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Interaction of Actinides with Carboxylates in Solution: Complexation of U(VI), Th(IV), and Nd(III) with Acetate at Variable Temperatures

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The complexation of uranium (VI), thorium (IV), and neodymium (III) with acetate was studied from 10 to 70 °C. The formation constants and the enthalpies of complexation were determined by titration potentiometry and calorimetry. The complexes become stronger at higher temperatures, despite that the enthalpy of complexation becomes more positive and unfavorable to the complexation as the temperature is increased. Extended X-ray Absorption Fine Structure Spectroscopy (EXAFS) and optical absorption spectroscopy provide additional information to support the thermodynamic results. The effect of temperature on the thermodynamic parameters is discussed in terms of the electrostatic model.

1. Introduction

Study of the interactions of actinides with organic materials remains an active and challenging subject due to recent activities in the environmental management of nuclear wastes. Many organic materials exist in the nuclear wastes (e.g. carboxylic acids) or occur in the natural environment (e.g. humic and fulvic materials, microorganisms). They form fairly stable complexes with actinides in different oxidation states and reduce some actinides, particularly neptunium and plutonium, in higher oxidation states. Previous studies show that the redox reactions proceed through intramolecular electron transfer in the intermediate complexes between the actinides and organic materials.[1, 2] As a result, the strength of complexation affects the rate of redox reactions. Therefore, studies of the complexation of actinides with organic materials are critically important to predict the chemical behavior of actinides in nuclear waste processing and in the environment.

We have studied the complexation of actinides with a series of carboxylates at variable temperatures because of the following reasons. 1) Many carboxylic acids are known to exist in the nuclear wastes and carboxylate is one of the most important functional groups in natural organic materials that participate in the complexation and redox reactions with actinides. Complexation of actinides with carboxylates affects their behavior in nuclear waste processing as well as geological disposal. 2) The temperature in the nuclear wastes in storage tanks and the geological repository is significantly higher than the ambient temperature due to the radioactive decay energy. Because the majority of the data in the literature on the complexation of actinides with carboxylates are obtained at or near 25 °C,[3] the thermodynamic parameters that are needed to predict the behavior of actinides in waste processing and disposal are unavailable. This paper focuses on the studies of the complexation of U(VI), Th(IV), and Nd(III) with acetate in solution at 10 – 70 °C. The formation constants, enthalpy and entropy of complexation for U(VI) acetate and Nd(III) acetate are reviewed and recalculated on the molality scale using a conversion approach different from that previously used.[4, 5] Recent data on Th(IV) acetate complexes are included. The thermodynamic parameters and the effect of temperature on the complexation of U(VI), Th(IV), and Nd(III) with acetate are discussed on a comparative basis.

2. Experimental

Chemicals. All the concentrations in molarity in this paper are referred to 25 °C. All chemicals are reagent grade or higher. Distilled water was used in preparations of all solutions. Descriptions on the preparation and standardization of the stock solutions of U(VI), Th(IV), and Nd(III) were given elsewhere.[4–6] Solutions of sodium acetate/acetic acid were prepared by adding calculated amounts of sodium hydroxide into solutions of acetic acid. The ionic strength of the solutions used in potentiometry and calorimetry was 1.0 mol dm^{-3} ($NaClO_4$) in the study of U(VI) and Th(IV), and 2.0 mol dm^{-3} ($NaClO_4$) in the study of Nd(III).

Procedures

Potentiometry. Details of the potentiometric titration setup have been provided elsewhere.[4–6] Electromotive force (*EMF*, in millivolts) was measured with a Metrohm pH meter (Model 713) equipped with a Ross combination pH electrode (Orion Model 8102) filled with 1.0 mol dm^{-3} sodium perchlorate to avoid clogging of the electrode frit glass septum due to the low solubility of $KClO_4$. The *EMF* of the glass electrode in the acidic region can be expressed by eq 1.

$$E = E^0 + RT/F \ln[H^+] + \gamma_H[H^+] \quad (1)$$

where *R* is the gas constant, *F* is the Faraday constant and *T* is the temperature in K. The last term is the electrode junction potential for the hydrogen ion ($\Delta E_{j,H+}$), assumed to be proportional to the concentration of the hydrogen ion. Prior to each titration, an acid/base titration with standard perchloric acid and sodium hydroxide was performed to obtain the electrode parameters of E^0 and γ_H. These parameters allowed the calculation of hydrogen ion concentrations from the *EMF*'s in the subsequent titration.

Fifty to seventy data points were collected in each titration. Multiple titrations were conducted at each temperature with solutions of different concentrations of the metal cations and perchloric acid. The complexation constants on the molarity scale were calculated with the program Hyperquad.[7]

Calorimetry. Details of the calorimeter and the calorimetric titrations have been given previously.[4] Usually, 50 – 70 values

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of experimental heat were obtained in each titration. The net heat of complexation was determined after correction for the heat of dilution and the heat due to acid/base neutralization. The enthalpy of metal acetate complexation was calculated by the computer program Letagrop.[8]

Optical Absorption Spectroscopy. Absorption spectra of Nd(III) acetate solutions were obtained on a Varian Cary-5G spectrophotometer equipped with a 1 × 1 peltier automatic temperature controller. Quartz cells with 1.0 cm optical length were used.

Extended X-ray Absorption Fine Structure (*EXAFS*) *Spectroscopy*. Uranium and thorium L_{III}-edge EXAFS spectra (up to $k_{max} \sim 15$ Å^{-1}) were collected on solutions of U(VI) and Th(IV) with different concentrations of acetate. The conditions of the solutions were selected, based on speciation calculation with the formation constants from this work, so that they contained different complexes as dominant species. The average ligand number, $\bar{n}$, ranged from 0 to 3.0 for U(VI) acetate and from 0 to 4.0 for Th(IV) acetate. Three scans were performed for each sample. Energy calibration was based on assigning the first inflection point of the absorption edge for UO_2 to 17166 eV and for ThO_2 to 16300 eV. The EXAFS spectra were fit with the R-space X-ray Absorption Package (RSXAP),[9] using parameterized phase and amplitude functions generated by the program FEFF8[10] with the reference crystal structures including $UO_2(OOCCH_3)_2 \cdot 2H_2O$ and $Na[UO_2(OOCCH_3)_3]$,[11–13] ThO_2 and $Na_6Th(CO_3)_5(H_2O)_{12}$.[14] Standard scattering paths were calculated from the reference structures and included in the data analysis. For the U(VI) data, the standard scattering paths include the single scattering U-O_{ax} (axial oxygen), U-O_{eq} (equatorial oxygen) and U-C, and the multiple scattering O=U=O (axial oxygens). For the Th(IV) data, the standard scattering paths include the single scattering Th-O, Th-C, and Th-Th.

Conversion of stability constants on the molarity scale to the molality scale. To allow the comparison at different temperatures, the constants in molarity (β_M) were converted to the constants in molality (β_m) by eq 2.[15]

$$\log_{10} \beta_m = \log_{10} \beta_M + \Sigma_r \nu_r \log_{10} \vartheta \qquad (2)$$

where ϑ is the ratio of the values of molality to molarity for the ϑ specific ionic medium and is equal to 1.05 and 1.10 dm^3 of solution per kg of water for 1.0 and 2.0 mol dm^{-3} $NaClO_4$. $\Sigma_r \nu_r$ is the stoichiometric coefficient of the reaction (ν_r is positive for products and negative for reactants) and is equal to $-j$ for the metal acetate complexation reactions ($M^{m+} + jAc^- = [M(Ac)_j]^{(m-j)+}$ where M^{m+} represents UO_2^{2+}, Th^{4+}, and Nd^{3+}, respectively). Therefore, the corrections for I = 1.0 and = 2.0 mol dm^{-3} $NaClO_4$ are performed by eq 3a and 3b, respectively.

$$\log_{10} \beta_{m,j} = \log_{10} \beta_{M,j} - 0.02 \times j \qquad (3a)$$

$$\log_{10} \beta_{m,j} = \log_{10} \beta_{M,j} - 0.04 \times j \qquad (3b)$$

3. Results and Discussion

U(VI) acetate

Thermodynamic parameters at 25 – 70 °C. The data from both potentiometry and calorimetry are consistent with the formation of three consecutive U(VI) acetate complexes defined by equilibrium 4.

$$\begin{aligned} &UO_2^{2+} + j\,CH_3COO^- \rightleftharpoons UO_2(OOCCH_3)_j^{(2-j)+} \quad j = 1, 2, 3 \\ &\beta_j = [UO_2(OOCCH_3)_j^{(2-j)+}]/([UO_2^{2+}][CH_3COO^-]^j) \end{aligned} \qquad (4)$$

The equilibrium constants and the corresponding Gibbs free energy, enthalpy and entropy of complexation are given in Table 1. The values of log β_M and ΔH were obtained by potentiometry and calorimetry, respectively. The values of log β_m were recalculated from the experimental log β_M using eq 3a. As shown by the data in Table 1, the overall stability constants of all three U(VI) acetate complexes increase as the temperature is elevated.

Structures of U(*VI*) *acetate complexes in solution.* The Fourier Transforms of the background-subtracted uranium L_{III}-edge EXAFS spectra for three U(VI) acetate solutions are shown in Figure 1. Based on the speciation calculation using the stability constants in Table 1, the average ligand number, $\bar{n}$, is equal to 1, 2, and 3 for Solutions I, II and III, respectively. The 1:1 and 1:3 complexes, $UO_2(OOCCH_3)^+$ and $UO_2(OOCCH_3)_3^-$, are the dominant species in Solutions I and III, respectively. However, Solution II contains a mixture of three complexes (1:1, 1:2, and 1:3) in comparable amounts without a dominant species.

Systematic changes in the Fourier Transforms of the EXAFS spectra are observed in the region around 2 Å (before the correction for the phase shift). From the 1:1 uranyl-acetate complex (Solution I), through the mixture (Solution II), to the 1:3 complex (Solution III), the broad peak at ~ 2 Å splits into two at 1.8 and 2.15 Å, respectively. The feature at 2.15 Å becomes more significant for Solution III, suggesting that

TABLE 1: Formation Constants and Corresponding Thermodynamic Parameters for Uranyl Acetate Complexation, I = 1.05 mol kg^{-1} ($NaClO_4$)

	t	log β_M	log β_m	ΔG	ΔH	ΔS
	°C			kJ mol^{-1}	kJ mol^{-1}	J K^{-1} mol^{-1}
$UO_2^{2+} + Ac^- = UO_2Ac^+$	25	2.58 ± 0.03	2.56 ± 0.03	–14.61	10.6 ± 0.8	85 ± 3
	35	2.67 ± 0.02	2.65 ± 0.02	–15.63	11.8 ± 0.5	89 ± 2
	45	2.74 ± 0.03	2.72 ± 0.03	–16.57	13.0 ± 0.6	93 ± 2
	55	2.85 ± 0.02	2.83 ± 0.02	–17.78	14.3 ± 0.5	98 ± 2
	70	2.98 ± 0.05	2.96 ± 0.05	–19.44	15.4 ± 0.7	102 ± 3
$UO_2^{2+} + 2Ac^- = UO_2Ac_2$	25	4.37 ± 0.14	4.33 ± 0.14	–24.71	20 ± 3	150 ± 13
	35	4.60 ± 0.08	4.56 ± 0.08	–26.90	21 ± 2	155 ± 8
	45	4.76 ± 0.10	4.72 ± 0.10	–28.75	22 ± 2	160 ± 8
	55	4.94 ± 0.06	4.90 ± 0.06	–30.78	24 ± 1	167 ± 4
	70	5.27 ± 0.09	5.23 ± 0.09	–34.36	27 ± 1	179 ± 5
$UO_2^{2+} + 3Ac^- = UO_2Ac_3^-$	25	6.86 ± 0.04	6.80 ± 0.04	–38.81	17.5 ± 0.6	189 ± 3
	35	7.11 ± 0.03	7.05 ± 0.03	–41.59	18.8 ± 0.3	196 ± 2
	45	7.23 ± 0.04	7.17 ± 0.04	–43.67	20.8 ± 0.3	203 ± 2
	55	7.38 ± 0.03	7.32 ± 0.03	–45.98	22.8 ± 0.3	210 ± 2
	70	7.62 ± 0.06	7.56 ± 0.06	–49.66	24.6 ± 0.4	216 ± 2

The error limits represent 3σ

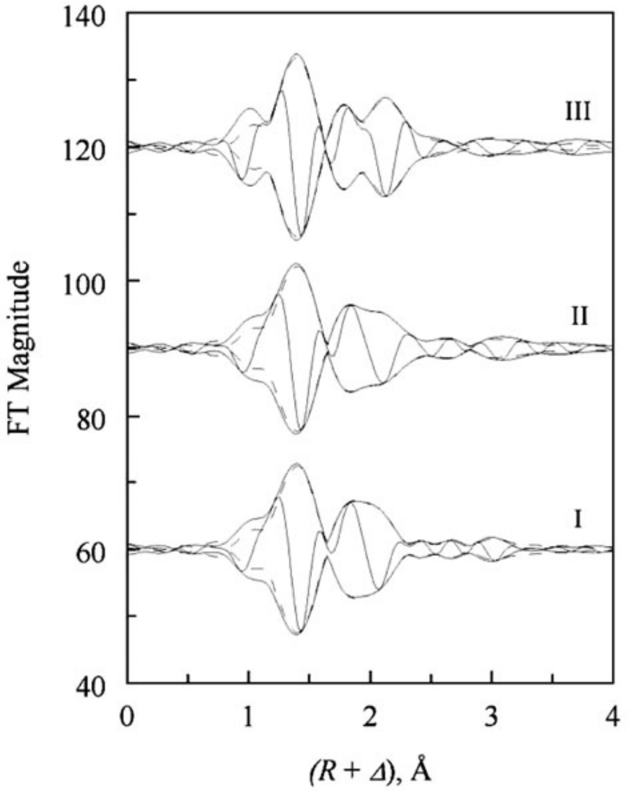

Figure 1. Experimental (solid lines) and fitted (dashed lines) uranium L_{III}-edge EXAFS data. (I) Solution I, $\bar{n}$ = 1, $UO_2(OOCCH_3)^+$ dominant; (II) Solution II, $\bar{n}$ = 2, no dominant species; (III) Solution III, $\bar{n}$ = 3, $UO_2(OOCCH_3)_3^-$ dominant.

more oxygens and/or carbons are found in a distant shell in the 1:3 complex than in the 1:1 complex. The best-fit parameters are summarized in Table 2.

As Denecke et al. showed,[16] the bidentate and unidentate acetate in the U(VI) complex can be differentiated by two features in EXAFS: (1) the $R_{U\text{-}O}$ is longer in the former (~ 2.45 – 2.48 Å) than in the latter (~ 2.35 Å); (2) the $R_{U\text{-}C}$ in the former is ~ 2.85 – 2.88 Å, easily identified by EXAFS. However, detecting the carbon in a unidentate acetate may be difficult due to its longer distance ($R_{U\text{-}C}$ 3.5 Å) and the overlap of oscillations resulting from the U-C single scattering and the linear O=U=O multiple scattering (1.78 × 2 Å). Therefore, data in Table 2 suggest the following: 1) The acetate ligand in the 1: 1 uranyl acetate complex (Solution I) is bidentate to uranium (two oxygens at 2.50 Å and one carbon at 2.91 Å). 2) In the 1:3 complex (Solution III), two acetates are bidentate (four oxygens at 2.48 Å and two carbons at 2.87 Å) and the third acetate is unidentate. One of the two oxygens at 2.34 Å is from the unidentate acetate while the other is from water. 3) Because no single species is dominant in Solution II, we cannot unambiguously assign the structure of the 1:2 complex based on the EXAFS data. However, the two carbons at 2.90 Å implies that there are two bidentate acetates per uranium by average in Solution II. Based on the EXAFS data, the structures of U(VI) acetate complexes in solution are proposed in Figure 2.

TABLE 2: Best Fit Parameters for Uranium L_{III}-Edge EXAFS

Samples	Shell	R,[a] Å	N[a]	σ, [b]Å	ΔE_0, eV
Solution I	U-O_{ax}	1.78	2.0	0.0411	-14.48
1:1 Uranyl/acetate	U-O_{eq1}	2.38	4.0	0.0703	-14.48
	U-O_{eq2}	2.5	2.0	0.0920	-14.48
	U-C	2.91	1.3	0.0500	-14.48
Solution II	U-O_{ax}	1.78	2.0	0.0370	-12.45
Mixture	U-O_{eq}	2.42	5.9	0.0888	-12.45
	U-C	2.9	2.2	0.0500	-12.45
Solution III	U-O_{ax}	1.78	2.0	0.0344	-12.37
1:3 Uranyl/acetate	U-O_{eq1}	2.34	1.9	0.0533	-12.37
	U-O_{eq2}	2.48	4.1	0.0482	-12.37
	U-C	2.87	2.1	0.0500	-12.37

[a] The 95% confidence limits for the bond lengths (R) and coordination numbers (N) for each shell are: U-O_{ax}, 0.01 Å and ± 15%; U-O_{eq}, 0.02 Å and ± 25%; U-C, 0.02 Å and ± 25%, respectively.

[b] σ is the EXAFS Debye-Waller term, which accounts for the effects of thermal and static disorder through damping of the EXAFS oscillations by the factor $\exp(-2k^2\sigma^2)$.

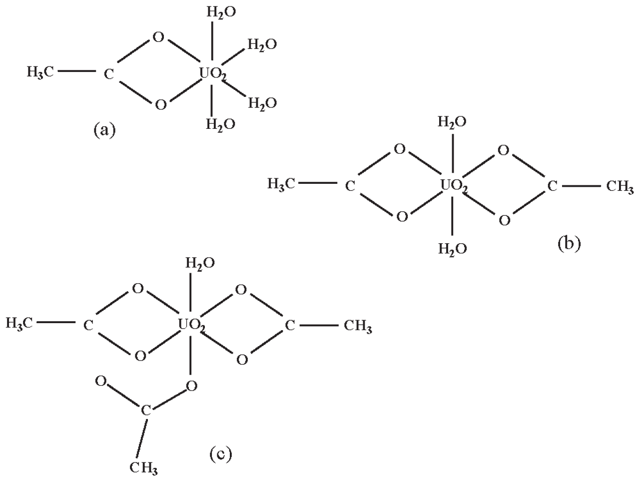

Figure 2. Proposed structures of uranyl acetate complexes in solution. (a) $UO_2(OOCCH_3)^+$. (b) $UO_2(OOCCH_3)_2(aq)$. (c) $UO_2(OOCCH_3)_3^-$.

Thermodynamic trends and the structure of complexes in solution. The stepwise enthalpy and entropy of complexation can be calculated from the data in Table 1. The trends are: (1) The first two steps are endothermic but the third is exothermic and the enthalpy of complexation decreases in the order: ΔH_1 (10 to 15 kJ mol^{-1}) > ΔH_2 (9 to 12 kJ mol^{-1}) >> ΔH_3 (about −2 kJ mol^{-1}). (2) The entropy change becomes smaller in the order: ΔS_1 (85 to 102 J K^{-1} mol^{-1}) > ΔS_2 (65 to 77 J K^{-1} mol^{-1}) > ΔS_3 (37 to 39 J K^{-1} $mo1^{-1}$) and ΔS_3 is less than 50% of ΔS_1. These trends can be rationalized in terms of the perturbation in the primary hydration sphere and the bulk structure of water upon complex formation. Since the degree of charge neutralization decreases as the stepwise complexation progresses, the energy required for restructuring the bulk solvent is expected to become less in successive steps. Thus the stepwise enthalpy change decreases in the order: $\Delta H_1 > \Delta H_2 > \Delta H_3$. Furthermore, the unidentate acetate in the third complex (Figure 2c) replaces only one water molecule in the primary hydration sphere so that it requires less desolvation energy than a bidentate coordination. Consequently, the enthalpy change in the third step is much less than the first two and, in this particular case, the stepwise formation of the third complex becomes exothermic.

Similarly, the trend in entropy can be interpreted based on the structural information of the uranyl acetate complexes in solution. In general, the entropy change upon the complexation consists of ΔS_t (translational), ΔS_r (rotational), and ΔS_c (conformational). The change in vibrational entropy (ΔS_v) can usually be neglected. Quantitative evaluation of the entropy effect in complexation is difficult because the quantities ΔS_t, ΔS_r, and ΔS_c are not easy to assess and the information on the solvation of the ligand is rarely available. However, integration of the thermodynamic data and structural information obtained in this work allows qualitative discussions. A larger gain in the translational entropy is certainly expected for a bidentate complex (steps 1 and 2) than a unidentate complex (step 3), because the former replaces more water molecules from the primary hydration sphere. Besides, higher degree of charge neutralization in steps 1 and 2 causes larger net increase

TABLE 3: Equilibrium Constants and Corresponding Thermodynamic Parameters for the Formation of Th(IV) Acetate Complexes

	t	log β_M	log β_m	ΔG	ΔH	ΔS
	°C			kJ mol^{-1}	kJ mol^{-1}	J K^{-1} mol^{-1}
$Th^{4+} + Ac^- = ThAc^{3+}$	10	3.71 ± 0.03	3.69 ± 0.03	–20.0	10.2± 0.23	107 ± 1
	25	3.81 ± 0.02	3.79 ± 0.02	–21.6	12.2± 0.18	114 ± 1
	40	3.96 ± 0.02	3.94 ± 0.02	–23.6	15.2± 0.75	124 ± 2
	55	4.11 ± 0.05	4.09 ± 0.05	–25.7	17.3 ± 0.8	131 ± 3
	70	4.30 ± 0.02	4.28 ± 0.02	–28.1	17.0 ± 0.9	131 ± 3
$Th^{4+} + 2Ac- = Th(Ac)_2^{2+}$	10	6.76 ± 0.02	6.72 ± 0.02	–36.4	12.7± 0.33	174 ± 1
	25	6.83± 0.02	6.79 ± 0.02	–38.8	16.9± 0.27	187 ± 1
	40	6.94 ± 0.04	6.90 ± 0.04	–41.4	20.7 ± 1.4	198 ± 5
	55	7.31 ± 0.06	7.27 ± 0.06	–45.7	25.5 ± 1.3	217 ± 4
	70	7.67 ± 0.02	7.63 ± 0.02	–50.1	28.3 ± 1.4	229 ± 4
$Th^{4+} + 3Ac^- = Th(Ac)_3^+$	10	8.58 ± 0.06	8.52 ± 0.06	–46.2	17.5 ± 1.1	225 ± 4
	25	8.77± 0.13	8.71 ± 0.13	–49.7	30.8 ± 0.7	270 ± 3
	40	9.05 ± 0.07	8.99 ± 0.07	–53.9	35.4 ± 2.6	285 ± 8
	55	9.41± 0.15	9.35 ± 0.15	–58.7	39.2 ± 3.7	298 ± 12
	70	9.75 ± 0.13	9.69 ± 0.17	–63.7	38.9 ± 4.7	299 ± 10
$Th^{4+} + 4Ac^- = Th(Ac)_4$	10	10.12 ± 0.12	10.04 ± 0.12	–54.4	29.1 ± 1.7	295 ± 6
	25	10.25 ± 0.19	10.17 ± 0.25	–58.0	30.7 ± 1.4	298 ± 7
	40	10.51 ± 0.12	10.43 ± 0.18	–62.5	44.8 ± 4.5	343 ± 6
	55	11.35 ± 0.11	11.27 ± 0.11	–70.8	65.9 ± 3.1	417 ± 10
	70	11.54 ± 0.20	11.46 ± 0.2	–75.3	99.5 ± 6.1	509 ± 18
$Th^{4+} + 5Ac^- = Th(Ac)_5^-$	10	11.37 ± 0.15	11.27 ± 0.15	–61.1	34.2 ± 1.2	337 ± 5
	25	11.51 ± 0.22	11.41 ± 0.22	–65.1	38.9 ± 0.8	349 ± 5
	40	11.69 ± 0.21	11.59 ± 0.21	–69.5	39.9 ± 3.5	349 ± 12
	55	12.48 ± 0.28	12.38 ± 0.28	–77.8	34.2 ± 3.2	341 ± 11
	70	12.94 ± 0.24	12.84 ± 0.24	–84.3	40.1 ± 4.2	363 ± 13

I = 1.05 mol kg^{-1} $NaClO_4$. The error limits represent 3σ

in the disorder of the bulk water. In addition, it is reasonable to assume that the structuring effect of a unidentate acetate on the bulk water could be stronger than a bidentate acetate because the former is more capable of forming hydrogen bonds with bulk water due to its "free" oxygen (Figure 2c). The combination of all these effects results in a much smaller ΔS_3 and the decreasing order of the stepwise entropy of complexation: $\Delta S_1 > \Delta S_2 >> \Delta S_3$.

Th(IV) acetate

Thermodynamic parameters at 10–70 °C. The data from both potentiometry and calorimetry are consistent with the formation of five consecutive Th(IV) acetate complexes. The equilibrium constants and the corresponding Gibbs free energy, enthalpy and entropy of complexation are given in Table 3.

EXAFS. The EXAFS spectra and associated Fourier Transforms of six Th(IV) solutions are shown in Figure 3. The values of $\bar{n}$ range from 0 to 4. The Fourier Transforms show prominent features in the region around 2 Å that represent the oxygen shell of coordinating water molecules or carboxylate groups of the acetate. The peak around 2 Å broadens from Solution I to VI as $\bar{n}$ is increased from 0 to 4, suggesting a single oxygen shell for Solution I ($\bar{n}$ = 0) but multiple oxygen shells for Solution VI ($\bar{n}$ = 4). Best fit of the EXAFS data indicate that the spectrum for Solution I is represented by a single Th-O shell with ~ 10 oxygen atoms at 2.45 Å, while the spectrum for Solution VI is represented by two distinct Th-O shells: 2–3 oxygen atoms at 2.37 Å and 8 oxygen atoms at 2.52 Å. The spectra for Solutions II–V are represented by gradual transition from a single Th-O shell (Solution I) to two Th-O shells (Solution VI).

Conclusive assignments of the two oxygen shells for Solution VI are difficult since there are no data on the crystal structure of Th(IV) acetate complexes. However, the most reasonable assignments can be made in comparison with the structural information on U(VI) acetate complexes in solution and crystalline $Na_6Th(CO_3)_5 \cdot 12H_2O$.[14] As discussed in previous sections, acetates coordinate to the linear UO_2^{2+} cation in the equatorial plane with either bidentate or unidentate modes. The $R_{U\text{-}Oeq}$ for the bidentate acetate is 2.45–2.48 Å, longer than the $R_{U\text{-}Oeq}$ for the unidentate acetate or the solvating water (~ 2.35 Å).[4, 16] Since the effective ionic radius of Th(IV) is larger than that of U(VI),[17] the $R_{Th\text{-}O}$ for bidentate or unidentate acetate should be slightly longer than corresponding $R_{U\text{-}O}$. This appears to be in agreement with the structural data of $Na_6Th(CO_3)_5 \cdot 12H_2O(c)$ where the five carbonate ligands are bidentate with the average

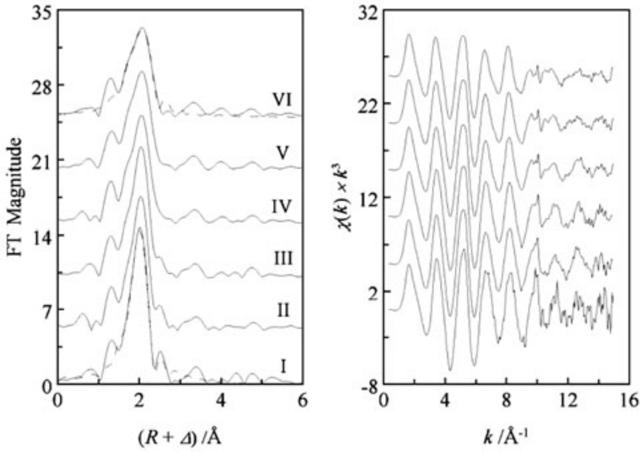

Figure 3. Experimental (solid line) and fitted (dotted line) thorium L_{III}-edge EXAFS spectra (right) and associated Fourier Transforms (left). (I-VI): Solutions I–VI, $\bar{n}$ = 0, 1.0, 1.5, 2.0, 3.0, 4.0, respectively.

TABLE 4: Formation Constants and Corresponding Thermodynamic Parameters for Nd(III) Acetate Complexation

	t	$\log \beta_M$	$\log \beta_m$	ΔG	ΔH	ΔS
	°C			kJ mol^{-1}	kJ mol^{-1}	J K^{-1} mol^{-1}
$Nd^{3+} + Ac^- = NdAc^{2+}$	25	1.92 ± 0.04	1.88 ± 0.04	−10.73	7.1 ± 0.03	59.8 ± 0.4
	45	2.05 ± 0.03	2.01 ± 0.03	−12.24	9.1 ± 0.3	67 ± 2
	70	2.24 ± 0.01	2.20 ± 0.01	−14.45	11.7 ± 0.2	76 ± 1
$Nd^{3+} + 2Ac^- = NdAc_2^+$	25	3.02 ± 0.05	2.94 ± 0.05	−16.78	14.6 ± 0.16	105 ± 2
	45	3.40 ± 0.05	3.32 ± 0.05	−20.2	17.5 ± 0.4	119 ± 3
	70	3.65 ± 0.03	3.57 ± 0.03	−23.4	20.1 ± 0.4	127 ± 2
$Nd^{3+} + 3Ac^- = NdAc_3$	25	3.58 ± 0.08	3.46 ± 0.08	−19.75	18.4 ± 0.46	128 ± 4
	45	4.36 ± 0.09	4.24 ± 0.09	−26.9	23.6 ± 0.5	159 ± 4
	70	4.71 ± 0.10	4.59 ± 0.10	−30.2	29.2 ± 0.5	173 ± 3

I = 2.20 mol kg^{-1} $NaClO_4$. The error limits represent 3σ

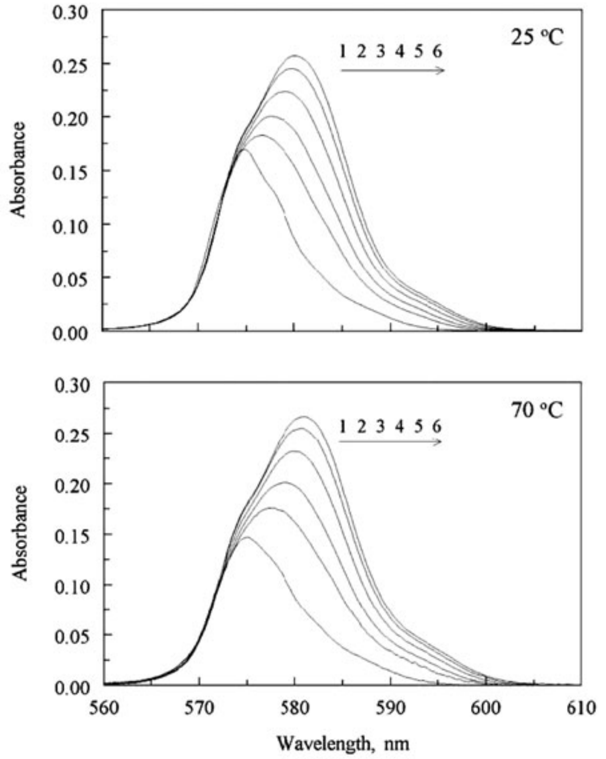

Figure 4. Absorption spectra of Nd/acetate solutions (the hypersensitive $^4I_{9/2} \rightarrow {}^4G_{5/2}, {}^2G_{7/2}$ transition) at 25 and 70 °C. Optical length: 1.0 cm, pH = 4.7, $[Nd(III)]_{total}$ = 0.025 mol dm^{-3}, the ratios of $C_{acetate}/C_{Nd}$ for spectra 1 – 6 are 0, 4, 8, 16, 28, and 40, respectively.

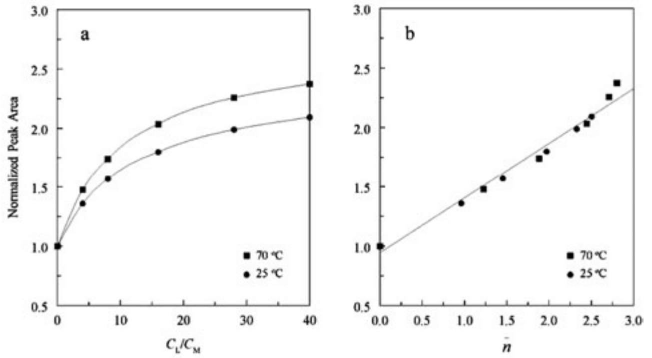

Figure 5. Normalized peak area for the $^4I_{9/2} \rightarrow {}^4G_{5/2}, {}^2G_{7/2}$ transition of Nd(III) vs. $C_{acetate}/C_{Nd}$ (a) and $\bar{n}$ (b) at 25 and 70 °C.

$R_{Th\text{-}O}$ = 2.505 Å.[14] Based on these results, the eight oxygens at 2.52 Å for Solution VI can be most reasonably assigned to the oxygens from bidentate acetate ligands, corresponding to four acetates by average for every Th^{4+}. Then the 2 – 3 oxygen atoms at 2.37 Å can be reasonably assigned to the solvating water molecules, making a total coordination number of 10 – 11 for Th^{4+}. It should be pointed out that the EXAFS data alone do not provide compelling evidence on the structures of the complexes in solution, but they are consistent with the thermodynamic results that suggest a value of $\bar{n} = 4$ for Solution VI.

Nd(III) acetate

Thermodynamic parameters at 25 – 70 °C. The equilibrium constants and the corresponding Gibbs free energy, enthalpy and entropy of complexation are given in Table 4. The values of log β_m were recalculated from the experimental log β_M using eq 3b.

Absorption Spectra at 25 and 70 °C. The absorption spectra of Nd(III) acetate solutions ($C_{Acetate}/C_{Nd}$ = 0, 4, 8, 16, 28, and 40) at 25 and 70 °C are shown in Figure 4. The data indicate that the $^4I_{9/2} \rightarrow {}^4G_{5/2}, {}^2G_{7/2}$ transition was significantly intensified as $C_{Acetate}/C_{Nd}$ was increased from 0 to 40, in a similar fashion at both temperatures. Attempts to deconvolute the spectra and calculate the oscillator strengths for individual species were not successful. However, when the peak area (normalized against the peak area in the absence of acetate) was plotted against $C_{Acetate}/C_{Nd}$, the data did indicate that the intensity of the $^4I_{9/2} \rightarrow {}^4G_{5/2}, {}^2G_{7/2}$ transition was enhanced by the complexation more significantly at 70 °C than at 25 °C (Figure 5a). Based on the generalization by Henrie et al.,[18] this difference implies that there are a greater number of coordinated acetate ligands around Nd^{3+} at 70 °C than at 25 °C when the ratio of $C_{Acetate}/C_{Nd}$ is constant. In other words, the spectrometric data suggest that Nd(III)/acetate complexation is stronger at 70 °C than at 25 °C. This is consistent with the trend in the thermodynamic constants obtained by potentiometry (Table 4). Figure 5b indicates that the peak area is proportional to the average number of acetate ligands around Nd^{3+} at both temperatures.

The effect of temperature on the complexation of U(VI), Th(IV), and Nd(III)

The stability of complexes. Data in Tables 1, 3, and 4 show that the U(VI), Th(IV), and Nd(III) acetate complexes become stronger as the temperature is increased. As discussed in previous publications, the effect of temperature on the formation constants of the complexes between a hard acid (e.g. actinide and lanthanide cations) and a hard base (e.g. oxygen donor ligands such as acetate) could be interpreted with an electrostatic model. Combining a modified Born equation[19] and the empirical expression for the dielectric constant of water ($\varepsilon = \varepsilon_0 \exp(-T/\vartheta)$, where $\varepsilon_0 = 305.7$; $\vartheta = 219$ K),[20, 21] the temperature coefficient of the complexation constant (β) is expressed as

$$\partial(\log \beta)/\partial T = Ne^2 Z_1 Z_2/(0.2303 R d_{12})(1/T - 1/\vartheta)/(\varepsilon T) \quad (5)$$

where the symbols are explained in Reference 19. Since ϑ is far below the freezing point of water, T is always higher than ϑ in the whole accessible temperature range of an aqueous solution. As a result, $(1/T - 1/\vartheta)$ is always negative. Thus, the electrostatic model predicts that the complexation between species of opposite charges is enhanced by the increase in temperature and that the magnitude of enhancement is proportional to $|Z_1Z_2|$. These predictions appear to agree with the data on the formation of 1:1 complexes of U(VI), Th(IV), and Nd(III) with acetate, as shown in Table 5. The agreement implies that the complexation between actinides and acetate is dominantly electrostatic interactions.

TABLE 5: Temperature Effect on the Formation Constants of Acetate Complexes

Reaction	Z_1Z_2	β_{70}/β_{25}[a]
$Nd^{3+} + Ac^- \rightarrow Nd(Ac)^{2+}$	−3	2
$UO_2^{2+} + Ac^- \rightarrow UO_2(Ac)^+$	−3.2[b]	2.5
$Th^{4+} + Ac^- \rightarrow Th(Ac)^{3+}$	−4	2.8

[a] Taken as a measure of the magnitude of temperature effect.

[b] Based on the effective charge on UO_2^{2+} in the literature.[19, 22]

Enthalpy and entropy of complexation. Data in Tables 1, 3, and 4 indicate that the overall complexation of U(VI), Th(IV), and Nd(III) with acetate is endothermic and is driven by large and positive entropies, consistent with the general observation for the interactions between "hard acid" cations and "hard base" anions. As shown in Figure 6, though the enthalpies become more positive and unfavorable to the complexation at higher temperatures, the complexes are more stable because of increasingly more positive entropy of complexation. These trends can be related to the perturbation of the solvent structure by thermal motions that results in a more disordered bulk water structure at higher temperatures. In the process of complexation, the highly ordered solvating water molecules are released to a more disordered bulk solvent. As a result, the gain in the entropy of complexation is larger at higher temperatures. This effect has been discussed in more detail elsewhere.[5, 23, 24]

Figure 6 shows that the overall enthalpies of formation of all the acetate complexes, except $Th(Ac)_4(aq)$, can be fitted with linear functions of the temperature, suggesting that the heat capacities of formation of these complexes are constant from 25 to 70 °C. From the slopes of the linear fits, the overall heat capacities of complexation ($J\ K^{-1}\ mol^{-1}$) are calculated to be: (110 ± 19) for UO_2Ac^+, (172 ± 48) for $UO_2(Ac)_2(aq)$, and (170 ± 12) for $UO_2(Ac)_3^-$; (125 ± 22) for $ThAc^{3+}$, (265 ± 11) for $Th(Ac)_2^{2+}$, (341 ± 94) for $Th(Ac)_3^+$, and (46 ± 68) for $Th(Ac)_5^-$; and (102 ± 13) for $NdAc^{2+}$, (122 ± 19) for $Nd(Ac)_2^+$, and (239 ± 27) for $Nd(Ac)_3(aq)$. Unlike these complexes, the enthalpy of formation of $Th(Ac)_4(aq)$ drastically increases in a non-linear manner when the temperature is increased from 10 to 70 °C. This suggests that heat capacity of formation of $Th(Ac)_4(aq)$ is large and temperature-dependent. This may not be surprising since the stepwise formation of $Th(Ac)_4(aq)$ is a reaction of complete charge neutralization:

$$Th(Ac)_3^+ + Ac^- \rightarrow Th(Ac)_4(aq) \tag{6}$$

The heat capacity of a reaction consists of electrostatic and non-electrostatic contributions and the former is expected to be dominant in the reaction between a "hard acid" and a "hard-base". For an isocolumbic reaction where the sign and magnitude of the electrical charges on the reactants and the products are identical, the electrostatic contributions from the reactants and products may balance out so that the heat capacity is small or near zero, and independent of temperature.[25] However, for the reactions where the electrical charges of the reactants and products are drastically different, large heat capacity changes are often associated. This could be particularly true for the reactions of complete charge neutralization such as Reaction 6. In fact, the heat capacities of the formation of $Nd(Ac)_3(aq)$ and $UO_2(Ac)_2(aq)$, also reactions of complete charge neutralization, are found to be large.

4. Summary

The complexation of U(VI), Th(IV), and Nd(III) with acetate becomes stronger as the temperature is increased from 10 to 70 °C, despite that the enthalpy of complexation becomes more endothermic and unfavorable to the complexation at higher temperatures. The enhancement of the complexation is mainly due to a larger entropy effect at higher temperatures and can be explained by the effect of temperature on the solvent structure and a simple electrostatic model.

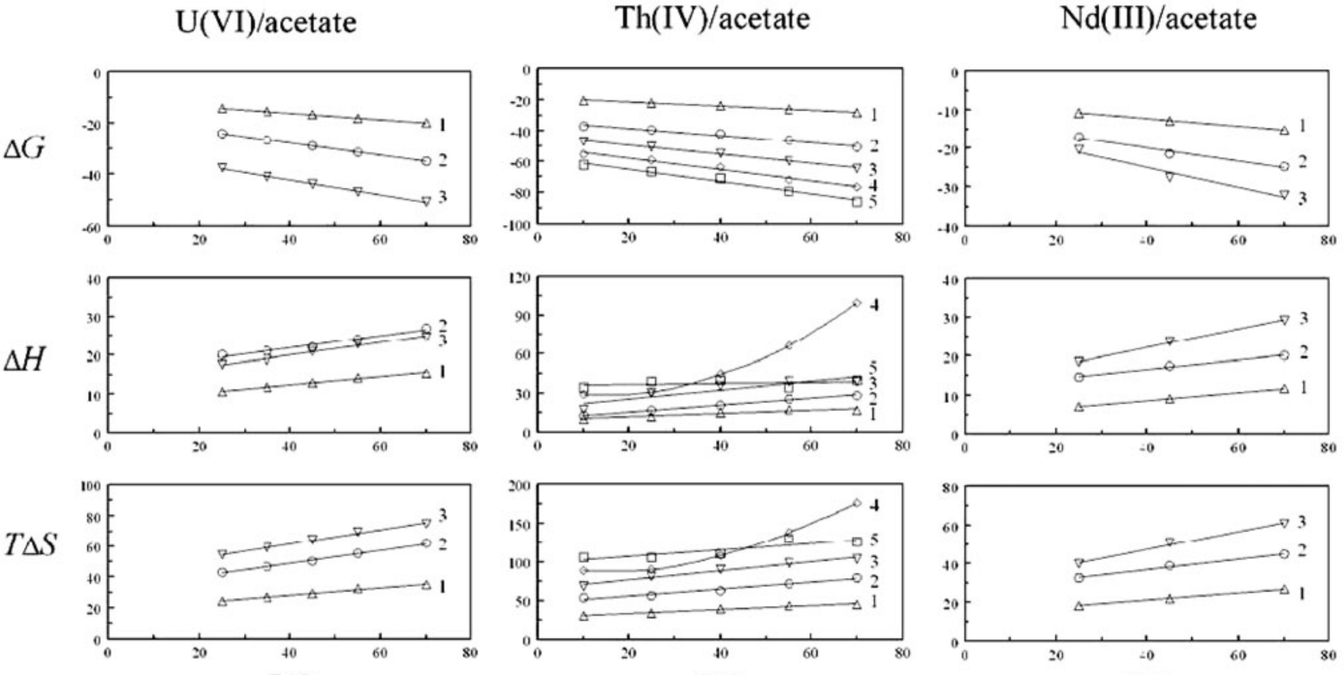

Figure 6. Overall thermodynamic parameters of U(VI), Th(IV) and Nd(III) acetate complexation at different temperatures, Symbols: (1) ML; (2) ML_2; (3) ML_3; (4) ML_4; (5) ML_5.

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