Thermodynamic Modeling of Neptunium(V)-Acetate Complexation in Concentrated NaCl Media.

Craig F. Novak¹, Marion Borkowski², and Gregory R. Choppin³

Abstract

The complexation of neptunium(V), Np(V), with the acetate anion, Ac⁻, was measured in sodium chloride media to high concentration using an extraction technique. The data were interpreted using the thermodynamic formalism of Pitzer, which is valid to high electrolyte concentrations. A consistent model for the deprotonation constants of acetic acid in NaCl and NaClO₄ media was developed. For the concentrations of acetate expected in a waste repository, only the neutral complex NpO₂Ac(aq) was important in describing the interactions between the neptunyl ion and acetate. The thermodynamic stability constant $\log \beta_{101}^0$ for the reaction $\text{NpO}_2^+ + \text{Ac}^- \leftrightarrow \text{NpO}_2\text{Ac}$ was calculated to be 1.46 ± 0.11 . This weak complexing behavior between the neptunyl ion and acetate indicates that acetate will not significantly enhance dissolved Np(V) concentrations in ground waters associated with nuclear waste repositories that may contain acetate.

Introduction

The Waste Isolation Pilot Plant (WIPP), a proposed repository for transuranic (TRU) wastes, is situated in bedded evaporite salts of Permian age. Associated with the various geologic layers important to the WIPP performance assessment are natural Na-K-Mg-Ca-Cl-SO₄-CO₃-B brines ranging in concentration to as high as ten times that of sea water. Under the design basis, the TRU wastes intended for the WIPP will not be reprocessed, and as such may contain organic anions such as acetate, citrate, oxalate, lactate, and ethylenediaminetetraacetic acid (EDTA). Estimates of the quantities of these ligands in the design-basis waste suggest that these ligands

¹ Sandia National Laboratories, MS 1320, P.O. Box 5800, Albuquerque, New Mexico 87185-1320 USA

² on leave, Institute of Nuclear Chemistry and Technology, Department of Radiochemistry, Dorodna SL 16, 03-195 Warsaw, Poland

³ Florida State University, Department of Chemistry, Tallahassee, Florida 32306-3006 USA

may be present in concentrations up to 0.01 Molar (Brush, 1990). It has been suggested that such concentrations of these ligands may significantly increase potential dissolved actinide concentrations and impact repository compliance with the applicable environmental regulations.

The WIPP has instituted a research program examining the potential of the above organic ligands to increase the concentrations of Am(III), Th(IV), Np(V), and U(VI) in concentrated electrolytes. This paper documents Np(V)-acetate interactions. The papers Chen and Choppin (1995) and Choppin et al. (1995), and Borkowski et al. (1995) document similar work on other actinides and organic ligands. In addition to examining the enhancement of actinide solubility caused by complexation with organic ligands, the program is also examining the competition of Mg^{2+} with the actinides for complexing organic ligands in concentrated NaCl systems. The goal of this program is a comprehensive thermodynamic model of the complexation of the actinides Am(III), Th(IV), Np(V), and U(VI) with the organic anions acetate, citrate, oxalate, lactate, and EDTA in dilute to concentrated NaCl and $MgCl_2/NaCl$ solutions. The stability constants for Pu(III), Pu(IV), Pu(V), and Pu(VI) with these ligands will be estimated from the actinide oxidation state analogs.

Experimental

1) Chemicals

Analytical grade sodium chloride (Fisher Lot 940518) and sodium acetate (NaAc) (Fisher lot 880514) were used with no additional purification. Distilled deionized water (E-Pure, Barustead) was used for all aqueous solutions. Di(2-ethylhexyl)phosphoric acid, HDEHP (minimum 95%) was obtained from Sigma (Lot 72H0681) and purified according to the procedure in McDowell et al. (1976). An extractant was prepared as n-heptane HDEHP solution with concentration $9.52 \times 10^{-3} M$ ($1.4 \times 10^{-2} m$, $d=0.68 g/ml$). ^{237}Np tracer was obtained from Oak Ridge National Laboratory and was purified by ion exchange method with Dowex 1 $\times$ 4. The oxidation state of Np was verified as Np(V) using spectrophotometry. The active daughter ^{233}Pa was removed by extraction from the tracer $^{237}NpO_2^+$ solution prior to the extraction experiments.

DISCLAIMER

Portions of this document may be illegible in electronic image products. Images are produced from the best available original document.

2) Extraction Procedure

Two series of solutions were prepared with stoichiometric ionic strengths of 0.30, 1.00, 2.00, 3.00, 4.00, and 5.00 m. The first series contained 0.15 m NaAc with the balance of the ionic strength from NaCl; the second series contained only NaCl. Fixed volumes of solutions of the same ionic strength were mixed to obtain various concentrations of acetate ion. The organic phase was preequilibrated over a NaCl solution at the ionic strength corresponding to the aqueous phase containing the acetate ion, and the pH_r , i.e., the meter reading, was adjusted to 5.0 ± 0.1 . All solutions were filtered through a Nalgene Disposable Filter (0.2 μm pore size). Into the vial containing 5.0 ± 0.1 ml of the aqueous solution with the $^{237}\text{NpO}_2^+$, 5.0 ± 0.1 mL of the extractant was added and shaken in a thermostated shaker at $25 \pm 0.5^\circ\text{C}$ for 2 hours. The extraction vials were centrifuged for 3 minutes; 1.00 ± 0.01 mL duplicate aliquots from the organic and aqueous phases were removed into 10 mL of Ecolume scintillation cocktail for alpha counting. A TriCarb 4000 Liquid Scintillation Counter (Packard) was used for measurements. After extraction, pH_r was measured in each aqueous solution.

3) pH_r vs pcH Calibration

A research pH meter (Accumet 950, Fischer Scientific) was used with a combination glass electrode. The KCl solution in the salt bridge was replaced with 5m NaCl. The electrode was calibrated with 4.01 ± 0.01 and 7.00 ± 0.01 NIST traceable standard pH buffers. The pH readings (pH_r) were converted to hydrogen ion concentrations in Molar units (pcH) using calibration curves obtained by a series of HCl or HClO_4 dilutions in NaCl or NaClO_4 , respectively, in a modified Gran titration method (Gran, 1950; 1952). This work resulted in the correlation $\text{pcH} = \text{pH}_r + 0.255m_{\text{NaCl}}$ for our electrode.

Thermodynamic Model and Data Base

The activity coefficient model of Pitzer (1991) is a semi-empirical formalism that successfully describes the chemical behavior of concentrated electrolyte systems. Model parameterizations exist for brine evaporite systems (Harvie et al., 1984; Felmy and Weare, 1986),

and the Pitzer formalism is increasingly being used to interpret and describe the chemical behavior of +III, +IV, and +V actinides in concentrated electrolytes (Fanghänel et al., 1995; Felmy et al., 1989; 1990; 1991; Felmy and Rai, 1992; Neck et al., 1995; Novak et al., 1995; Novak and Roberts, 1995). The model is general enough to describe systems from dilute to high concentration, and is formalized for complex background electrolytes such as natural brines. Activity coefficients are represented by a virial expansion with the following form when truncated to include only cation-anion interactions:

$$\ln \gamma_m = z_m^2 F + \sum_{a=1}^{N_a} m_a (2 B_{ma}(I) + \left(\sum_{i=1}^N |z_i| m_i \right) C_{ma}) + |z_m| \sum_{c=1}^{N_c} \sum_{a=1}^{N_a} m_c m_a C_{ca} \quad (1)$$

for cation "m" with the general cations and anions represented by "c" and "a" respectively, and where F represents the Debye-Hückel term. A similar expression holds for anions. The complete forms of the equations and extensive discussion are given elsewhere (see for example, Harvie et al., 1984). The second virial coefficients $B_{ma}(I)$ are given by the relationship

$$B_{mx}(I) \equiv \beta_{mx}^{(0)} + \beta_{mx}^{(1)} g(\alpha_{1mx} \sqrt{I}) + \beta_{mx}^{(2)} g(\alpha_{2mx} \sqrt{I}) \quad (2)$$

The constants α_{1mx} and α_{2mx} have the values 2.0 and 12 for 1-($n \geq 1$) electrolytes, 1.4 and 12 for 2-2 electrolytes, and 1.4 and 50 for 2-($n \geq 3$) electrolytes, respectively. The parameters $\beta_{mx}^{(0)}$, $\beta_{mx}^{(1)}$, and $\beta_{mx}^{(2)}$ are important at high, intermediate, and low ionic strength, respectively, and $g(y)$ is a decaying exponential function of the argument. The third virial coefficients C_{mx} are related to the usually tabulated value C_{mx}^ϕ by

$$C_{mx}^\phi = 2 \sqrt{|z_m| |z_x|} C_{mx} \quad (3)$$

The concentration dependence of the activity coefficient for neutral species is

$$\ln \gamma_N = \sum_c m_c + \sum_a \lambda_{Na} m_a + \sum_c \sum_a \zeta_{Nca} \quad (4)$$

(Felmy and Weare, 1986), where λ_{Nc} and λ_{Na} are neutral-cation and neutral-anion interaction parameters, respectively, and ζ_{Nca} is a neutral-cation-anion interaction parameter.

Parameters for use with the Pitzer equations are not unique; different sets of parameters can be used to provide an identical description of the same data (see the discussion for the deprotonation model for acetic acid below for an illustration). Therefore, it is imperative that parameters are not mixed and matched indiscriminately. Judicious selection of new parameters and careful referencing to a specified "base" model is required. For this and other work for the Waste Isolation Pilot Plant (WIPP) Actinide Source Term Program, the data base developed by Harvie et al. (1984) and extended in Felmy and Weare (1986) is the reference base model. Parameter values from Harvie et al. (1984) and Felmy and Weare (1986) are used in the process of fitting all new experimental data and calculating parameter values for new species and ion interactions. This process ensures that the new parameters are consistent with and can be used in combination with the reference data base. The standard chemical potentials and ion interaction parameters from this data base needed for constructing the Np(V)-Ac complexation model are given in Table 1.

Model for Deprotonation of Acetic Acid in NaCl and NaClO₄ Media

A reliable model for the deprotonation of acetic acid in dilute to concentrated NaCl is required to interpret Np(V) complexation behavior with acetate in NaCl media. The necessary thermodynamic parameters are the standard chemical potentials $\mu_f^0(\text{HAc(aq)})$ and $\mu_f^0(\text{Ac}^-)$ and ion interaction parameters with acetate, including the cation-anion parameters $\beta_{\text{NaAc}}^{(0)}$, $\beta_{\text{NaAc}}^{(1)}$, and C_{NaAc}^ϕ ; the anion-anion parameters θ_{ClAc} and $\theta_{\text{ClO}_4\text{Ac}}$; the anion-anion-cation

parameters ψ_{ClAcNa} and $\psi_{\text{ClO}_4\text{AcNa}}$; the neutral-ion interaction parameters $\lambda_{\text{HAc(aq),Na}}$, $\lambda_{\text{HAc(aq),Cl}}$, and $\lambda_{\text{HAc(aq),ClO}_4}$; and the neutral-cation-anion parameters $\zeta_{\text{HAc(aq),c,a}}$.

A model for the ionization of acetic acid in NaCl(aq) media is given by Mesmer et al. (1989). For 25°C, the parameters in this model are

$$2\beta_{\text{NaAc}}^{(0)} + 2\theta_{\text{HNa}} + 2\theta_{\text{ClAc}} - \delta = 0.1777 \quad (5)$$

$$\beta_{\text{NaAc}}^{(1)} = 0.22 \quad (6)$$

$$C_{\text{NaAc}}^{\phi} + \psi_{\text{HNaCl}} + \psi_{\text{NaClAc}} = 0 \quad (7)$$

$$K_{a1} = 10^{-4.757} \quad (\text{Mesmer et al., 1989}) \quad (8)$$

where δ is the Setchenow coefficient, equivalent to a linear combination of $\lambda_{\text{HAc(aq),Na}}$ and $\lambda_{\text{HAc(aq),Cl}}$.

The standard chemical potential for HAc(aq) is -392 kJ/mole (Weast, 1980), or $\frac{\mu_f^0(\text{HAc(aq)})}{RT} = -158.3$. From this value and the equilibrium constant, Equation 8, the dimensionless standard chemical potential of the acetate ion is calculated to be $\frac{\mu_f^0(\text{Ac}^-)}{RT} = -147.347$.

The parameters in Equations 5 and 7 cannot be determined independently from the presentation in Mesmer et al. (1989). Indeed, every set of values satisfying the linear combinations of Equations 5 to 7 will result in an identical prediction of the HAc(aq) deprotonation behavior in NaCl media, and thus any set is arguably as good as any other. However, the parameters θ_{ClAc} and ψ_{NaClAc} are not used for describing the HAc(aq) deprotonation behavior in NaClO₄ media, for example, which would instead have the analogous parameters $\theta_{\text{ClO}_4\text{Ac}}$ and $\psi_{\text{NaClO}_4\text{Ac}}$. The differences in chemical behavior in the different media may provide an indication of the generality of the chosen parameter set, as illustrated in the application of this model to NaClO₄ media.

Values for θ_{HNa} and ψ_{HNaCl} are known, see Table 1. Pitzer (1991, p. 102) gives the values $\beta_{\text{NaAc}}^{(0)} = 0.1426$, $\beta_{\text{NaAc}}^{(1)} = 0.3237$, and $C_{\text{NaAc}}^{\phi} = -0.00629$. However,

$\beta_{\text{NaAc}}^{(0)}$

$\beta_{\text{NaAc}}^{(1)}$

C_{NaAc}^{ϕ}

this value for $\beta_{\text{NaAc}}^{(1)}$ from Pitzer (1991) is incompatible with the value from Mesmer et al. (1989) as specified by Equation 6. Substituting the Pitzer (1991) values for $\beta_{\text{NaAc}}^{(0)}$ and C_{NaAc}^ϕ and defining the Setchenow coefficient to be zero, i.e., $\delta \equiv 0$, the values $\theta_{\text{ClAc}} = -0.090$ and $\psi_{\text{NaClAc}} = 0.01029$ are calculated.

To test the reliability of this model, we conducted a series of potentiometric titration measurements of the apparent deprotonation constants for acetic acid in NaCl and NaClO₄ media. The apparent stability constants from Chen et al. (manuscript in progress) and Du (1995) are reproduced in Table 2; a comparison of these values with the model is shown in Figure 1. The model accurately predicts experimental values in both NaCl and NaClO₄ media to high concentration, requiring no additional parameters describing ion interactions between acetic acid species and the perchlorate anion. Thus, the differences in acetic acid deprotonation behavior between NaCl and NaClO₄ media are adequately described with this model, and the parameter assignments are reasonable.

Np(V)-Ac Data Analysis and Model Development

The extraction experiments provide the relative proportions of ²³⁷Np in the organic and aqueous phases. The distribution coefficient, D, is defined as

$$D \equiv \frac{m_{\text{Np(o)}}}{m_{\text{Np(aq)}}} \quad (9)$$

where $m_{\text{Np(o)}}$ and $m_{\text{Np(aq)}}$ are the total Np molality in the organic and aqueous phases, respectively. Hydrolysis of Np(V) under our experimental conditions is negligible, so $m_{\text{Np(aq)}} = m_{\text{NpO}_2^+} + \sum_i m_{\text{NpO}_2\text{Ac}_i^{1-i}}$. The quantity D^0 is defined as the distribution coefficient with no acetate present.

The extraction of NpO_2^+ by HDEHP is given by the reaction

where $\text{HX(o)} \equiv \text{HDEHP}$ and $\text{NaX(o)} \equiv \text{NaDEHP}$. The stoichiometry of the extraction reaction depends on the H^+ and Na^+ concentrations and the ionic strength of the aqueous phase. The H^+ dependence at each NaCl molality was determined by additional extraction experiments in the absence of acetate for the range $3 < \text{pH}_T < 5$. The equilibrium relationship for Reaction 10 can be written as

$$\begin{aligned} \log D = & \left[y \log(K_H^{\text{ex}} a_{\text{HX(o)}}) + (1-y) \log(K_{\text{Na}}^{\text{ex}} a_{\text{NaX(o)}}) - \log \gamma_{\text{NpO}_2\text{X(o)}} \right] \\ & + \left[\log \gamma_{\text{NpO}_2^+} - (1-y) \log a_{\text{Na}^+} \right] + y(-\log(\gamma_{\text{H}^+} m_{\text{H}^+})) \end{aligned} \quad (11)$$

where K_H^{ex} and $K_{\text{Na}}^{\text{ex}}$ are the equilibrium constants for the reaction when $y=1$ and $y=0$, respectively. The first bracketed term, characterizing the organic phase, is of no particular interest other than for allowing characterization of the aqueous phase. The experiments were designed so that, for a given aqueous ionic strength, the organic phase parameters can be assumed to be constant. The second bracketed term, characterizing the aqueous phase, is nearly constant for each ionic strength under our experimental conditions. Values for y , the extraction dependence on hydrogen ion activity, are given in Table 3.

The pH_T of the aqueous phase varied slightly after contact with the organic phase. The measured D values were adjusted to $\text{pH}_T=5.0$ using the equation

$$\log D^{\text{adj}} = \log D^{\text{meas}} + y(5.0 - \text{pH}_T) \quad (12)$$

(c.f. Equation 10). Aqueous phase concentrations, pH_T values, and measured and adjusted distribution coefficients are given in Table 4.

The data give no indication of the formation of the $\text{NpO}_2\text{Ac}_2^-$ or higher complexes, even at >0.1 m total acetate concentration. Thus, only formation of $\text{NpO}_2\text{Ac}(\text{aq})$ was assumed in the model development. The complexation reaction was:

$$\begin{aligned} \beta_{101}^0 &= \exp \left[-\frac{\mu^\circ(\text{NpO}_2\text{Ac}(\text{aq}))}{RT} + \frac{\mu^\circ(\text{NpO}_2^+)}{RT} + \frac{\mu^\circ(\text{Ac}^-)}{RT} \right] \\ &= \frac{\gamma_{\text{NpO}_2\text{Ac}(\text{aq})} m_{\text{NpO}_2\text{Ac}(\text{aq})}}{\gamma_{\text{NpO}_2^+} m_{\text{NpO}_2^+} \gamma_{\text{Ac}^-} m_{\text{Ac}^-}} \end{aligned} \quad (14)$$

The unknowns in this equation are standard chemical potential of the neptunyl acetate complex, which is a constant, and the activity coefficient $\gamma_{\text{NpO}_2\text{Ac}(\text{aq})}$, which is a function of solution composition. The thermodynamic fitting code MacNONLIN 2.0* was used to determine the quantity $\frac{\mu^\circ(\text{NpO}_2\text{Ac}(\text{aq}))}{RT} + \ln \gamma_{\text{NpO}_2\text{Ac}(\text{aq})}$ for each sodium concentration; these values are plotted in Figure 2. The data suggest no dependence of the activity coefficient for $\text{NpO}_2\text{Ac}(\text{aq})$ on m_{NaCl} . Therefore, we assign $\lambda_{\text{NpO}_2\text{Ac}(\text{aq}),i} = 0$ for $i = \text{all ions}$ and $\zeta_{\text{NpO}_2\text{Ac}(\text{aq}),c,a} = 0$ for $c = \text{all cations}$ and $a = \text{all anions}$. The average value $\frac{\mu_f^\circ(\text{NpO}_2\text{Ac}(\text{aq}))}{RT} = -519.8 \pm 0.5$ (2σ) was calculated from these data, giving the stability constant value $\log \beta_{101}^0 = 1.46 \pm 0.22$. The complete model is summarized in Table 1. Figure 3 compares experimental and predicted values for the normalized distribution coefficients as a function of free acetate concentration: both axis are on a linear scale. The model accurately reproduces the measured behavior over the entire ionic strength range.

Model Implications and Conclusions

* MacNONLIN 2.0 is the Macintosh version of NONLIN. NONLIN, developed by A.R. Felmy, uses the MINPACK nonlinear least-squares programs combined with a chemical equilibrium program based on the Gibbs free-energy minimization procedure of Harvie et al. (1987).

This model suggests that, depending on the NaCl concentration, a free acetate concentration of 0.03 to 0.07 molal is required to attain a concentration of $\text{NpO}_2\text{Ac(aq)}$ equal to that of NpO_2^+ . That is, approximately 0.1 m Ac^- would be required to raise the dissolved Np(V) concentration by a factor of 2 if acetate complexation were the only significant complexation reaction. This illustrates that acetate complexation with Np(V) will have a negligible effect at acetate concentrations less than 0.1 m, and thus can be safely ignored in most environmental applications.

Acknowledgment

This work was performed as part of the Waste Isolation Pilot Plant (WIPP) Actinide Source Term Program, supported at Sandia National Laboratories by the United States Department of Energy under Contract DE-AC04-94AL85000, and at Florida State University under contract AH-5590. This work was performed under an NQA-1 equivalent Quality Assurance program.

References

- Borkowski, M., S. Lis, and G.R. Choppin. 1995. "Complexation Study of UO_2^{2+} and NpO_2^+ Ions with Several Organic Ligands in Aqueous Solutions of High Ionic Strength." to be published in the proceedings of Migration '95.
- Brush, L.H. 1990. *Test Plan for Laboratory and Modeling Studies of Repository and Radionuclide Chemistry for the Waste Isolation Pilot Plant*. SAND90-0266. Albuquerque, New Mexico: Sandia National Laboratories.
- Choppin, G.R. and J-F. Chen. 1995. "Complexation of Am^{3+} by Oxalate in NaClO_4 Media." to be published in the proceedings of Migration '95.
- Choppin, G.R., H.N. Erten, and Y-X. Xia. 1995. "Variation of Stability Constants of Thorium Citrate Complexes and of Thorium Hydrolysis Constants with Ionic Strength." to be published in the proceedings of Migration '95.
- Cox, J.D., D.D. Wagman, and V.A. Medvedev. 1989. *CODATA Key Values for Thermodynamics*. New York: Hemisphere Publishing Corporation.
- Du, M. 1995. *f-Element Complexation in Solutions to High Ionic Strength*. Doctoral Thesis, The Florida State University. Ann Arbor, Michigan: University Microfilms.
- Fanghänel, Th., V. Neck, and J.I. Kim. 1995. "Thermodynamics of Neptunium(V) in Concentrated Salt Solutions: II. Ion Interaction (Pitzer) Parameters for Np(V) Hydrolysis Species and Carbonate Complexes." *Radiochimica Acta* submitted.
- Felmy, A.R., D. Rai, and R.W. Fulton. 1990. "The Solubility of $\text{AmOHCO}_3(\text{c})$ and the Aqueous Thermodynamics of the System $\text{Na}^+ - \text{Am}^{3+} - \text{HCO}_3^- - \text{OH}^- - \text{H}_2\text{O}$." *Radiochimica Acta* vol. 50: 193-240.
- Felmy, A.R., and D. Rai. 1992. "An Aqueous Thermodynamic Model for a High Valence 4:2 Electrolyte $\text{Th}^{4+} - \text{SO}_4^{2-}$ in the System $\text{Na}^+ - \text{K}^+ - \text{Li}^+ - \text{NH}_4^+ - \text{SO}_4^{2-} - \text{HSO}_4^- - \text{H}_2\text{O}$ to High Concentration." *Journal of Solution Chemistry* vol. 21 #5: 407-423.
- Felmy, A.R., D. Rai, and M.J. Mason. 1991. "The Solubility of Hydrated Thorium(IV) Oxide in Chloride Media: Development of an Aqueous Ion-Interaction Model." *Radiochimica Acta* vol. 55: 177-185.

- Felmy, A.R., D. Rai, J.A. Schramke, and J.L. Ryan. 1989. "The Solubility of Plutonium Hydroxide in Dilute Solution and in High-Ionic-Strength Chloride Brines." *Radiochimica Acta* vol. 48: 29-35.
- Felmy, A.R., and J.H. Weare. 1986. "The Prediction of Borate Mineral Equilibria in Natural Waters: Application to Searles Lake, California." *Geochimica et Cosmochimica Acta* vol. 50: 2771-2783.
- Fuger, J. and F.L. Oetting. 1976. *The Chemical Thermodynamics of Actinide Elements and Compounds: Part 2. The Actinide Aqueous Ions*. Vienna, Austria: International Atomic Energy Agency.
- Gran, G. 1950. "Determination of the Equivalent Point in Potentiometric Titrations." *Acta Chemica Scandinavica* vol. 4: 559-577.
- Gran, G. 1952. "Determination of the Equivalent Point in Potentiometric Titrations. Part II." *The Analyst* vol. 77: 661-671.
- Harvie, C.E., J.P. Greenberg, and J.H. Weare. 1987. "A Chemical Equilibrium Algorithm for Highly Non-ideal Multiphase Systems: Free Energy Minimization." *Geochimica et Cosmochimica Acta* vol. 51: 1045-1057.
- Harvie, C.E., N. Møller, and J.H. Weare. 1984. "The Prediction of Mineral Solubilities in Natural Waters: The Na-K-Mg-Ca-H-Cl-SO₄-OH-HCO₃-CO₃-CO₂-H₂O System to High Ionic Strength at 25°C." *Geochimica et Cosmochimica Acta* vol. 48: 723-751.
- McDowell, W.J., P.T. Perdue, and G.N. Case. 1976. "Purification of di(2-ethylhexyl)phosphoric acid." *Journal of Inorganic and Nuclear Chemistry* vol. 38: 2127-2129.
- Mesmer, R.E., C.S. Patterson, R.H. Busey, and H.F. Holmes. 1989. "Ionization of Acetic Acid in NaCl(aq) Media: A Potentiometric Study to 573K and 130 Bar." *Journal of Physical Chemistry* vol. 93: 7483-7490.
- Neck, V., Th. Fanghänel, G. Rudolph, and J.I. Kim. 1995. "Thermodynamics of Neptunium(V) in Concentrated Salt Solutions: Chloride Complexation and Ion Interaction (Pitzer) Parameters for the NpO₂⁺ Ion." *Radiochimica Acta* in press.
- Novak, C.F., and K.E. Roberts. 1995. "Thermodynamic Modeling of Neptunium(V) Solubility in Na-CO₃-HCO₃-Cl-ClO₄-H-OH-H₂O Electrolytes." *Materials Research Society Symposium Proceedings. Volume 353. Scientific Basis for Nuclear Waste Management XVIII*. T. Murakami and R.C. Ewing, editors. Pittsburgh, Pennsylvania: Materials Research Society. Vol. 353 Part 2, 1119-1128.
- Novak, C.F., C.C. Crafts, and N.J. Dhooge. 1995. "A Data Base for Thermodynamic Modeling of +III Actinide Solubility in Concentrated Na-Cl-SO₄-CO₃-PO₄ Electrolytes." to be published in the proceedings of Migration '95.
- Pitzer, K.S. 1991. *Activity Coefficients in Electrolyte Solutions*. Boca Raton, Florida: CRC Press.
- Weast, R.C. 1980. *CRC Handbook of Chemistry and Physics* 60th ed. Chemical Rubber Publishing Company, Boca Raton, Florida. p. D-79.

Table 1. Summary of thermodynamic parameters used and developed for the HAc(aq) deprotonation model. All parameters are from Harvie et al. (1984) unless otherwise noted. All neutral-ion and neutral-cation-anion parameters for HAc(aq) and $\text{NpO}_2\text{Ac(aq)}$ are zero.

Species	$\frac{0}{RT} \mu_f$	Species	$\frac{0}{RT} \mu_f$	source
H_2O	-95.663	ClO_4^-	-73.81	Cox et al., 1989
H^+	0.0	HAc(aq)	-158.3	Weast, 1980
Na^+	-105.651	Ac^-	-147.347	Mesmer et al., 1989
Cl^-	-52.955	NpO_2^+	-369.1	Fuger and Oetting, 1976
OH^-	-63.435	$\text{NpO}_2\text{Ac(aq)}$	-519.8±0.25	this work

i	j	$\beta_{ij}^{(0)}$	$\beta_{ij}^{(1)}$	C_{ij}^ϕ	Source
Na^+	Cl^-	0.0765	0.2664	0.00127	
Na^+	ClO_4^-	0.0554	0.2755	-0.00118	Pitzer, 1991
Na^+	OH^-	0.0864	0.253	0.0044	
Na^+	Ac^-	0.1428		-0.00629	Pitzer, 1991
Na^+	Ac^-		0.22		Mesmer et al., 1989
H^+	Cl^-	0.1775	0.2945	0.0008	
H^+	ClO_4^-	0.1747	0.2931	0.00819	Pitzer, 1991
H^+	OH^-	0	0	0	
H^+	Ac^-	0	0	0	Mesmer et al., 1989
NpO_2^+	Cl^-	0.1415	0.281	0	Neck et al., 1995
NpO_2^+	ClO_4^-	0.257	0.180	0.0081	Neck et al., 1995
NpO_2^+	OH^-	0	0	0	
NpO_2^+	Ac^-	0	0	0	

i	j	θ_{ij}	$\psi_{ij\text{Cl}^-}$	$\psi_{ij\text{ClO}_4^-}$	$\psi_{ij\text{OH}^-}$	$\psi_{ij\text{Ac}^-}$
Na^+	H^+	0.036	-0.004	-0.016	0	0

i	j	θ_{ij}	$\psi_{ij\text{Na}^+}$	$\psi_{ij\text{H}^+}$
Cl^-	ClO_4^-	0	0	0
Cl^-	OH^-	-0.05	-0.006	0
Cl^-	Ac^-	-0.090 [this work]	0.01029 [this work]	0
ClO_4^-	OH^-	0	0	0
ClO_4^-	Ac^-	0	0	0
OH^-	Ac^-	0	0	0

Table 2. Summary of apparent deprotonation constants for acetic acid in NaCl and NaClO₄ media.

NaCl Concentration, molal	logK _{a1} in NaCl (molal units) (Chen et al. manuscript in preparation)	NaClO ₄ Concentration, molal	logK _{a1} in NaClO ₄ (molal units) (Du, 1995)
0.1	-4.567	0.104	-4.568
0.3	-4.520	0.508	-4.538
0.5	-4.506	1.042	-4.605
1.0	-4.526	3.509	-4.973
2.0	-4.640	6.501	-5.447
3.0	-4.796	10.018	-6.023
5.0	-5.174	11.974	-6.360
		14.061	-6.618

Table 3. Dependence of extraction equilibrium on hydrogen ion activity as a function of NaCl molality.

m _{NaCl}	y, as used in Equations 10-12
0.3	1.0
1.0	0.93
2.0	0.15
3.0	0.08
4.0	0.0
5.0	0.0

DISCLAIMER

This report was prepared as an account of work sponsored by an agency of the United States Government. Neither the United States Government nor any agency thereof, nor any of their employees, makes any warranty, express or implied, or assumes any legal liability or responsibility for the accuracy, completeness, or usefulness of any information, apparatus, product, or process disclosed, or represents that its use would not infringe privately owned rights. Reference herein to any specific commercial product, process, or service by trade name, trademark, manufacturer, or otherwise does not necessarily constitute or imply its endorsement, recommendation, or favoring by the United States Government or any agency thereof. The views and opinions of authors expressed herein do not necessarily state or reflect those of the United States Government or any agency thereof.

Table 4. Measured and adjusted distribution coefficients, see Equation 12, for Np extraction from NaCl media as a function of acetate concentration.

pH _r	D _{meas}	D _{adj}	m _{Ac⁻}	m _{Cl⁻}	m _{Na⁺}
0.30m NaCl Set#3					
4.701	0.794	1.581	0.0000	0.3000	0.3000
4.884	0.921	1.204	0.0075	0.2925	0.3000
4.955	1.305	1.448	0.0150	0.2850	0.3000
4.952	1.110	1.240	0.0300	0.2700	0.3001
4.987	1.035	1.066	0.0600	0.2401	0.3001
4.996	0.768	0.775	0.0901	0.2101	0.3002
5.005	0.679	0.671	0.1201	0.1802	0.3002
5.011	0.613	0.598	0.1501	0.1502	0.3003
1.00m NaCl Set#3					
5.046	6.313	5.721	0.0000	1.0000	1.0000
4.954	6.104	6.736	0.0075	0.9924	0.9999
4.967	6.122	6.571	0.0150	0.9849	0.9999
4.983	5.384	5.583	0.0300	0.9697	0.9997
5.010	4.364	4.272	0.0600	0.9394	0.9995
5.021	4.003	3.827	0.0901	0.9092	0.9992
5.027	3.294	3.109	0.1201	0.8789	0.9990
5.032	2.674	2.497	0.1501	0.8486	0.9987
1.00m NaCl Set#2					
5.425	9.066	3.649	0.0000	1.0000	1.0000
4.950	8.111	9.028	0.0075	0.9924	0.9999
4.953	8.021	8.871	0.0150	0.9849	0.9999
4.959	7.577	8.272	0.0300	0.9697	0.9997
4.971	6.302	6.706	0.0600	0.9394	0.9995
4.975	5.300	5.591	0.0901	0.9092	0.9992
4.982	4.564	4.743	0.1201	0.8789	0.9990
4.987	3.794	3.901	0.1501	0.8486	0.9987
2.00m NaCl Set#2					
4.999	0.901	0.902	0.0000	2.0000	2.0000
4.905	0.843	0.871	0.0075	1.9928	2.0003
4.906	0.723	0.747	0.0151	1.9856	2.0006
4.913	0.681	0.701	0.0302	1.9711	2.0013
4.923	0.458	0.471	0.0603	1.9422	2.0026
4.932	0.384	0.393	0.0905	1.9134	2.0038
4.931	0.323	0.331	0.1206	1.8845	2.0051
4.935	0.262	0.268	0.1508	1.8556	2.0064
2.00m NaCl Set#3					
5.020	5.788	5.748	0.0000	2.0000	2.0000
5.002	5.475	5.471	0.0075	1.9928	2.0003
5.000	5.193	5.193	0.0151	1.9856	2.0006
4.994	4.315	4.324	0.0302	1.9711	2.0013
4.991	3.537	3.548	0.0603	1.9422	2.0026
4.989	2.806	2.817	0.0905	1.9134	2.0038
4.990	2.246	2.254	0.1206	1.8845	2.0051
4.989	1.735	1.741	0.1508	1.8556	2.0064
3.00m NaCl Set#2					
4.613	1.497	1.608	0.0000	3.0000	3.0000

4.877	1.339	1.369	0.0075	2.9925	3.0000
4.898	1.181	1.203	0.0150	2.9850	3.0000
4.923	0.925	0.938	0.0300	2.9699	2.9999
4.950	0.692	0.698	0.0601	2.9398	2.9999
4.965	0.427	0.430	0.0901	2.9097	2.9998
4.977	0.410	0.412	0.1202	2.8796	2.9998
4.987	0.317	0.318	0.1502	2.8495	2.9997
3.00m NaCl Set#3					
4.929	3.918	3.970	0.0000	3.0000	3.0000
4.967	3.113	3.132	0.0075	2.9925	3.0000
4.967	2.956	2.974	0.0150	2.9850	3.0000
4.967	2.345	2.359	0.0300	2.9699	2.9999
4.985	1.625	1.629	0.0601	2.9398	2.9999
4.995	1.251	1.252	0.0901	2.9097	2.9998
5.006	1.049	1.048	0.1202	2.8796	2.9998
5.010	0.833	0.832	0.1502	2.8495	2.9997
4.00m NaCl Set#2					
4.865	3.003	3.003	0.0000	4.0000	4.0000
4.909	2.894	2.894	0.0075	3.9924	3.9999
4.914	2.617	2.617	0.0150	3.9848	3.9998
4.930	2.035	2.035	0.0301	3.9695	3.9996
4.951	1.523	1.523	0.0602	3.9390	3.9992
4.967	1.084	1.084	0.0902	3.9085	3.9987
4.973	0.877	0.877	0.1203	3.8780	3.9983
4.980	0.679	0.679	0.1504	3.8475	3.9979
4.00m NaCl Set#3					
4.980	4.914	4.914	0.0000	4.0000	4.0000
4.927	4.339	4.339	0.0075	3.9924	3.9999
4.959	4.642	4.642	0.0150	3.9848	3.9998
4.983	4.154	4.154	0.0301	3.9695	3.9996
4.999	2.611	2.611	0.0602	3.9390	3.9992
5.008	2.268	2.268	0.0902	3.9085	3.9987
5.019	1.795	1.795	0.1203	3.8780	3.9983
5.024	1.418	1.418	0.1504	3.8475	3.9979
5.00m NaCl Set#3					
4.211	7.024	7.024	0.0000	5.0000	5.0000
4.920	4.443	4.443	0.0075	4.9924	4.9999
4.975	4.697	4.697	0.0150	4.9847	4.9997
4.958	4.072	4.072	0.0300	4.9694	4.9995
4.998	2.610	2.610	0.0601	4.9389	4.9990
4.998	1.407	1.407	0.0901	4.9083	4.9984
5.014	1.169	1.169	0.1202	4.8778	4.9979
5.051	0.981	0.981	0.1502	4.8472	4.9974

Figure 1. Comparison of independent measured values of apparent deprotonation constants for acetic acid in NaCl and NaClO₄ media with model calculations.

Figure 2. Calculated quantity $\mu_{RT}^0(\text{NpO}_2\text{Ac(aq)}) + \ln \gamma_{\text{NpO}_2\text{Ac(aq)}}$ as a function of m_{NaCl} .

Figure 3. Np(V) extraction data (symbols) as a function of acetate and sodium chloride concentrations, with model developed from these data (curves).