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

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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 $NaClO_4$ media was developed. For the concentrations of acetate expected in a waste repository, only the neutral complex $NpO_2Ac(aq)$ was important in describing the interactions between the neptunyl ion and acetate. The thermodynamic stability constant β^0_{101} for the reaction $NpO_2^+ + Ac^- \leftrightarrow NpO_2Ac$ was calculated to be 1.46 ± 0.22. 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 wastes, is examining the potential of organic ligands to increase the concentrations of Am(III), Th(IV), Np(V), and U(VI) in concentrated electrolytes. The ligands under study are acetate, citrate, oxalate, lactate, and ethylenediaminetetraacetic acid (EDTA). This paper documents Np(V)-acetate interactions; related work with other actinides and organic ligands is documented elsewhere [1–3]. 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), Na(V), and U(VI) with the organic anions acetate, citrate, oxalate, lactate, and EDTA in dilute to concentrated NaCl and $MgCl_2$/NaCl solutions.

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 [4]. An extractant was prepared as n-heptane HDEHP solution with concentration 9.52×10^{-3} M (1.4×10^{-2} m, d = 0.68g/ml). ^{237}Np tracer was obtained from Oak Ridge National Laboratory and was purified by ion exchange method with Dowex 1×4. 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.

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 $^{237}NpO_2^+$, 5.0 ± 0.1 ml of the extractant was added and shaken in a thermostated shaker at 25 ± 0.5 °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 5 m 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 [5, 6]. For our electrode, this work resulted in the correlation $pcH = pH_r + 0.255\, m_{NaCl}$.

Thermodynamic model and database

The activity coefficient formalism of Pitzer [7] with a database for the brine evaporite system [8, 9] was used to interpret the Np(V)-acetate complexation data. This model represents activity coefficients with a virial expansion with the second the third virial coefficients $B_{mx}(I)$ and C^{ϕ}_{mx} (technically C_{mx}). Here, $B_{ma}(I)$ is a function of ionic strength given by

$$B_{mx}(I) \equiv \beta^{(0)}_{mx} + \beta^{(1)}_{mx}\, g(\alpha_{1mx}\sqrt{I}) + \beta^{(2)}_{mx}\, g(\alpha_{2mx}\sqrt{I}). \quad (1)$$

The α and β parameters are constants, and $g(y)$ is a decreasing exponential function. C^{ϕ}_{mx} is a constant. Activity coefficients for neutral species are given by

$$\ln \gamma_N = \sum_c m_c + \sum_a \lambda_{Na} M_a + \sum_c \sum_a \zeta_{nca} \quad (2)$$

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. Details are given in [7–9].

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 WIPP, the database developed by Harvie *et al.* [8] and extended in Felmy and Weare [9] is the reference base model. The reference database is used for calculating new parameters values when additional species and ion interactions are included, maintaining and ensuring internal consistency with the reference database. The standard chemical potentials and ion interaction parameters from this database needed for constructing the Np(V)-Ac complexation model are given in Table 1.

Model for deprotonation of acetic acid in NaCl and $NaClO_4$ 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 $\mu^0_f(HAc(aq))$ and $\mu^0_f(Ac^-)$ and ion interaction parameters with acetate, including the cation-anion parameters $\beta^{(0)}_{NaAc}$, $\beta^{(1)}_{NaAc}$, and C^{ϕ}_{NaAc}; the anion-anion parameters θ_{ClAc} and θ_{ClO_4Ac}; the anion-anion-cation parameters ψ_{ClAcNa} and ψ_{ClO_4AcNa}; the neutral-ion interaction parameters $\lambda_{HAc(aq),Na}$, $\lambda_{HAc(aq),Cl}$, and $\lambda_{HAc(aq),ClO_4}$; and the neutral-cation-anion parameters $\zeta_{HAc(aq),c,a}$.

A model for the ionization of acetic acid in NaCl(aq) media is given by Mesmer *et al.* [10]. For 25°C, the parameters in this model are

$$2\,\beta^{(0)}_{NaAc} + 2\,\theta_{HNa} + 2\,\theta_{ClAc} - \delta = 0.1777 \quad (3)$$

$$\beta^{(1)}_{NaAc} = 0.22 \quad (4)$$

$$C^{\phi}_{NaAc} + \psi_{HNaCl} + \psi_{NaClAc} = 0 \quad (5)$$

$$K_{a1} = 10^{-4.757} \quad \text{from Ref. [10]} \quad (6)$$

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

The standard chemical potential for HAc(aq) is −392 kJ/mole [11], of $\frac{\mu^0_f(HAc(aq))}{RT} = -158.3$. From this value and the equilibrium constant, equation (6), the dimensionless standard chemical potential of the acetate ion is calculated to be $\frac{\mu^0_f(Ac^-)}{RT} = -147.347$.

The parameters in equations (3) and (5) cannot be determined independently from the presentation in [10]. Indeed, every set of values satisfying the linear combinations of equations (3) to (5) 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 $NaClO_4$ media, for example, which would instead have the analogous parameters θ_{ClO_4Ac} and ψ_{NaClO_4Ac}. 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 $NaClO_4$ media.

Values for θ_{HNa} and ψ_{HNaCl} are known, see Table 1. Pitzer [7, p. 102] gives the values $\beta^{(0)}_{NaAc} = 0.1426$, $\beta^{(1)}_{NaAc} = 0.3237$, and $C^{\phi}_{NaAc} = -0.00629$. However, this value for $\beta^{(1)}_{NaAc}$ from [7] is incompatible with the value from [10] as specified by equation (6). Substituting the Pitzer [7] values for $\beta^{(0)}_{NaAc}$ and C^{ϕ}_{NaAc} and defining the Setchenow coefficient to be zero, i.e., $\delta \equiv 0$, the values $\theta_{ClAc} = -0.090$ and $\psi_{NaClAc} = 0.01029$ 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 $NaClO_4$ media. The apparent stability constants from Chen *et al.* (manuscript in progress) and [12] are reproduced in Table 2; a comparison of these values with the model is shown in Fig. 1. The model accurately predicts experimental values in both NaCl and $NaClO_4$ media to high concentration, requiring no additional parameters describing ion interactions be-

Table 1. Summary of thermodynamic parameters used and developed for the HAc(aq) deprotonation model. All parameters are from Harvie *et al.* [8] unless otherwise noted. All neutral-ion and neutral-cation-anion parameters for HAc(aq) and $NpO_2Ac(aq)$ are zero

Species	$\frac{\mu_f^0}{RT}$	Species	$\frac{\mu_f^0}{RT}$	Source
H_2O	−95.663	ClO_4^-	−73.81	Cox *et al.* [13]
H^+	0.0	HAc(aq)	−158.3	Weast [11]
Na^+	−105.651	Ac^-	−147.347	Mesmer *et al.* [10]
Cl^-	−52.955	NpO_2^+	−369.109	Fuger and Oetting [14]
OH^-	−63.435	$NpO_2Ac(aq)$	−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 [7]
Na^+	OH^-	0.0864	0.253	0.0044	
Na^+	Ac^-	0.1426		−0.00629	Pitzer [7]
Na^+	Ac^-		0.22		Mesmer *et al.* [10]
H^+	Cl^-	0.1775	0.2945	0.0008	
H^+	ClO_4^-	0.1747	0.2931	0.00819	Pitzer [7]
H^+	OH^-	0	0	0	
H^+	Ac^-	0	0	0	Mesmer *et al.* [10]
NpO_2^+	Cl^-	0.1415	0.281	0	Neck *et al.* [15]
NpO_2^+	ClO_4^-	0.257	0.180	0.0081	Neck *et al.* [15]
NpO_2^+	OH^-	0	0	0	
NpO_2^+	Ac^-	0	0	0	

i	j	θ_{ij}	$\psi_{ij Cl^-}$	$\psi_{ij ClO_4^-}$	$\psi_{ij OH^-}$	$\psi_{ij Ac^-}$
Na^+	H^+	0.036	−0.004	−0.016	0	0

i	j	θ_{ij}	$\psi_{ij Na^+}$	$\psi_{ij H^+}$
Cl^-	Cl_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. Apparent deprotonation constants for acetic acid in NaCl and $NaClO_4$ media

NaCl concentration,	$\log K_{a1}$ in NaCl (molal units) (Chen *et al.* manuscript in preparation)	$NaClO_4$ concentration, molal	$\log K_{a1}$ in $NaClO_4$ (molal units) [12]
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

tween acetic acid species and the perchlorate anion. The differences in acetic acid deprotonation behavior between NaCl and $NaClO_4$ media are adequately described, and the parameter assignments are reasonable.

Np(V)-Ac data analysis and model development

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

$$D \equiv \frac{m_{Np(o)}}{m_{Np(aq)}} \tag{7}$$

where $m_{Np(o)}$ and $m_{Np(aq)}$ are the total Np molality in the organic and aqueous phases, respectively. Hydrolysis of Np(V) under the experimental conditions was negligible, so $m_{Np(aq)} = m_{NpO_2^+} + \sum_i m_{NpO_2Ac_i^{1-i}}$. The quantity D^0 is defined as the distribution coefficient with no acetate present.

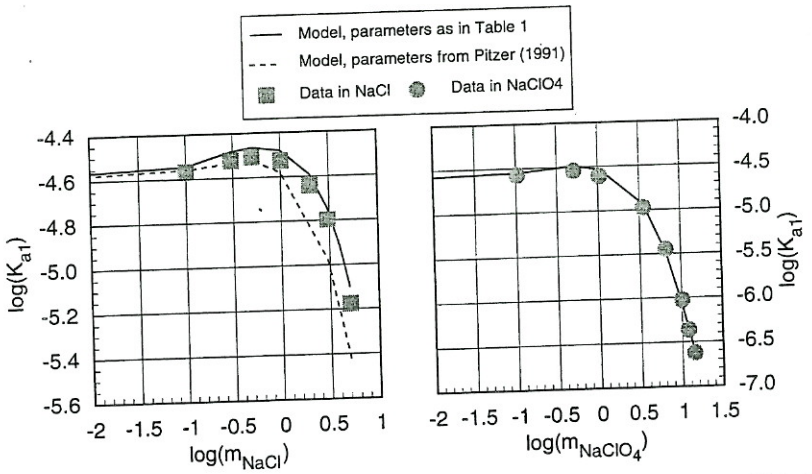


Fig. 1. Comparison of independent measured values of apparent deprotonation constants for acetic acid in NaCl and $NaClO_4$ media with model calculations.

Table 3. Dependence of extraction equilibrium on hydrogen ion activity in NaCl media

m_{NaCl}	y, as used in equation (10)
0.3	1.0
1.0	0.93
2.0	0.15
3.0	0.08
4.0	0.0
5.0	0.0

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

$$NpO_2^+ + y\,HX(o) + (1-y)NaX(o) \leftrightarrow NpO_2X(o) + yH^+ + (1-y)Na^+ \quad (8)$$

where HX(o) ≡ HDEHP and NaX(o) ≡ 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 $3 < pH_r < 5$. The equilibrium relationship for reaction (9) can be written as

$$\log D = [y \log(K^{ex}_{H\,HX(o)}) + (1-y)\log(K^{ex}_{Na}\, a_{NaX(o)}) - \log\gamma_{NpO_2X(o)}] + [\log\gamma_{NpO_2^+} - (1-y)\log a_{Na^+}] + y(-\log(\gamma_{H^+} m_{H^+}) \quad (9)$$

where K^{ex}_H and K^{ex}_{Na} 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_r of the aqueous phase varied slightly after contact with the organic phase. The measured D values were adjusted to $pH_r = 5.0$ using the equation

$$\log D^{adj} = \log D^{meas} + y(5.0 - pH_r) \quad (10)$$

(c.f. equation (8)). The results obtained are presented in Fig. 3.

The data give no indication of the formation of the $NpO_2Ac_2^-$ or higher complexes, even at >0.1 m total acetate concentration. Thus, only formation of $NpO_2Ac(aq)$ was assumed in the model development. The complexation reaction was:

$$NpO_2^+ + Ac^- \leftrightarrow NpO_2Ac(aq) \quad (11)$$

$$\beta^0_{101} \equiv \exp\left[-\frac{\mu^0}{RT}(NpO_2Ac(aq)) + \frac{\mu^0}{RT}(NpO_2^+) + \frac{\mu^0}{RT}(Ac^-)\right] = \frac{\gamma_{NpO_2Ac(aq)}\, m_{NpO_2Ac(aq)}}{\gamma_{NpO_2^+}\, m_{NpO_2^+}\, \gamma_{Ac^-}\, m_{Ac^-}}. \quad (12)$$

The unknowns in this equation are standard chemical potential of the neptunyl acetate complex, which is a constant, and the activity coefficient $\gamma_{NpO_2Ac(aq)}$, which is a function of solution composition. The thermodynamic fitting code MacNONLIN 2.0* was used to determine the quantity $\frac{\mu^0}{RT}(NpO_2Ac(aq)) + \ln\gamma_{NpO_2Ac(aq)}$ for each sodium concentration; these values are plot-

* 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 [16].

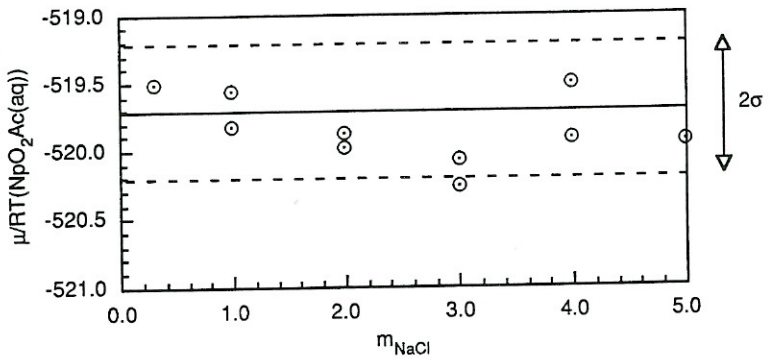


Fig. 2. Calculated quantity $\frac{\mu_f^0}{RT}(NpO_2Ac(aq)) + \ln\gamma_{NpO_2Ac(aq)}$ as a function of m_{NaCl}.

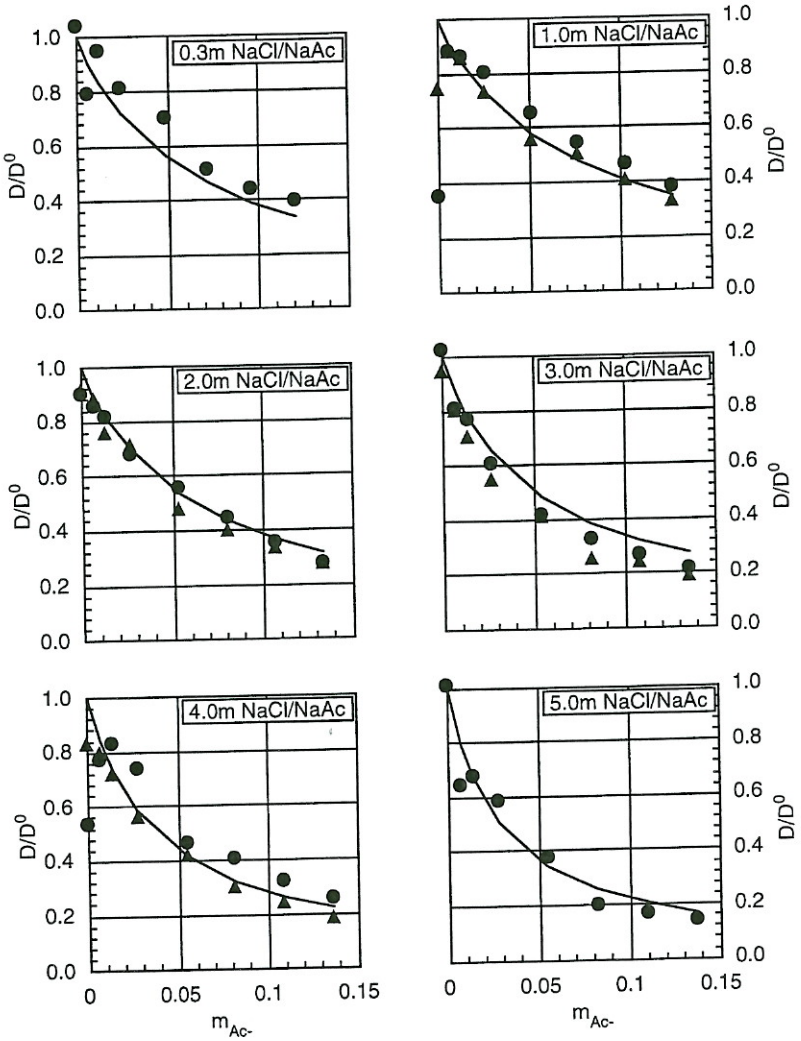


Fig. 3. Np(V) extraction data (symbols) as a function of acetate and sodium chloride concentrations, with model developed from these data (curves).

ted in Fig. 2. The data suggest no dependence of the activity coefficient for $NpO_2Ac(aq)$ on m_{NaCl}. Therefore, we assign $\lambda_{NpO_2Ac(aq),i} = 0$ for i = all ions and $\zeta_{NpO_2Ac(aq),c,a} = 0$ for c = all cations and a = all anions. The average value $\frac{\mu_f^0(NpO_2Ac(aq))}{RT} = -519.8 \pm 0.5$ (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. Fig. 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

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 $NpO_2Ac(aq)$ 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 two 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.

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