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THERMODYNAMIC MODELING OF NEPTUNIUM(V) SOLUBILITY IN CONCENTRATED Na-CO₃-HCO₃-Cl-ClO₄-H-OH-H₂O SYSTEMS, Craig F. Novak* and Kevin E. Roberts**

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ABSTRACT

Safety assessments of nuclear waste repositories often require estimation of actinide solubilities as a function of groundwater composition. Although considerable amounts of research has been done on the solubility and speciation of actinides,^{1,2} relatively little has been done to unify these data into a model applicable to concentrated brines. Numerous authors report data on the aqueous chemical properties of Np(V) in NaClO₄, Na₂CO₃, and NaCl media, but a consistent thermodynamic model for predicting these properties is not available. To meet this need, a model was developed to describe the solubility of Np(V) in Na-Cl-ClO₄-CO₃ aqueous systems, based on the Pitzer activity coefficient formalism for concentrated electrolytes. Hydrolysis and/or carbonate complexation are the dominant aqueous reactions with neptunyl in these systems. Literature data for neptunyl extraction and solubility, and solubility data that we developed, are used to parameterize an integrated model for Np(V) solubility in the Np(V)-Na-CO₃-HCO₃-Cl-ClO₄-H-OH-H₂O system. The resulting model is tested against additional solubility data, and compared with Np(V) solubility experiments in complex synthetic brines.

THE PITZER ACTIVITY COEFFICIENT MODEL

The Pitzer activity coefficient model³ is a semi-empirical formalism describing the thermodynamics of concentrated electrolyte systems. Model parameterizations exist for brine evaporite systems^{4,5} and, in a more limited fashion, for +III and +IV actinides in brines.^{6,7,8,9} The model is general enough to describe solutions from dilute to high concentration, and is formalized for complex electrolytes such as natural brines. Activity coefficients are represented by a virial expansion which, truncated to binary interactions, has the form

$$\ln \gamma_m = z_m^2 F + 2 \sum_{a=1}^{N_a} m_a B_{ma}(I) \quad \text{for cation "m"}$$

where F represents the Debye-Hückel term, N_a is the number of anions, and z_m is the charge on cation m . A similar expression holds for anions. The complete forms of the equations and extensive discussion are given elsewhere.^{3,4} The second virial coefficients $B_{ma}(I)$ are functions of the ionic strength, and are given by the relationship

$$B_{ma}(I) \equiv \beta_{ma}^{(0)} + \beta_{ma}^{(1)} g(\alpha_{ma}\sqrt{I}) + \beta_{ma}^{(2)} g(12\sqrt{I}) \quad \text{for cation "m," anion "a"}$$

where $\beta_{ma}^{(0)}$, $\beta_{ma}^{(1)}$, and $\beta_{ma}^{(2)}$ are parameters that are important at high, intermediate, and low ionic strength, respectively, and $g(y)$ is a decaying exponential function of the argument. When only the $\beta_{ma}^{(0)}$ coefficient is nonzero, this model is similar to SIT,¹⁰ although a species molality, not the total ionic strength, multiplies this coefficient. The following sections discuss the process of determining $\beta_{ma}^{(0)}$ and $\beta_{ma}^{(1)}$ values and standard chemical potentials for the Np(V) system.

DEVELOPING AND TESTING THE Np(V) SOLUBILITY MODEL

Brief descriptions of the data used to parameterize and test the model are given below. Data interpretation was performed using NONLIN;*† comparison of the parameterization with the

* NONLIN, developed by A.R. Felmy, uses the MINPACK nonlinear least-squares programs in combination with a chemical equilibrium program based on the Gibbs free-energy minimization procedure of Harvie et al.¹³

† Version MacNONLIN 94.05.13b for solubility and MacNONLINex 94.07.09 for extraction

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experimental data were made using either NONLIN or FMT[‡]. Selection of data sets for model development was based in part on endorsements in reviews or compilation for actinides.^{1,11,12} Experimental details can be found in the source reports; only brief descriptions are given here.

The general parameterization process begins with the least complex data sets, or data sets from which one can determine the fewest number of parameters. As each parameter is generated, it is tested whenever possible by comparison against independent data. When an acceptable fit is obtained, these parameter values are fixed and held constant through the remaining parameter determinations. The data sets used to parameterize and test the Np(V) solubility model are summarized in Table 1. Most of the data in Table 1 were taken at 25°C, although several of the experiments were at 20°C,¹⁴ as is the work first reported here. The slight temperature dependence of the equilibrium constants and Pitzer ion interaction parameters over this small temperature range were neglected in this study. In total, the model parameterization calculated eight standard chemical potentials and six ion interaction parameters. Fixed parameters from the literature are in Table 2; calculated standard chemical potentials and ion interaction parameters are in Table 3.

Neptunyl Interactions with Perchlorate and Chloride (Data Series P1, P2; T1, T2)

Data measuring the extraction of Np(V) with sodium dinonylnaphthalenesulfonate (NaDNNS) from 0.2 - 5M NaClO₄ or NaCl solutions¹⁵ were used to determine interaction parameters between NpO₂⁺ and ClO₄⁻, and NpO₂⁺ and Cl⁻. The experimental distribution coefficients $D = m_{\text{Np(o)}}/m_{\text{Np(aq)}}$ are shown in Fig. 1a along with the fitted models. Note that neither Cl⁻ nor ClO₄⁻ complexes were required to fit the data. These values are used to predict Np(V) extraction equilibria in NaCl/NaClO₄ mixtures at 2M total ionic strength¹⁶ and 5M total ionic strength,¹⁵ where D^0 is the measured distribution coefficient when no Cl⁻ is present. Fig. 1b shows that the model prediction compares quite well with experimental values.

Figure 1. Solvent extraction data of Np(V) with NaDNNS from (a) NaCl or NaClO₄ media,¹⁵ with the fitted model $\beta_{\text{NpO}_2^+-\text{ClO}_4^-}^{(0)} = 0.312$ and $\beta_{\text{NpO}_2^+-\text{Cl}^-}^{(0)} = 0.169$; (b) NaCl/NaClO₄ mixtures maintained at 2M and 5M constant ionic strength.^{16,15} Predicted lines use parameter values obtained in Fig. 1a.

Neptunyl Hydroxide Solids and Neptunyl Hydrolysis (Data Series P3; T3)

The solubility of NpO₂OH(am/aged) in 0.1, 1, and 3M NaClO₄ as a function of H⁺ concentration were investigated,^{17,18} and the data are plotted in Fig. 2. The solubility of NpO₂OH(aged) is lower than NpO₂OH(am), and the system shows amphoteric behavior. These data can be interpreted using the solubility and hydrolysis reactions

Because the solubility was determined in relatively high NaClO_4 concentrations, the data interpretation requires the ion interaction parameters for $\text{NpO}_2^+-\text{ClO}_4^-$, calculated in the previous section. Although these data, Fig. 2, represent two solid phases with different standard chemical potentials, the hydrolysis behavior is independent of the solid phase and thus must be the same for both. The "low" pH data ($\log(m_{\text{OH}^-}) < \sim -3$) were used to determine standard chemical potentials for the solid phases in Reactions 1 and 2, see Table 3. The agreement between the model and the solubility data at low pH values as a function of NaClO_4 concentration, Fig. 2, indicates that the $\beta^{(0)}$ value determined from solvent extraction data is reliable. The standard chemical potential for $\text{NpO}_2(\text{OH})_2^-$ was fitted from the high m_{OH^-} values where this species dominates; the standard chemical potential for $\text{NpO}_2\text{OH(aq)}$ was fitted from the intermediate m_{OH^-} values, also in Table 3. No ion interaction parameters between hydrolysis species and either Na^+ or ClO_4^- were required.

The reliability of the standard chemical potential for $\text{NpO}_2\text{OH(am)}$ and the Pitzer ion interaction parameter for NpO_2^+ with Cl^- determined above were tested using data that we measured for the solubility of $\text{NpO}_2\text{OH(am)}$ in NaCl solutions; see the Appendix for details. Good agreement between the measured and predicted solubility of $\text{NpO}_2\text{OH(am)}$ in NaCl solutions (Fig. 3) indicates that the values for $(\mu_f^\circ/\text{RT})_{\text{NpO}_2\text{OH(am)}}$ and $\beta_{\text{NpO}_2^+-\text{Cl}^-}^{(0)}$ are reliable.

Figure 2. Data^{17,18} used to calculate standard chemical potentials for neptunium hydroxide solid and hydrolysis species, and to build confidence in the value for $\beta_{\text{NpO}_2^+-\text{ClO}_4^-}^{(0)}$.

Figure 3. Experimental data and model predictions of $\text{NpO}_2\text{OH}(\text{am})$ solubility in NaCl solutions.

Standard Chemical Potentials for $\text{NaNpO}_2\text{CO}_3(\text{s})$, $\text{NpO}_2\text{CO}_3^-$, and $\text{NpO}_2(\text{CO}_3)_2^{3-}$; and Ion Interactions for $\text{Na}^+-\text{NpO}_2\text{CO}_3^-$ and $\text{Na}^+-\text{NpO}_2(\text{CO}_3)_2^{3-}$ (Data Series P4, P5; T5, T6)

Neptunyl complexation with carbonate and the solubility of $\text{NaNpO}_2\text{CO}_3(\text{s})$ in several media under different conditions have been reported by various authors.^{14,15,19,20,21} These data were used to develop and test the model for neptunyl complexation with carbonate. The bulk of the data was taken at constant $\text{CO}_2(\text{g})$ pressure in 0.1, 1.0, 3.0, and 5.0M NaClO_4 (Neck et al.¹⁵; Kim et al.²⁰), although Maya²¹ reported solubility both in solutions with fixed total inorganic carbon and with fixed $\text{CO}_2(\text{g})$ partial pressure. During analysis, a discrepancy of up to 1.1 log units was noted in some of the data^{15,20} between the reported hydrogen ion and carbonate concentrations and the Harvie-Møller-Weare model⁴ predictions. This may indicate the need for improved models describing the solubility of $\text{CO}_2(\text{g})$ in NaClO_4 media, or a lack of equilibrium between the CO_2 in the gas and aqueous phases. This discrepancy rendered it unrealistic to use pH/pcH values and fixed $\text{CO}_2(\text{g})$ pressures for parameterization, thus the reported carbonate concentrations were considered primary data. This interpretation is reasonable because the data of Maya,²¹ in which Np(V) solubilities were measured both for fixed solution composition and solutions in equilibrium with a gas phase, overlie the data from Kim et al.²⁰ for 1.0M NaClO_4 solutions. These data, plotted in Fig. 4, were used to calculate thermodynamic parameters for $\text{NaNpO}_2\text{CO}_3(\text{s})$, $\text{NpO}_2\text{CO}_3^-$, and $\text{NpO}_2(\text{CO}_3)_2^{3-}$. The behavior of neptunyl in the presence of carbonate can be described by the reactions

Data for $\log(m_{\text{CO}_3^{2-}}) < \sim -5$, where Reaction 5 dominates,⁸ were used to determine the standard chemical potential of the solid, and to test the value for $\beta_{\text{NpO}_2^+-\text{ClO}_4^-}$. The mono- and di-carbonato species dominate in the intermediate carbonate concentration range, $\sim -5 < \log(m_{\text{CO}_3^{2-}}) < \sim -2.5$; these data were used to calculate $(\mu_i^0/\text{RT})_{\text{NpO}_2\text{CO}_3^-}$, $(\mu_i^0/\text{RT})_{\text{NpO}_2(\text{CO}_3)_2^{3-}}$, and the binary ion interaction parameters $\beta_{\text{Na}^+-\text{NpO}_2\text{CO}_3^-}^{(0)}$ and $\beta_{\text{Na}^+-\text{NpO}_2(\text{CO}_3)_2^{3-}}^{(0)}$. These parameter values were tested against

extraction data,¹⁹ producing the favorable comparison shown in Fig. 5. The region where $\log(m_{\text{CO}_3^{2-}}) > \sim -2.5$ is discussed in the following section.

Figure 4. Data^{15,20,21} for parameterizing and testing the model for neptunyl-carbonate reactions.

Figure 5. Comparison of model with data¹⁹ for extraction of neptunyl carbonate complexes in 1.0M NaClO₄.

Standard Chemical Potential for $\text{NpO}_2(\text{CO}_3)_3^{5-}$ and $\text{Na}^+-\text{NpO}_2(\text{CO}_3)_3^{5-}$ Ion Interactions (Data Series P6; T7)

Calculating thermodynamic parameters for the neptunyl triscarbonato species requires data extending to high carbonate concentration. Ueno and Saito¹⁴ examined the solubility of $\text{NaNpO}_2\text{CO}_3(\text{s})$ in 0.05 to 1.6M Na_2CO_3 solutions. Although $\text{Na}_3\text{NpO}_2(\text{CO}_3)_2(\text{s})$ has been reported to be the stable phase in these high concentration ranges,¹¹ $\text{NaNpO}_2\text{CO}_3(\text{s})$ was most probably the metastable equilibrium solid over the reported one to two day equilibration period. Assuming the $\text{NaNpO}_2\text{CO}_3(\text{s})$ solid phase, and using the thermodynamic parameters previously developed in this paper, these solubility data are well represented

by the triscarbonato species from Reaction 8 and the ion interaction parameters $\beta_{\text{Na}^+-\text{NpO}_2(\text{CO}_3)_3^{5-}}^{(0)}$ and $\beta_{\text{Na}^+-\text{NpO}_2(\text{CO}_3)_3^{5-}}^{(1)}$, as shown by the comparison in Fig. 6. The predicted solubilities of $\text{NaNpO}_2\text{CO}_3(\text{s})$ in NaClO_4 solutions are consistent with the data sets given in Fig. 4 for $\log(m_{\text{CO}_3^{2-}}) > \sim -2.5$, where the species $\text{NpO}_2(\text{CO}_3)_3^{5-}$ is also important. Thus the solid phase identified by Ueno and Saito is supported, and the values for the neptunyl triscarbonato complex can be calculate from these data. Although $\text{NpO}_2(\text{CO}_3)_3^{3-}$ never dominates under the conditions of Fig. 6, this species is dominant under the conditions of Fig. 4 for $\sim -4 < \log(m_{\text{CO}_3^{2-}}) < \sim -2$.

Figure 6. Data¹⁴ and model fit of $\text{NaNpO}_2\text{CO}_3(\text{s})$ solubility in Na_2CO_3 solutions.

Reactions 1 through 4, are $\log K_{\text{sp}} = -8.72$, $\log K_{\text{sp}} = -9.32$, $\log \beta_{101} = 2.58$, and $\log \beta_{102} = 4.27$, respectively; the thermodynamic equilibrium constants for the carbonate system, Reactions 5 through 8, are $\log K_{\text{sp}} = -11.3$, $\log \beta_{101} = 5.39$, $\log \beta_{102} = 5.81$, and $\log \beta_{103} = 5.19$, respectively. Comparison with parameter values reported for 1-1, 3-1, and 5-1 electrolytes²² show that all the values for activity coefficient parameters are reasonable, e.g., our calculated value for the 5:1 electrolyte $\beta_{\text{Na}^+ - \text{NpO}_2(\text{CO}_3)_3}^{(1)} = 16$ compares favorably with the value $\beta_{\text{Na}^+ - \text{P}_3\text{O}_{10}}^{(1)} = 21.66$ of Pitzer.²²

TESTING THE PREDICTIVE ABILITY OF THE MODEL

Although the model explains many simple data sets, additional testing of the model is necessary to generate confidence that the model can predict total dissolved Np(V) concentrations in complex natural systems. Two comparisons are given here to provide some confidence in this model, and indicate some directions for future work.

Most of the data used to develop this model were obtained in NaClO_4 media; little data in NaCl media were available. However, in natural systems, NaCl is likely to be the dominant electrolyte, and thus it is essential to establish the applicability of this model to sodium chloride solutions. Then, is it possible that the solubility behavior of Np(V) in more complex natural brines, e.g., containing small amounts of K-Mg-Ca-SO_4 , can be approximated by this model. These points are tested against additional experimental data.

The solubility of $\text{NaNpO}_2\text{CO}_3(\text{s})$ is reported¹⁵ as a function of pH in 5M NaCl at constant $\log P_{\text{CO}_2(\text{g})}$ of -3.5 . In contrast with these authors' similar data in NaClO_4 , the reported hydrogen ion and carbonate concentrations are consistent with the Harvie-Møller-Weare model.⁴ Thus the system can be modeled as open to the gas phase. A comparison of these data with the model developed above is presented in Fig. 7 along with calculated species concentrations. The model follows the trend of the data quite well, especially for high carbonate concentrations, but is offset for lower carbonate concentrations, particularly in the region where the mono- and dicarbonato species dominate. Although this may indicate that additional species are necessary to describe this system, there was no need to invoke neptunyl chloride species to describe the simpler experimental systems above. Possible reasons for the discrepancy between the observed and calculated concentrations, include: (1) the standard chemical potential may be different for this solid phase; (2) additional specific ion interaction parameters, e.g., $\text{NpO}_2^+ - \text{Na}^+ - \text{Cl}^-$ or $\text{NpO}_2\text{CO}_3^- - \text{Cl}^-$, may be required; or (3) equilibrium may not have been attained. Additional experiments at

DISCUSSION OF MODEL AND PARAMETERS

The model developed here is a comprehensive, unified description of Np(V) solubility behavior in $\text{Na-CO}_3\text{-Cl-ClO}_4$ media. The model is based on the formation of important aqueous species and binary cation-anion interactions between neptunyl species and bulk solution ions. The model is a synthesis of, and explains, nine different data sets representing two types of experiments. Model species and parameters are summarized in Tables 3 and 4. The thermodynamic equilibrium constants for the hydrolysis system,

different NaCl concentrations in NaCl/Na₂CO₃ media are needed to refine the values for ion interaction parameters for this system.

Figure 7. Comparison of model with $\text{NaNpO}_2\text{CO}_3(\text{s})$ solubility data¹⁵ in 5M NaCl.

A further test of this model is comparison with solubility measurements in complex synthetic brines. Oversaturation experiments with $^{237}\text{Np}(\text{V})$ were conducted in the brines listed in Table 5. These ongoing experiments are similar to others conducted with Pu in these same brines.²³ Sufficient neptunyl was added to cause oversaturation and precipitation of a neptunium solid phase. The operational hydrogen ion concentration was controlled within ± 0.1 units, and the aqueous neptunium concentration was monitored. An approximate steady-state aqueous concentration was reached after about 400 days. The solid phases were characterized by X-ray diffraction as $\text{NaNpO}_2\text{CO}_3(\text{s})$. These brines are predominantly sodium chloride (Table 4), so previous electrode titrations, as discussed in the Appendix, were used as pH/pcH calibrations. The measured total dissolved Np(V) concentration in AISinR Brine at $-\log(m_{\text{H}^+}) = 7.7 \pm 0.2$ is 2×10^{-6} molal; the model predicts 6×10^{-6} to 2×10^{-5} molal. The measured total dissolved Np(V) concentration in H-17 Brine at $-\log(m_{\text{H}^+}) = 7.8 \pm 0.2$ is 1×10^{-6} molal; the model predicts 2×10^{-6} to 3×10^{-6} molal. The comparison is very good, with an order of magnitude or less difference between the measured and calculated values. Although more data in complex brines are required to support the model, this work suggests that this building block approach will prove successful for predicting dissolved neptunyl concentrations in complex brines.

CONCLUDING REMARKS

The Np(V) solubility model developed here explains many different data sets from different types of experiments. As such, it appears to be robust and may be usable to obtain order-of-magnitude estimates of neptunium solubility in predominantly NaCl groundwaters. Additional experimental measurement of Np(V) chemistry in NaCl/Na₂CO₃ media would allow refinement of the model and improve the predictive ability in high chloride systems.

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APPENDIX

Green $\text{NpO}_2\text{OH}(\text{am})$ was synthesized¹⁷ and added to 0.3, 0.6, 1.0, 1.8, 3.0, and 5.6m NaCl solutions and allowed to react for 37 days. Experiments, including solution preparations, were performed in an argon atmosphere glove box using freshly distilled, deionized water to avoid introduction of carbon dioxide. No conversion to $\text{NpO}_2\text{OH}(\text{aged})$ was noted, although this conversion was seen in concentrated NaClO_4 within this time span¹⁷. Phases were separated by filtering aliquots of solution through presaturated 4.1 nm filters (Amicon Corp., Danvers, MA). Aqueous neptunium concentrations were determined by γ -pulse height analysis of the 29.38 keV gamma emission from the ^{237}Np in the supernatant. Hydrogen ion concentrations were measured using a Ross combination pH electrode (Orion Research Inc., Boston, MA) at the time of each assay. The operational pH read by the glass electrode was related to the actual proton concentration in each NaCl solution by earlier potentiometric titration of standardized solutions of HCl with NaOH, both adjusted to the desired NaCl concentration.

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Table 1. Experimental systems used to parameterize (P) and test (T) the Np(V) solubility model. A single value was determined for each of the fourteen parameters using data in the P series. These values were tested as often as appropriate against the data listed as the T series. The final two experimental systems provided an overall comparison of the model with data.

P/T	System	Medium	Type	Parameters Calculated	Ref.
P1	$\text{NpO}_2^+-\text{Cl}^-$	0.2 - 5.0M NaCl	extr	$\beta_{\text{NpO}_2^+-\text{Cl}^-}^{(0)}$	15
P2	$\text{NpO}_2^+-\text{ClO}_4^-$	0.2 - 5.0M NaClO ₄	extr	$\beta_{\text{NpO}_2^+-\text{ClO}_4^-}^{(0)}$	15
P3	$\text{NpO}_2\text{OH}(\text{am})$, $\text{NpO}_2\text{OH}(\text{aged})$; $\text{NpO}_2^+-\text{OH}^-$	0.1, 1, 3M NaClO ₄	sol	$(\mu_f^\circ/\text{RT})_{\text{NpO}_2\text{OH}(\text{aq})}$; $(\mu_f^\circ/\text{RT})_{\text{NpO}_2(\text{OH})_2^-}$; $(\mu_f^\circ/\text{RT})_{\text{NpO}_2\text{OH}(\text{am})}$; $(\mu_f^\circ/\text{RT})_{\text{NpO}_2\text{OH}(\text{aged})}$	17, 18
P4	$\text{NpO}_2^+-\text{CO}_3^{2-}$	0.1, 1.0, 3.0, 5.0M NaClO ₄ ; $\log(m_{\text{CO}_3^{2-}}) < \sim -5$	sol	$(\mu_f^\circ/\text{RT})_{\text{NaNpO}_2\text{CO}_3(\text{s})}$	15, 20, 21
P5	$\text{NpO}_2^+-\text{CO}_3^{2-}$	0.1, 1.0, 3.0, 5.0M NaClO ₄ ; $\sim -5 < \log(m_{\text{CO}_3^{2-}}) < \sim -2.5$	sol	$(\mu_f^\circ/\text{RT})_{\text{NpO}_2\text{CO}_3^-}$, $\beta_{\text{Na}^+-\text{NpO}_2\text{CO}_3^-}^{(0)}$; $(\mu_f^\circ/\text{RT})_{\text{NpO}_2(\text{CO}_3)_2^{3-}}$; $\beta_{\text{Na}^+-\text{NpO}_2(\text{CO}_3)_2^{3-}}^{(0)}$	15, 20, 21
P6	$\text{NpO}_2^+-\text{CO}_3^{2-}$	0.05 - 1.6M Na ₂ CO ₃	sol	$(\mu_f^\circ/\text{RT})_{\text{NpO}_2(\text{CO}_3)_3^{5-}}$; $\beta_{\text{Na}^+-\text{NpO}_2(\text{CO}_3)_3^{5-}}^{(0)}$, $\beta_{\text{Na}^+-\text{NpO}_2(\text{CO}_3)_3^{5-}}^{(1)}$	14

	System	Medium	Type	Parameters Tested	Ref.
T1	$\text{NpO}_2^+-\text{Cl}^-$	5.0M NaCl/NaClO ₄ mixtures	extr	$\beta_{\text{NpO}_2^+-\text{Cl}^-}^{(0)}$, $\beta_{\text{NpO}_2^+-\text{ClO}_4^-}^{(0)}$	15
T2	$\text{NpO}_2^+-\text{Cl}^-$	2.0M NaCl/NaClO ₄ mixtures	extr	$\beta_{\text{NpO}_2^+-\text{Cl}^-}^{(0)}$, $\beta_{\text{NpO}_2^+-\text{ClO}_4^-}^{(0)}$	16
T3	$\text{NpO}_2\text{OH}(\text{am})$, $\text{NpO}_2\text{OH}(\text{aged})$	0.1, 1, 3M NaClO ₄	sol	$\beta_{\text{NpO}_2^+-\text{ClO}_4^-}^{(0)}$	17, 18
T4	$\text{NpO}_2\text{OH}(\text{am})$ solubility	0.3 - 5.6 m NaCl	sol	$\beta_{\text{NpO}_2^+-\text{Cl}^-}^{(0)}$, $(\mu_f^\circ/\text{RT})_{\text{NpO}_2\text{OH}(\text{am})}$	this work
T5	$\text{NpO}_2^+-\text{CO}_3^{2-}$	0.1, 1.0, 3.0, 5.0M NaClO ₄ ; $\log(m_{\text{CO}_3^{2-}}) < \sim -5$	sol	$\beta_{\text{NpO}_2^+-\text{ClO}_4^-}^{(0)}$	15, 20, 21
T6	$\text{NpO}_2^+-\text{CO}_3^{2-}$	1M NaClO ₄	extr	$(\mu_f^\circ/\text{RT})_{\text{NpO}_2\text{CO}_3^-}$, $\beta_{\text{Na}^+-\text{NpO}_2\text{CO}_3^-}^{(0)}$; $(\mu_f^\circ/\text{RT})_{\text{NpO}_2(\text{CO}_3)_2^{3-}}$; $\beta_{\text{Na}^+-\text{NpO}_2(\text{CO}_3)_2^{3-}}^{(0)}$	19
T7	$\text{NpO}_2^+-\text{CO}_3^{2-}$	0.1, 1.0, 3.0, 5.0M NaClO ₄ ; $\log(m_{\text{CO}_3^{2-}}) > \sim -2.5$	sol	$(\mu_f^\circ/\text{RT})_{\text{NpO}_2(\text{CO}_3)_3^{5-}}$, $\beta_{\text{Na}^+-\text{NpO}_2(\text{CO}_3)_3^{5-}}^{(0)}$; $\beta_{\text{Na}^+-\text{NpO}_2(\text{CO}_3)_3^{5-}}^{(1)}$	15, 20, 21

	System	Medium	Type	Overall Comparison	Ref.
	$\text{NpO}_2^+-\text{CO}_3^{2-}$	5.0M NaCl	sol	for comparison with model	15
	Np(V) in complex synthetic brines	0.8 and 3.0 Ionic Strength	sol	for comparison with model	this work

Table 2. Fixed parameters for model fitting (from Harvie et al.⁴ unless otherwise noted).

Standard Chemical Potentials					
Species	μ_f^0/RT	Species	μ_f^0/RT	Species	μ_f^0/RT
H ₂ O	-95.6635	ClO ₄ ⁻	-73.805 [24]	HCO ₃ ⁻	-236.751
H ⁺	0.0	Cl ⁻	-52.955	CO ₃ ²⁻	-212.944
OH ⁻	-63.435	CO ₂ (aq)	-155.68	NpO ₂ ⁺	-369.127 [25]
Na ⁺	-105.651				

Binary Electrolyte Parameters							
	$\beta^{(0)}$	$\beta^{(1)}$	C [‡]		$\beta^{(0)}$	$\beta^{(1)}$	C [‡]
Na ⁺ -OH ⁻	0.0864	0.253	0.0044	Na ⁺ -Cl ⁻	0.0765	0.2664	0.00127
Na ⁺ -ClO ₄ ⁻	0.0554 [26]	0.2755 [26]	-0.00118 [26]	H ⁺ -Cl ⁻	0.1775	0.2945	0.0008
Na ⁺ -CO ₃ ²⁻	0.0399	1.389	0.0044	H ⁺ -ClO ₄ ⁻	0.1747 [26]	0.2931 [26]	0.00819 [26]
Na ⁺ -HCO ₃ ⁻	0.0277	0.0411	0				

Ternary Electrolyte Parameters					
Na ⁺ -H ⁺	0.036	Cl ⁻ -CO ₃ ²⁻	-0.02	OH ⁻ -CO ₃ ²⁻	0.10
Na ⁺ -H ⁺ -ClO ₄ ⁻	-0.016 [26]	Cl ⁻ -CO ₃ ²⁻ -Na ⁺	0.0085	OH ⁻ -CO ₃ ²⁻ -Na ⁺	-0.017
Na ⁺ -H ⁺ -Cl ⁻	-0.004	Cl ⁻ -HCO ₃ ⁻	0.03	CO ₃ ²⁻ -HCO ₃ ⁻	-0.04
Cl ⁻ -OH ⁻	-0.050	Cl ⁻ -HCO ₃ ⁻ -Na ⁺	-0.015	CO ₃ ²⁻ -HCO ₃ ⁻ -Na ⁺	0.002
Cl ⁻ -OH ⁻ -Na ⁺	-0.006				

Neutral Ion Parameters			
Na ⁺ -CO ₂ (aq)	0.100	Cl ⁻ -CO ₂ (aq)	-0.005

Table 3. Standard chemical potentials for neptunyl species calculated in this paper

Species	μ_f^0/RT	Species	μ_f^0/RT
NpO ₂ OH(am)	-452.642	NaNpO ₂ CO ₃ (s)	-713.707
NpO ₂ OH(aged)	-454.010	NpO ₂ CO ₃ ⁻	-594.492
NpO ₂ OH(aq)	-438.518	NpO ₂ (CO ₃) ₂ ³⁻	-808.403
NpO ₂ (OH) ₂ ⁻	-505.829	NpO ₂ (CO ₃) ₃ ⁵⁻	-1019.918

Table 4. Pitzer parameters calculated in this paper

$\beta_{\text{NpO}_2^+ \text{ClO}_4^-}^{(0)}$	0.312	$\beta_{\text{Na}^+ \text{NpO}_2 \text{CO}_3^-}^{(0)}$	0.161	$\beta_{\text{Na}^+ \text{NpO}_2 (\text{CO}_3)_3^{5-}}^{(0)}$	1.97
$\beta_{\text{NpO}_2^+ \text{Cl}^-}^{(0)}$	0.169	$\beta_{\text{Na}^+ \text{NpO}_2 (\text{CO}_3)_2^{3-}}^{(0)}$	0.407	$\beta_{\text{Na}^+ \text{NpO}_2 (\text{CO}_3)_3^{5-}}^{(1)}$	16

Table 5. Compositions of synthetic brines in Np(V) solubility experiments

molal concentrations	AlSinR	H-17
Na ⁺	0.643	2.54
K ⁺	0.00820	0.0325
Mg ²⁺	0.0215	0.0783
Ca ²⁺	0.0171	0.0306
Cl ⁻	0.580	2.64
SO ₄ ²⁻	0.0796	0.0793
B	0.00279	0.00421
Br ⁻	0	0.00101
Ionic Strength	0.841	2.97
logP _{CO₂(g)}	-2.71	-2.56

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