus, the model we developed for the $\text{Np(IV)}\text{-ISA}$ system is applicable to a wide range in pH values (2–14), $\text{HISA}(\text{aq})$ concentrations (0.0001–0.1 *M*), and NaClO_4 concentrations (0.103–6.54 *m*) in the acidic region.

2. MATERIALS AND METHODS

2.1. Preparation of $\text{NpO}_2(\text{am})$

The Np(IV) stock solution in HCl was prepared electrolytically. Over time, the Np stock that initially contained a significant amount of Np(III) converted to Np(IV) . UV-Vis-NIR spectroscopic analyses of the stock solution prior to each use confirmed the absence of detectable amounts of all oxidation states other than Np(IV) . The acidic Np(IV) stock solution was spiked into 20-mL of degassed

water containing 0.01 *M* Na₂S₂O₄ in 50-mL glass centrifuge tubes. NpO₂(am) was precipitated by titrating with 5 *M* NaOH to pH values of approximately 10–10.5. The precipitate was washed twice with 20- to 30-mL aliquots of degassed water containing 0.01 *M* Na₂S₂O₄. The centrifuge tubes were kept tightly sealed with Nalgene caps to minimize exposure to the chamber atmosphere.

2.2. Preparation of NaISA Stock Solution

A stock solution of NaISA for use with the Ca(ISA)₂(c) and NpO₂(am) solubility studies was prepared using the following procedure: (1) dissolving Ca(ISA)₂(c) in 2 *M* NaOH by shaking the suspension for a few days, where dissolved Ca precipitates as Ca(OH)₂ leaving NaISA in the aqueous phase, (2) centrifuging and separating the supernatant containing NaISA and a portion of unreacted NaOH, (3) analyzing the concentration of ISA by carbon analysis, and (4) making appropriate pH adjustments, using HCl, and dilutions of NaISA needed for experiments.

2.3. Procedures

Experiments were conducted in an atmosphere-controlled chamber under an Ar atmosphere for Np experiments or an N₂ atmosphere for Ca(ISA)₂(c) experiments. Deionized distilled water, degassed by boiling and cooling in the Ar or N₂ atmosphere, was used in all cases. Solubility was approached from the undersaturation direction.

2.3.1. Solubility of Ca(ISA)₂(c) in NaISA

The Ca(ISA)₂(c) used in this study was prepared by the same method described by Rai *et al.*⁽¹⁴⁾ A 0.2 g of Ca(ISA)₂(c) was added to 50-mL centrifuge tubes containing NaISA solutions ranging in concentrations from 0.01 to 0.2 *M*. The pH values of the suspensions were adjusted to 8.3 and the suspensions shaken continuously until analyzed. After 48 days of equilibration, the pH values were measured using a combination Orion–Ross glass electrode calibrated against standard pH buffers. The suspensions were centrifuged and aliquots of the supernatant were withdrawn for C analyses to quantify isosaccharinate concentrations and to filter them through CentriPrep membrane filters with 30,000 molecular weight cut-offs. The filtered solutions were analyzed for Ca using inductively coupled plasma spectroscopy. Data are listed in Appendix Table A.I.

2.3.2. Solubility of NpO₂(am) in NaISA

Because Np(IV) can be oxidized to Np(V) by O₂ and such oxidation proceeds more easily in solutions of higher pH, special precautions need to be taken to maintain the Np(IV) oxidation state. Several measures developed in previous

studies^(15,19) were taken to minimize oxidation during the preparation of stock solutions and throughout the solubility experiments. These measures included (1) preparing the concentrated Np(IV) stock solutions (~ 250 g Np/L) in approximately 3.5 *M* HCl [where Np(IV) is relatively stable] and storing the solutions under argon, (2) conducting the experiments in the presence of a reducing agent (0.01 *M* Na₂S₂O₄), and (3) sealing the sample tubes during equilibration and sealing the ion-specific electrodes into the sample containers during measurements to avoid O₂ diffusion.

Two sets of experiments were conducted to determine NpO₂(am) solubility in the presence of isosaccharinate. For each sample in the first experimental set, 2.5-mL aliquots of 0.1 *M* Na₂S₂O₄ were added to 50-mL centrifuge tubes, followed by 5.2 mL of 0.4 *M* NaISA and 5 mg of washed NpO₂(am) precipitate. Degassed water or standard NaOH solution was added to bring the sample volume to 25 mL. The pH of the solution was adjusted using NaOH or HCl to several pH values ranging from 5 to 12. Additional samples were prepared in standard NaOH solutions ranging in concentration from 0.01 to 1.0 *M*. Samples in the second set were prepared similarly, except the pH was fixed (about 12) and the concentration of NaISA was varied from 0.0002 to 0.1 *M*. For both sets, the centrifuge tubes were tightly capped and placed on a shaker. Periodically, pH values of the suspensions were measured using an Orion–Ross combination glass electrode calibrated against pH buffers; the electrode was sealed in the tubes to avoid contact of suspensions with the chamber atmosphere.

The suspensions were centrifuged at 2000/g for at least 10 min after different equilibration periods (4–6, 12–14, 20, or 28 days). The supernatant was then filtered through Amicon Centriplus filters (Amicon Corp.) with a 30,000 nominal molecular-weight cutoff and approximately 0.004- μ m pore size. An aliquot of the filtrate was spiked into a liquid scintillation cocktail for total Np analysis by liquid scintillation counting.

Oxidation state analyses were performed on all samples using a solvent extraction technique involving thenoyltrifluoroacetone.⁽²⁰⁾ Data are listed in Tables A.II and A.III. The percentage Np(IV) listed in these tables is based on the portion of total soluble Np extracted by thenoyltrifluoroacetone. Using this technique, the unextracted amount [100-% Np(IV)] is assumed to represent % Np(V).

2.3.3. Solvent Extraction Experiments

Our previous publication⁽²¹⁾ describes the preparation of stock solutions of Np(IV) ($\sim 60,000$ dpm in 10 μ L) and NaClO₄ (0.103, 0.53, 1.07, 2.22, 3.48, 4.91, and 6.54 *m*), the purification procedure for dibenzoylmethane (DBM), the quantification of H⁺ concentrations containing NaClO₄ solutions, and the general procedure for determining distribution coefficients (*D*, ratio of Np in the organic to the aqueous phases). Only a brief description is provided here. The negative

logarithm of H^+ ion concentrations (pC_{H^+}) in different solutions were determined from the observed pH electrode readings (pH_{obs}) using the equation [$pC_{H^+} = pH_{obs} + A$]. The values of A for different $NaClO_4$ solutions (0.03 for 0.103 m , 0.14 for 0.53 m , 0.27 for 1.07 m , 0.48 for 2.22 m , 0.69 for 3.48 m , 0.90 for 4.91 m , and 1.12 for 6.54 m) were determined using a Gran type of titration procedure.⁽²²⁾ Isosaccharinate stock solution was prepared from $Ca(ISA)_2(c)$. All extractions were performed in borosilicate glass scintillation vials, which were silanized using Caceci and Choppin's⁽²³⁾ procedure. A reducing agent, $NH_2OH.HCl$, was used to maintain Np in the tetravalent oxidation state.

Five-milliliter aliquots of $NaClO_4$ adjusted to the appropriate pC_{H^+} and containing 0.01 M $NH_2OH.HCl$, 10 μL of Np(IV) stock solution, and a known concentration of ISA (but varying between 0.0002 to 0.0028 m) were shaken with 5.0 mL of DBM in toluene at room temperature ($25 \pm 1^\circ C$) for 1 hr. The concentration of DBM was adjusted depending upon the $NaClO_4$ molality and pC_{H^+} of the solution so that the distribution ratio (D) fell between 0.1 and 10. Kinetic studies confirmed that the extraction equilibrium was attained in about 10 min. The vials were centrifuged and 1.0-mL aliquots were taken from both phases to measure the alpha activity. A Wallac 1415 liquid scintillation counter was used to count the activity in HiSafe cocktail (Wallac). The remaining aqueous phase was used for pH_{obs} measurements. Extraction data along with normalized Np(IV) aqueous concentrations used in thermodynamic analyses are reported in Table A.IV.

2.4. Thermodynamic Model

The ion-interaction model of Pitzer^(24,25) was used to interpret the solubility data. This aqueous thermodynamic model emphasizes a detailed description of specific ion interactions in solution. The effects of specific ion interactions on the excess solution free energy are contained in the expressions for the activity coefficients. The activity coefficients can be expressed in a virial-type expansion as

$$\ln \gamma_i = \ln \gamma_i^{DH} + \sum_j \beta_{ij}(I) m_j + \sum_j \sum_k C_{ijk} m_j m_k + \dots \quad (1)$$

where m is the molality, γ_i^{DH} is a modified Debye–Hückel activity coefficient that is a universal function of ionic strength, and $\beta_{ij}(I)$ and C_{ijk} are specific for each ion interaction and are functions of ionic strength. The third virial coefficient, C , is understood to be independent of ionic strength. A detailed description of the exact form of Eq. (1) is contained in the nonlinear least-squares programs [NONLIN and INSIGHT]⁽²⁶⁾ for estimating the activity coefficients and calculating chemical equilibria involving multiple solid and aqueous species. We have used these programs extensively in the past to interpret solubility data for many systems including those involving isosaccharinic acid and Np(IV).^(14,15,21,27) For calculation

and plotting purposes of $\text{NpO}_2(\text{am})$ and $\text{Ca}(\text{ISA})_2(\text{c})$ data, it was assumed that the measured molarities equal molalities because all of the solutions are either of very low ionic strength or the calculated molalities (e.g., for 1.0 M NaOH) are not significantly different than the molarity values. Since the solvent extraction experiments were conducted in relatively dilute to concentrated NaClO_4 solutions, appropriate corrections were made to convert concentrations from molarity to molality units.

3. RESULTS AND DISCUSSION

3.1. Acid Dissociation and Dehydrolysis Constants of $\text{HISA}(\text{aq})$ and Complexation of Ca^{2+} with ISA^-

Rai *et al.*⁽¹⁴⁾ obtained extensive data on $\text{Ca}(\text{ISA})_2(\text{c})$ solubility as a function of pH and Ca concentrations. Because preparation techniques for NaISA were unavailable at that time, they were not able to conduct studies as a function of ISA^- concentrations. These data are now presented in Fig. 2 and show a progressive decrease in Ca concentrations at a fixed pH value of 8.3 with an increase in NaISA concentrations, similar to data presented recently by Van Loon *et al.*⁽¹⁷⁾ These data on $\text{Ca}(\text{ISA})_2(\text{c})$ as a function of NaISA concentrations are critical in defining the Ca-ISA complexes in pH values of >5 . Rai *et al.*⁽¹⁴⁾ interpreted $\text{Ca}(\text{ISA})_2(\text{c})$ solubility as a function of pH using $\text{HISA}(\text{aq})$, ISA^- , and $\text{Ca}(\text{ISA})_2(\text{aq})$ species. However, this model does not explain the behavior observed in Fig. 2, predicts constant Ca concentration as opposed to observed decrease in Ca concentrations with the increase in NaISA concentrations, and is not consistent with NMR data,⁽¹⁶⁾ which definitively shows that both $\text{HISA}(\text{aq})$ and $\text{ISL}(\text{aq})$ are the important species under acidic conditions, and not $\text{HISA}(\text{aq})$ alone. The NMR data⁽¹⁶⁾ provided a reliable value for the proton dissociation constant of $\text{HISA}(\text{aq})$. However, the NMR data were not sufficient to provide reliable values for equilibrium constants of reactions involving $\text{ISL}(\text{aq})$. To develop a model that is consistent with all of these data, we reinterpreted the entire data set using the Pitzer model. For these interpretations, we relied on the $\text{HISA}(\text{aq})$ dissociation constant value [$\log K^0$ of -3.27 ± 0.02 for $\text{HISA}(\text{aq}) \rightleftharpoons \text{ISA}^- + \text{H}^+$] based on our NMR data⁽¹⁶⁾ and fitted the values for other species. The new model (Tables I and II) is consistent with all of the data, includes $\text{HISA}(\text{aq})$, $\text{ISL}(\text{aq})$, ISA^- , and CaISA^+ species along with a revised value for the solubility product of $\text{Ca}(\text{ISA})_2(\text{c})$ and does not require $\text{Ca}(\text{ISA})_2(\text{aq})$. A comparison of experimental data reported in Rai *et al.*⁽¹⁴⁾ and obtained in this study to those predicted by the new model show close agreement (Figs. 2 and 3). Our values of 1.44 ± 0.07 and -6.26 ± 0.07 , respectively, for the log of the equilibrium constant for $[\text{Ca}^{2+} + \text{ISA}^- \rightleftharpoons \text{CaISA}^+]$ and for $[\text{Ca}(\text{ISA})_2(\text{c}) \rightleftharpoons \text{Ca}^{2+} + 2\text{ISA}^-]$ are very similar to the values (1.7 and -6.54 , respectively) recently reported for these reactions by Van Loon *et al.*⁽¹⁷⁾ and the values (1.7 and -6.36 ± 0.10 , respectively) reported by Vercammen *et al.*⁽¹⁸⁾ A low CaISA^+

Fig. 2. Solubility of $\text{Ca}(\text{ISA})_2(\text{c})$ as a function of NaISA concentration and at a fixed pH of approximately 8.3 and 48-day equilibration period. Solid line depicts predicted total concentration; other lines represent concentrations of different species, as identified, using modeling parameters reported in Tables I and II.

formation constant value shows that the isosaccharinate complexes with Ca^{2+} are rather weak and that this species does not contribute significantly to the total Ca concentrations (Figs. 2 and 3). The $\log K^0$ value of 0.37 ± 0.07 for $[\text{HISA}(\text{aq}) \rightleftharpoons \text{ISL}(\text{aq}) + \text{H}_2\text{O}]$ determined from these data is dependent on the value selected for the proton dissociation constant of $\text{HISA}(\text{aq})$. However, these data show that $\text{ISL}(\text{aq})$, as compared with $\text{HISA}(\text{aq})$, are the dominant species, which is consistent with the NMR studies⁽¹⁶⁾ and lends support to the accuracy of these values for use in developing reliable models for $\text{Np}(\text{IV})$ systems involving $\text{ISL}(\text{aq})$, $\text{HISA}(\text{aq})$, ISA^- , and CaISA^+ species.

3.2. Solubility of $\text{NpO}_2(\text{am})$ in the Presence of ISA^-

Aqueous Np concentrations in most of the samples were relatively low (Tables A.II and A.III), so direct spectrophotometric analyses for the oxidation

Table I. Pitzer Ion-Interaction Parameters Used in the Model^a

Species	$\beta^{(0)}$	$\beta^{(1)}$	$\beta^{(2)}$	C^ϕ	Reference
Binary Interactions					
$\text{H}^+ - \text{Cl}^-$	0.1775	0.2945	0.00	0.0008	(32)
$\text{Na}^+ - \text{Cl}^-$	0.0765	0.2664	0.00	0.00127	(32)
$\text{Na}^+ - \text{OH}^-$	0.0864	0.253	0.00	0.0044	(32)
$\text{Np}^{4+} - \text{Cl}^-$	1.644	15.5	0.00	0.0995	(28) ^a
$\text{Np}^{4+} - \text{ClO}_4^-$	2.26	17.53	0.00	0.0995	This study ^b
$\text{NpOH}^{3+} - \text{Cl}^-$	1.0	7.856	0.00	0.00	(28) ^a
$\text{NpOH}^{3+} - \text{ClO}_4^-$	1.4	9.0	0.00	0.00	This study ^b
Ternary Interactions					
$\text{H}^+ - \text{Na}^+$	0.036				(32)
$\text{H}^+ - \text{Na}^+ - \text{Cl}^-$	-0.004				(32)
$\text{Cl}^- - \text{OH}^-$	-0.05				(32)
$\text{Cl}^- - \text{OH}^- - \text{Na}^+$	-0.006				(32)
$\text{Np}(\text{OH})_3\text{ISA}(\text{aq}) - \text{ClO}_4^-$	0.045				This study ^{b,c}

^a Assuming corresponding U(IV) parameters reported in the quoted reference apply to the Np(IV) system; our recent solvent extraction studies⁽²¹⁾ with Np(IV) in low to concentrated chloride solutions are consistent with these assumptions.

^b These parameters are primarily important in solvent extraction data; see text for details.

^c The use of this value for the reported parameter or for $\text{Np}(\text{OH})_3\text{ISA}(\text{aq}) - \text{Na}^+$ provides identical fits. However, due to the limitations of the experimental data, it is, at present, not possible to assign this value to one of these parameters only.

state and speciation were not possible. Therefore, oxidation state distribution of aqueous Np was determined by solvent extraction, and the results in nearly all cases (different pH, ISA⁻ concentrations, and times) indicated that 75–90% of total aqueous Np was present in the tetravalent state.

The aqueous Np(IV) concentrations in equilibrium with $\text{NpO}_2(\text{am})$ are similar at different equilibration periods in each set containing (1) 0.0016 M NaISA in a range of pH values (Fig. 4), or (2) variable NaISA concentrations at a fixed pH value of about 12 (Fig. 5), indicating that steady-state conditions are reached in less than 5–6 days. Our previous studies with $\text{NpO}_2(\text{am})$ ⁽²⁷⁾ and other tetravalent actinide hydrous oxides^(28,29) show that equilibrium between tetravalent actinide hydrous oxides and a wide variety of electrolyte solutions with a broad range in H^+ concentrations is reached within a few days. The attainment of steady-state conditions in this study and the use of sampling times that exceeded the minimum required to reach equilibrium⁽²⁷⁾ provided assurance that equilibrium is attained in our experiments.

There is a dramatic decrease in aqueous Np(IV) concentrations with increasing pH at pH < 7 (Fig. 4). The $\text{NpO}_2(\text{am})$ solubility in the acidic region is several orders of magnitude higher than that predicted in the absence of isosaccharinate⁽²⁷⁾ (Fig. 4). The measured Np concentrations are in close agreement with the data

Table II. Important Chemical Reactions Included in the Model

Reaction	log K^o	Reference
$\text{Ca(ISA)}_2(\text{c}) \rightleftharpoons \text{Ca}^{2+} + 2\text{ISA}^-$	-6.26 ± 0.07	This study
	-6.54	(17)
	-7.62	(14)
	-6.36 ± 0.10	(18)
$\text{Ca}^{2+} + \text{ISA}^- \rightleftharpoons \text{CaISA}^+$	1.44 ± 0.07	This study
	1.70	(17)
	1.7	(18)
$\text{Ca}^{2+} + 2\text{ISA}^- \rightleftharpoons \text{Ca(ISA)}_2(\text{aq})$	NN	This study ^a
	5.4	(14)
$\text{HISA}(\text{aq}) \rightleftharpoons \text{ISL}(\text{aq}) + \text{H}_2\text{O}$	0.37 ± 0.07	This study
$\text{HISA}(\text{aq}) \rightleftharpoons \text{ISA}^- + \text{H}^+$	-3.27 ± 0.02	(16) ^b
	-4.46	(14)
$\text{Np}^{4+} + \text{H}_2\text{O} \rightleftharpoons \text{NpOH}^{3+} + \text{H}^+$	-0.5	(33) ^c
$\text{NpO}_2(\text{am}) + \text{ISA}^- + \text{H}^+ + \text{H}_2\text{O} \rightleftharpoons \text{Np(OH)}_3\text{ISA}(\text{aq})$	2.57 ± 0.37	This study
	2.76	(15)
$\text{NpO}_2(\text{am}) + 2\text{ISA}^- + \text{H}^+ + \text{H}_2\text{O} \rightleftharpoons \text{Np(OH)}_3(\text{ISA})_2^-$	4.68 ± 0.37	This study
$\text{NpO}_2(\text{am}) + \text{ISA}^- + 2\text{H}_2\text{O} \rightleftharpoons \text{Np(OH)}_4\text{ISA}^-$	-4.76 ± 0.37	This study
$\text{NpO}_2(\text{am}) + 2\text{ISA}^- + 2\text{H}_2\text{O} \rightleftharpoons \text{Np(OH)}_4(\text{ISA})_2^{2-}$	-2.90 ± 0.37	This study

^aNN = not needed.

^bBased on NMR data⁽¹⁶⁾ and consistent with the data presented in this study.

^cThe equilibrium constant value is assumed to be identical to that for corresponding U reaction and as reported in Rai *et al.*⁽³⁴⁾ This reaction does not contribute significantly to Np(IV) concentrations at any of the experimental conditions in the NpO₂(am) solubility study, but becomes important in solvent extraction study.

obtained by Rai *et al.*⁽¹⁵⁾ under identical conditions in the presence of isosaccharinate and where the experimental pH values overlap in both studies. The significant result obtained in this study is that the measured Np solubility remains low and constant under alkaline conditions exhibiting no pH dependence at pH values $\gtrsim 7$. A continued decrease in Np concentration with increasing pH is not observed under alkaline conditions, as predicted by the solubility model developed from low pH data only.⁽¹⁵⁾ The low Np solubility and lack of a pH dependence under alkaline conditions may truly be due to Np(IV)-ISA complexes or to detection limit problems and/or the presence of colloids. However, as is demonstrated by the results of the variable ISA⁻ experiments (Fig. 5), the actual detection limit is approximately an order of magnitude lower than the measured concentrations; only ionic Np(IV) is quantified in solvent extraction tests used in this study. Therefore, the lack of pH dependence under highly alkaline conditions is not an experimental artifact, but is due to the presence of different Np-ISA species under alkaline conditions.

The Np(IV) concentration in equilibrium with NpO₂(am) increases approximately one order of magnitude with an order of magnitude increase in NaISA

Fig. 3. Solubility of $\text{Ca(ISA)}_2(\text{c})$ as a function of pH and 75-day equilibration period [experimental data of Rai *et al.*⁽¹⁴⁾]. Solid lines depict predicted total concentrations; other lines represent concentrations of different species, as identified, using modeling parameters reported in Tables I and II.

concentration at a fixed pH of 12 (Fig. 5). These Np(IV) concentrations are also similar to those observed in equilibrium with 0.0016 M ISA as a function of pH (an average of 18 data points at pH values >8.5 from Fig. 4, plotted as a solid circle in Fig. 5), thereby providing additional assurance about the consistency

Fig. 4. Aqueous Np(IV) concentrations in equilibrium with $\text{NpO}_2(\text{am})$ as a function of pH and at a fixed total ISA concentration of 0.0016 m . Relatively low pH data from Rai *et al.*⁽¹⁵⁾ The pH values > 12 reported in this figure are calculated from INSIGHT based on input molarities of NaOH and other ions present in the system. Solid line represents total concentration, while other lines represent concentrations of different species, as identified, predicted using modeling parameters reported in Tables I and II. The line “ $\text{Np}(\text{OH})^{3+}$ ” represents predicted Np concentrations in the absence of ISA.

and the reliability of the data as a function of NaISA concentrations. Increases in Np(IV) concentrations with increases in ISA^- concentration were also observed for $\text{NpO}_2(\text{am})$ suspensions equilibrated at pH 5 (Fig. 6). However, the measured Np concentrations are nearly three orders of magnitude higher at pH 5 (Fig. 6) than at pH 12 (Fig. 5). Although increases in $\text{NpO}_2(\text{am})$ solubility are observed in both acidic and alkaline conditions, the dominant species must certainly be different in these two regimes. Reasons for these differences are (1) the solubility of $\text{NpO}_2(\text{am})$ decreases with the increase in pH at values between 2 and 7 (Figs. 4), which would require species, such as $\text{Np}(\text{OH})_x(\text{ISA})_y^{4-(x+y)}$, where x would have a value of less than 4 and y a value ≥ 1 , and (2) the solubility of $\text{NpO}_2(\text{am})$ is nearly constant at pH values between about 8 and 14 (Fig. 4), which would require species such as $\text{Np}(\text{OH})_4(\text{ISA})_y^{-y}$ with $y \geq 1$. Consistent with this observation, Rai *et al.*⁽¹⁵⁾ proposed $\text{Np}(\text{OH})_3\text{ISA}^0$ and $\text{Np}(\text{OH})_2(\text{ISA})_2^-$ species to explain the observed $\text{NpO}_2(\text{am})$ solubility behavior in the acidic region. Thermodynamic interpretations of the data currently available are discussed in the next section.

Fig. 5. Aqueous Np(IV) concentrations in equilibrium with $\text{NpO}_2(\text{am})$ as a function of time and NaISA concentrations at a fixed pH of ~ 12 . The solid circle with horizontal lines represents the mean and standard deviation of Np(IV) concentration ($\log m_{\text{Np(IV)}} = -7.292 \pm 0.09$) of 16 samples with pH values > 8.5 , which are plotted in Fig. 4. Solid line represents total concentrations, while other lines represent concentrations of different species, as identified, predicted using modeling parameters reported in Tables I and II.

3.3. Thermodynamic Analyses of $\text{NpO}_2(\text{am})$ Solubility Data

Because of the revised value of the dissociation constant of $\text{HISA}(\text{aq})$ and the new values involving CaISA^+ and $\text{ISL}(\text{aq})$ determined in this study (Table II), and because of the need to develop a comprehensive model for the Np(IV)-ISA system, the experimental data and those presented by Rai *et al.*⁽¹⁵⁾ were interpreted together to develop a reliable model that would be consistent with all of the available data. The aqueous $\text{Np}(\text{OH})_3\text{ISA}(\text{aq})$, $\text{Np}(\text{OH})_3(\text{ISA})_2^-$, $\text{Np}(\text{OH})_4(\text{ISA})^-$, and $\text{Np}(\text{OH})_4(\text{ISA})_2^{2-}$ make up the combination of complex species that provided close

Fig. 6. Aqueous Np(IV) concentrations in equilibrium with $\text{NpO}_2(\text{am})$ as a function of NaISA concentrations⁽¹⁵⁾ at a fixed pH value of ~ 5 . Solid line represents total concentrations, while other lines represent concentrations of different species, as identified, predicted using modeling parameters reported in Tables I and II.

agreement with the observed $\text{NpO}_2(\text{am})$ solubilities in a range of pH values varying from 2 to 14 and at fixed NaISA concentrations of 0.0016 or 0.008 *M* (Figs. 4 and 7) and NaISA concentrations ranging from 0.0001 to 0.1 *M* and at fixed pH values of 5 or 12 (Figs. 5 and 6). The relative distribution of these species as a function of pH and NaISA concentrations are shown in Figs. 4 through 7. These data show that at a given isosaccharinate concentration, primarily two species are required to explain the observed $\text{NpO}_2(\text{am})$ solubility from pH values of 2 all the way to approximately 14. The species $\text{Np}(\text{OH})_3\text{ISA}(\text{aq})$ or $\text{Np}(\text{OH})_3(\text{ISA})_2^-$ are required for pH values of $\lesssim 7$ and $\text{Np}(\text{OH})_4(\text{ISA})^-$ or $\text{Np}(\text{OH})_4(\text{ISA})_2^{2-}$ are required for pH values of $\gtrsim 7$. The species $\text{Np}(\text{OH})_3\text{ISA}^0$ or $\text{Np}(\text{OH})_4(\text{ISA})^-$ are important at total ISA concentrations of $\lesssim 0.01$ *M*, while $\text{Np}(\text{OH})_3(\text{ISA})_2^-$ or $\text{Np}(\text{OH})_4(\text{ISA})_2^{2-}$ are important at total ISA concentrations of $\gtrsim 0.01$ *M*. The $\text{NpO}_2(\text{am})$ solubility

Fig. 7. Aqueous Np(IV) concentrations⁽¹⁵⁾ in equilibrium with $\text{NpO}_2(\text{am})$ as a function of time and pH at a fixed total ISA concentration of 0.008 *m*. Solid line represents total concentrations, while other lines represent concentrations of different species, as identified, predicted using modeling parameters reported in Tables I and II.

reactions involving these species are reported in Eqs. (2–5)

The equilibrium constants for these reactions calculated from these data were 2.57 ± 0.37 , 4.68 ± 0.37 , -4.76 ± 0.37 , and -2.90 ± 0.37 , respectively. When these equilibrium reactions for the dissolution of $\text{NpO}_2(\text{am})$ (Eqs. 2–5) are combined with the $\text{NpO}_2(\text{am})$ solubility product ($\log K_{\text{sp}} = -54.9$),⁽²⁷⁾ they provide

the logarithm of the equilibrium constant of 43.47 for $[\text{Np}^{4+} + 3\text{OH}^- + \text{ISA}^- \rightleftharpoons \text{Np}(\text{OH})_3\text{ISA}^0]$, 45.58 for $[\text{Np}^{4+} + 3\text{OH}^- + 2\text{ISA}^- \rightleftharpoons \text{Np}(\text{OH})_3(\text{ISA})_2^-]$, 50.14 for $[\text{Np}^{4+} + 4\text{OH}^- + \text{ISA}^- \rightleftharpoons \text{Np}(\text{OH})_4\text{ISA}^-]$, and 52.00 for $[\text{Np}^{4+} + 4\text{OH}^- + 2\text{ISA}^- \rightleftharpoons \text{Np}(\text{OH})_4(\text{ISA})_2^-]$. No values of isosaccharinate complexes of Np(IV) or of other tetravalent actinides are available other than those Rai *et al.*⁽¹⁵⁾ determined for Np-ISA complexes, based on the limited data under acidic conditions or for those Moreton⁽⁵⁾ and Greenfield *et al.*^(3,4) proposed for Pu(IV)-ISA complexes based on a few samples at pH 12, and Vercammen *et al.*⁽¹²⁾ proposed for Th(IV) based on studies with ion-exchange resin at pH 13.3. Rai *et al.*⁽¹⁵⁾ proposed two species $[\text{Np}(\text{OH})_3\text{ISA}^0]$ and $[\text{Np}(\text{OH})_2(\text{ISA})_2^-]$ and the value for the equilibrium constant they determined for $\text{Np}(\text{OH})_3\text{ISA}^0$ is very similar to the value determined in this study (Table II). This is not surprising since both values are based on the same experimental data. However, reanalyses of Rai *et al.*⁽¹⁵⁾ data using a revised thermodynamic model (Tables I and II) showed that the species $\text{Np}(\text{OH})_2(\text{ISA})_2^-$ were not required to fit the data.

As we observed in this study for Np(IV), Moreton⁽⁵⁾ and Greenfield *et al.*^(3,4) also observed an increase in Pu(IV) concentration with the increase in ISA^- concentration at pH 12. Rather than interpreting the data under highly alkaline conditions, as we did using mixed hydroxy-ISA complexes $[\text{Np}(\text{OH})_4\text{ISA}^-]$ and $[\text{Np}(\text{OH})_4(\text{ISA})_2^-]$, they interpreted their data assuming complexes with isosaccharinate-containing deprotonated hydroxyl groups. The reactions they proposed are

where ISAH_{-m} represents the deprotonation of m hydroxyl groups of isosaccharinate.⁵ Like Reactions 4 and 5, Reactions 6 and 7 have no explicit pH dependence, so Pu(IV) solubility is expected to remain constant as a function of pH. Unfortunately, Pu(IV) solubility measurements were not made as a function of pH at constant isosaccharinate concentration and the predicted behavior cannot be verified. However, because the behavior of Pu(IV) and Np(IV) are expected to be similar and Np(IV) solubility does not exhibit a pH dependence under alkaline conditions (Fig. 4), the deprotonation reactions (Eqs. 6 and 7) of isosaccharinate hydroxyl groups can also explain our solubility data under alkaline conditions. Spectroscopic techniques, such as nuclear magnetic resonance (NMR), are required to distinguish between the mixed hydroxy-ISA complexes proposed in Eqs. 4 and 5 and the hydroxyl deprotonation reactions proposed in Eqs. 6 and 7. Our ¹³C-NMR studies with Na and Ca solutions of isosaccharinate⁽¹⁶⁾ show that

⁵Species similar to those in Reaction 6 for Th $[\text{Th}(\text{ISAH}_{-4})^-]$ were also proposed by Vercammen *et al.*⁽¹²⁾ to interpret their adsorption data for an ion-exchange resin at pH 13.3.

deprotonation of the carboxylic acid is complete by about pH 5 and that no further deprotonation reactions of isosaccharinate are apparent in the pH range from 5 to 12. These preliminary data support the formation of mixed hydroxy-ISA complexes and are consistent with our modeling results, which indicated that species of the type $\text{Np}(\text{OH})_4(\text{ISA})_y^{-y}$ (with $y \geq 1$) control the Np solubility from pH 8 to 14 (Figs. 4 and 5). The complexation of isosaccharinate with tetravalent actinides may shift the deprotonation of the hydroxyl group to lower pH values such that studies specifically with complexed tetravalent actinides would be required to determine whether the complexation involves deprotonation of hydroxyl groups or hydrolyzed tetravalent actinides. However, regardless of how the complexes are formed, the overall net reactions are well understood and provide reliable data for predicting Np behavior in a wide range of pH values and isosaccharinate concentrations.

3.4. Extending the Thermodynamic Model to High Acidity and Ionic Strength

The thermodynamic model described above is based on the $\text{NpO}_2(\text{am})$ solubility data obtained in relatively dilute electrolytes. For this purpose, we conducted extensive solvent extraction studies in the pC_{H^+} range of 1.5 to 1.9, total isosaccharinate concentrations varying from 0.0002 to 0.0028 *m*, and NaClO_4 concentrations fixed at different molalities ranging from 0.103 to 6.54 *m* (Table A.IV). Based on the model described above, the dominant Np-ISA complex species in the solvent extraction data is expected to be $\text{Np}(\text{OH})_3\text{ISA}^0$, and Np^{4+} and NpOH^{3+} are expected to become more important than in the solubility data. Therefore, Pitzer ion-interaction parameters cannot be ignored for Np^{4+} and NpOH^{3+} in these concentrated electrolytes. Pitzer parameters are not available for these species with ClO_4^- , the major electrolyte anion in this system. However, it has been suggested⁽²¹⁾ that binary parameters⁽²⁸⁾ for $\text{U}^{4+}-\text{Cl}^-$ and $\text{UOH}^{3+}-\text{Cl}^-$ can be used for the ClO_4^- interactions with corresponding Np species. Defining these parameters from these solvent extraction studies alone in relatively constant pC_{H^+} values and as a function of a limited range in ISA^- concentrations is difficult. Therefore, several different modeling runs were conducted to quantify these parameters. The parameters that provided the best fits to all of the data included $\beta^{(0)} = 2.26$ and $\beta^{(1)} = 17.53$ for $\text{Np}^{4+}-\text{ClO}_4^-$, and $\beta^{(0)} = 1.4$ and $\beta^{(1)} = 9.0$ for $\text{NpOH}^{3+}-\text{ClO}_4^-$, whereas the only other reported experimental values⁽²⁸⁾ for the ion-interaction parameters of tetravalent actinides are $\beta^{(0)} = 1.644$ and $\beta^{(1)} = 15.5$ for $\text{U}^{4+}-\text{Cl}^-$, and $\beta^{(0)} = 1.0$ and $\beta^{(1)} = 7.856$ for $\text{UOH}^{3+}-\text{Cl}^-$, indicating that the perchlorate system requires larger values for these parameters than the chloride system. We believe that the values of these parameters with perchlorate are reasonable because (1) the reported $\beta^{(0)}$ and $\beta^{(1)}$ values⁽²⁵⁾ for trivalent rare earths with

ClO_4^- are approximately 30 and 17%, respectively, higher than the values for the corresponding parameters with Cl^- ; the values that we determined in this study with ClO_4^- are consistent with this expectation; (2) Felmy *et al.*⁽³⁰⁾ reported orders of magnitude lower $\text{ThO}_2(\text{am})$ solubility in NaClO_4 solutions as compared with NaCl , indicating that higher values for $\beta^{(0)}$ and $\beta^{(1)}$ will be required for NaClO_4 solutions as compared with NaCl , again consistent with our findings; and (3) in trying to explain the observed $\text{ThO}_2(\text{am})$ solubility as a function of Na_2CO_3 in NaCl solutions, Felmy *et al.*⁽³¹⁾ determined $\theta = 1.8$ for $\text{Th}(\text{CO}_3)_5^{6-} - \text{Cl}^-$ as compared to $\theta = 5.5$ for $\text{Th}(\text{CO}_3)_5^{6-} - \text{ClO}_4^-$, indicating higher values for Pitzer parameters in perchlorate than in chloride systems. In addition to parameters for $\text{Np}^{4+} - \text{ClO}_4^-$ and $\text{NpOH}^{3+} - \text{ClO}_4^-$, the solvent extraction data also required a value of 0.045 for $\text{Np}(\text{OH})_3\text{ISA}^0 - \text{ClO}_4^-$ or for $\text{Np}(\text{OH})_3\text{ISA}^0 - \text{Na}^+$ (because the experiments were done in concentrated NaClO_4 solutions only, it is currently not possible to definitively assign the value to one of these parameters) to closely fit the data, especially in relatively concentrated solutions. This value for $\text{Np}(\text{OH})_3\text{ISA}^0 - \text{ClO}_4^-$ is in the range of reported values for interactions of other neutral species with monovalent ions.⁽²⁵⁾

The normalized aqueous $\text{Np}(\text{IV})$ concentrations from solvent extraction experiments in NaClO_4 concentrations ranging from 0.103 to 6.54 *m* show close agreement with the concentrations predicted using the thermodynamic data (Tables I and II) described above (Fig. 8), indicating that the model developed in this study is consistent with the solvent extraction data. Xia *et al.*,⁽²¹⁾ in interpreting their solvent extraction data for $\text{Np}(\text{IV})$ -sulfate in NaClO_4 concentrations ranging from 0.103 to 6.54 *m*, assumed that the $\beta^{(0)}$ and $\beta^{(1)}$ for $\text{Np}^{4+} - \text{ClO}_4^-$ and for $\text{NpOH}^{3+} - \text{ClO}_4^-$ are identical to those for the corresponding $\text{U}(\text{IV})$ system. It is of interest to know whether the new parameters for $\text{Np}^{4+} - \text{ClO}_4^-$ and $\text{NpOH}^{3+} - \text{ClO}_4^-$ impact the predictions made in Xia *et al.*⁽²¹⁾ Therefore, modeling runs with the Xia *et al.*⁽²¹⁾ data were performed and results indicated that the inclusion of these parameters did not significantly impact the predictions made in Xia *et al.*⁽²¹⁾ This, we believe, is because the concentrations of both the Np^{4+} and NpOH^{3+} are very low as compared with the total soluble Np in the $\text{Np}(\text{IV})$ -sulfate system investigated by Xia *et al.*⁽²¹⁾

4. CONCLUSIONS

The results presented in this paper show that significant complexation of $\text{Np}(\text{IV})$ by ISA^- can occur under acidic as well as basic conditions and that the overall effect in solubilizing $\text{NpO}_2(\text{am})$ is dependent on the pH and ISA^- concentration. The data reported in this study in conjunction with the data reported by Rai *et al.*^(14,15) provide a basis to develop a comprehensive model for predicting $\text{NpO}_2(\text{am})$ solubility behavior in a wide range of ISA^- concentrations

Fig. 8. Normalized aqueous Np(IV) concentrations ($[\text{Np(IV)}]_n$) as a function of total ISA concentrations. Solid line represents total concentrations, while other lines represent concentrations of different species, as identified, predicted using modeling parameters reported in Tables I and II.

Fig. 8. Continued.

(0.0001–0.1 *M*), very acidic to highly alkaline conditions (pH $\sim$ 2–14), and in dilute to concentrated NaClO₄ (0.1–6.5 *m*) solutions in the acidic region. The Pitzer ion-interaction parameters and the equilibrium constants developed/used in this study for the $\text{Np(IV)}\text{--H}^+\text{--Na}^+\text{--Ca}^{2+}\text{--HISA(aq)}\text{--ISA}^-\text{--ISL(aq)}\text{--OH}^-\text{--H}_2\text{O}$ and the $\text{Ca}^{2+}\text{--H}^+\text{--HISA(aq)}\text{--ISA}^-\text{--ISL(aq)}\text{--OH}^-\text{--H}_2\text{O}$ systems are summarized in Tables I and II.

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APPENDIX

Table A.I. Ca(ISA)₂(c) Solubility in NaISA Solutions of pH Values ~8.2, Equilibrated for 48 Days

log m_{NaISA}		
Initially added	At equilibrium	log m_{Ca}
-1.940	-1.63	-2.239
-1.636	-1.49	-2.444
-1.464	-1.46	-2.568
-1.347	-1.35	-2.702
-1.170	-1.17	-2.829
-0.959	-0.96	-2.991
-0.724	-0.70	-3.336

Table A.II. NpO₂(am) Solubility in 0.0016 M NaISA Containing 0.01 M Na₂S₂O₄ and as a Function of pH and Equilibration Period

5-6 Days			13 Days		
pH	log m_{Np}	% Np(IV)	pH	log m_{Np}	% Np(IV)
5.04	-5.534	89	5.09	-5.433	96
5.56	-6.292	54	5.55	-5.975	94
6.03	-6.070	24	6.02	-6.341	91
6.51	-6.437	20	6.54	-6.239	93
7.03	-7.214	58	7.01	-6.775	83
7.49	-6.561	29	7.48	-6.752	25

Table A.II. Continued

5-6 Days			13 Days		
pH	$\log m_{\text{Np}}$	% Np(IV)	pH	$\log m_{\text{Np}}$	% Np(IV)
7.99	-6.744	37	7.96	-6.940	88
8.47	-6.880	54	8.39	-6.976	85
8.81	-7.155	62	8.72	-7.214	81
9.24	-7.247	55	9.03	-7.557	74
9.64	-7.319	66	9.36	-7.342	73
10.18	-7.307	69	9.94	-7.206	78
10.78	-7.371	68	10.6	-7.243	77
11.87	-7.433	60	11.8	-7.284	76
12.98 ^a	-7.256	71	12.98 ^a	-7.360	72
13.82 ^b	-7.262	69	13.82 ^b	-7.262	71

^apH calculated by NONLIN from 0.125 *m* NaOH initially added to the solutions.

^bpH calculated by NONLIN from 1.00 *m* NaOH initially added to the solutions.

Table A.III. NpO₂(am) Solubility at pH Values of ~12 in 0.01 *M* Na₂S₂O₄ and as a Function of NaISA Concentrations

$\log m_{\text{ISA}}$	4 days		12 days		20 days	
	$\log m_{\text{Np}}$	% Np(IV) ^a	$\log m_{\text{Np}}$	% Np(IV)	$\log m_{\text{Np}}$	% Np(IV)
-3.699	-8.490	NL	-8.208	60	-8.092	46
-3.398	-8.227	73	-8.247	79	-7.845	68
-3.097	-8.051	77	-7.946	78	-7.706	73
-2.796	-7.666	89	-7.651	89	-7.305	83
-2.495	-7.365	87	-7.408	88	-7.028	92
-2.201	-7.137	94	-6.991	91	-6.058	95
-1.900	-6.604	92	-6.442	93	-8.155	97
-1.600	-5.929	91	-5.908	91	-5.516	98
-1.301	-5.077	98	-4.977	96	-4.571	98
-1.000	-4.758	95	-4.641	97	-4.294	96

^aNL represents a sample for which a value is not available.

Table A.IV. Solvent Extraction Data^a for Np(IV) from ISA Solutions in Different Concentrations of NaClO₄

$-\log m_{\text{H}}^{+}$	$\log m_{[\text{ISA}]t}^{\text{b}}$	$\log m_{[\text{Np(IV)]O}}^{\text{b}}$	$\log m_{[\text{Np(IV)]aq}}^{\text{b}}$	D	$\log m_{[\text{Np(IV)]n}}^{\text{b}}$
0.103 <i>m</i> NaClO ₄					
1.890	0.000	-4.887	-4.723	0.685	-5.836
1.897	-3.686	-5.134	-4.596	0.290	-5.462
1.899	-3.385	-5.301	-4.538	0.173	-5.238
1.905	-3.209	-5.432	-4.516	0.121	-5.084
1.908	-3.084	-5.531	-4.524	0.098	-4.993
1.914	-2.987	-5.638	-4.545	0.081	-4.908
1.919	-2.908	-5.687	-4.517	0.068	-4.830

Table A.IV. Continued

$-\log m_{\text{H}}^{+}$	$\log m_{[\text{ISA}]t}^b$	$\log m_{[\text{Np(IV)]O}}^b$	$\log m_{[\text{Np(IV)]aq}}^b$	D	$\log m_{[\text{Np(IV)]n}}^b$
1.930	-2.841	-5.779	-4.525	0.056	-4.746
1.932	-2.783	-5.811	-4.519	0.051	-4.708
1.940	-2.732	-5.875	-4.521	0.044	-4.647
1.941	-2.686	-5.916	-4.534	0.041	-4.618
0.53 <i>m</i> NaClO ₄					
1.840	0.000	-4.772	-4.726	0.901	-5.955
1.839	-3.674	-4.946	-4.638	0.492	-5.692
1.849	-3.197	-5.208	-4.563	0.227	-5.355
1.849	-3.072	-5.264	-4.549	0.192	-5.284
1.856	-2.975	-5.358	-4.523	0.146	-5.165
1.863	-2.896	-5.417	-4.499	0.121	-5.082
1.867	-2.829	-5.512	-4.513	0.100	-5.001
1.875	-2.771	-5.532	-4.508	0.095	-4.976
1.877	-2.719	-5.588	-4.505	0.083	-4.918
1.880	-2.674	-5.647	-4.478	0.068	-4.831
1.07 <i>m</i> NaClO ₄					
1.840	0.000	-5.004	-4.721	0.520	-5.716
1.839	-2.766	-5.496	-4.583	0.122	-5.087
1.840	-2.740	-5.530	-4.582	0.113	-5.052
1.840	-2.715	-5.542	-4.582	0.110	-5.040
1.847	-2.692	-5.581	-4.586	0.101	-5.004
1.851	-2.648	-5.616	-4.581	0.092	-4.965
1.857	-2.628	-5.604	-4.570	0.093	-4.966
1.868	-2.609	-5.619	-4.574	0.090	-4.954
1.879	-2.590	-5.634	-4.574	0.087	-4.940
1.881	-2.573	-5.650	-4.572	0.083	-4.922
1.886	-2.556	-5.701	-4.569	0.074	-4.867
2.22 <i>m</i> NaClO ₄					
1.7917	0.000	-4.761	-4.710	0.890	-5.949
1.7847	-3.654	-4.805	-4.643	0.689	-5.838
1.7867	-3.353	-4.856	-4.618	0.578	-5.762
1.7927	-3.177	-4.914	-4.619	0.508	-5.706
1.7947	-3.052	-4.930	-4.564	0.431	-5.634
1.8037	-2.875	-5.000	-4.547	0.352	-5.546
1.8197	-2.809	-5.050	-4.548	0.315	-5.498
1.8237	-2.751	-5.087	-4.561	0.298	-5.474
1.8287	-2.699	-5.129	-4.549	0.263	-5.420
1.8327	-2.654	-5.155	-4.526	0.235	-5.371
3.48 <i>m</i> NaClO ₄					
1.7275	0.000	-4.697	-4.661	0.919	-5.963
1.7275	-3.635	-4.736	-4.622	0.769	-5.886
1.7275	-3.333	-4.761	-4.595	0.684	-5.835
1.7305	-3.157	-4.785	-4.562	0.599	-5.777
1.7365	-3.032	-4.811	-4.568	0.572	-5.757
1.7415	-2.936	-4.845	-4.565	0.526	-5.721

Table A.IV. Continued

$-\log m_{\text{H}}^{+}$	$\log m_{[\text{ISA}]t}^b$	$\log m_{[\text{Np(IV)]O}}^b$	$\log m_{[\text{Np(IV)]aq}}^b$	D	$\log m_{[\text{Np(IV)]n}}^b$
1.7455	-2.856	-4.872	-4.547	0.474	-5.676
1.7615	-2.731	-4.914	-4.525	0.408	-5.611
1.7675	-2.680	-4.938	-4.498	0.364	-5.561
1.7755	-2.635	-4.978	-4.522	0.350	-5.544
4.91 <i>m</i> NaClO ₄					
1.642	0.000	-4.617	-4.675	1.143	-6.058
1.642	-3.609	-4.642	-4.644	1.003	-6.001
1.645	-3.308	-4.642	-4.619	0.947	-5.976
1.650	-3.132	-4.656	-4.623	0.928	-5.968
1.658	-2.910	-4.652	-4.614	0.917	-5.962
1.667	-2.831	-4.696	-4.610	0.820	-5.914
1.674	-2.764	-4.718	-4.631	0.818	-5.913
1.678	-2.655	-4.751	-4.594	0.698	-5.844
6.54 <i>m</i> NaClO ₄					
1.554	0.000	-4.605	-4.675	1.173	-6.069
1.553	-3.582	-4.611	-4.669	1.143	-6.058
1.554	-3.281	-4.613	-4.655	1.102	-6.042
1.571	-2.883	-4.626	-4.641	1.035	-6.015
1.577	-2.804	-4.639	-4.639	0.999	-6.000
1.585	-2.737	-4.676	-4.647	0.935	-5.971
1.597	-2.627	-4.666	-4.607	0.874	-5.941
1.605	-2.582	-4.687	-4.588	0.798	-5.902

^aExtraction with DBM in toluene using 1:1 volume ratio of aqueous to organic phases.

^b m_{xi} represents molality of the subscripted species *x* and the subscript *i* refers to total for *i* = t, organic phase for *i* = o, aqueous phase for *i* = aq, and normalized for *i* = n. The normalized Np(IV) aqueous molality $[m_{[\text{Np(IV)]n}}]$ was calculated by assuming $[\text{Np(IV)}]_0 = 1.0 \times 10^{-6}$ and then dividing this number by *D*, the distribution ratio $(m[\text{Np(IV)}]_O/m[\text{Np(IV)}]_{\text{aq}})$.

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