ELSEVIER

Journal of Alloys and Compounds 408–412 (2006) 1252–1259

Journal of ALLOYS AND COMPOUNDS

www.elsevier.com/locate/jallcom

Complexation of thorium(IV) with malonate at variable temperatures

Thandankorai G. Srinivasan [a], PierLuigi Zanonato [b], Plinio Di Bernardo [b],
Arturo Bismondo [c], Linfeng Rao [a,*]

[a] *Chemical Sciences Division, Lawrence Berkeley National Laboratory, Berkeley, CA 94720, USA*
[b] *Dipartimento di Scienze Chimiche, Università di Padova, via Marzolo 1, 35131 Padova, Italy*
[c] *Istituto di Chimica Inorganica e delle Superfici del C.N.R. of Padova, Corso Stati Uniti 4, 35127 Padova, Italy*

Abstract

Complexation between thorium(IV) and malonate in 1.05 mol kg^{-1} $NaClO_4$ was studied from 10 to 70 °C by potentiometry and calorimetry. Three complexes, ThL^{2+}, ThL_2 and ThL_3^{2-}, where L stands for malonate, were identified. The stability constants, the enthalpies and entropies of complexation at variable temperatures were determined. Despite that the enthalpies of complexation become more endothermic, the complexes become more stable due to increasingly larger entropies of complexation that exceed the unfavorable contribution of enthalpies of complexation at higher temperatures. The thermodynamic trends are explained in terms of an electrostatic model and the change in the structure of water with temperature. The data are compared with previous results on the complexation of U(VI) and Nd(III) with malonate and other carboxylate ligands.

Keywords: Thorium; Malonate; Complexation; Stability constants; Enthalpy; Entropy; Temperature effect

1. Introduction

The necessity to treat and dispose of large amounts of nuclear wastes in a safe and economical manner has generated significant interest in recent years in the coordination chemistry of actinides in solution, especially at elevated temperatures. It is well known that the temperature of the waste in the storage tanks can be up to 90 °C, while that in the vicinity of the waste forms in the repository can be as high as 100–300 °C [1,2]. Thus, complexation of actinides with ligands in solution at elevated temperatures should be understood. However, the majority of the literature data are obtained at or near 25 °C [3]. Though the data can be extrapolated to higher temperatures with the van't Hoff isochore if the enthalpy of complexation is known and assumed to be constant [4,5], such attempts could lead to large uncertainties. Theoretical models such as the HKF equation permit the prediction of thermodynamic properties under geothermal conditions with fairly good accuracy [6–8]. However, use of these models for actinides is hindered by the lack of parameters.

The properties of water vary significantly as the temperature is changed. For example, the dielectric constant decreases by about 35% [9] and the ionic product ($K_w = [H^+][OH^-]$) increases by almost three orders of magnitude [10] from 0 to 100 °C. The change in the dielectric constant is likely to affect the complexation of actinides because the actinide-ligand interactions are dominantly electrostatic. The increase in K_w could enhance the hydrolysis of actinides and weaken their complexation with other ligands. Besides, the thermal perturbation of the structure of water at elevated temperatures certainly increases the degree of disorder of the bulk water, thus affecting the entropy of complexation that involves the release of water molecules from the primary hydration sphere of the metal ion to the bulk water. Therefore, the study of the complexation of actinides at elevated temperatures can provide insight into the nature and energetics of metal–ligand interaction and improve the fundamental understanding of actinide complexation.

For the above-mentioned practical and fundamental reasons, we have initiated studies on the complexation of

---

* Corresponding author.
E-mail address: lrao@lbl.gov (L. Rao).

0925-8388/$ – see front matter © 2005 Elsevier B.V. All rights reserved.
doi:10.1016/j.jallcom.2005.04.122

actinides and lanthanides with carboxylic acids at variable temperatures, including the complexation of Nd(III), U(VI) and Th(IV) with acetate [5,11,12], U(VI) with malonate [13], Sm(III) and U(VI) with oxydiacetate [14], as well as the hydrolysis of U(VI) [15] and Np(V) [16]. This paper reports the results of the complexation of Th(IV) with malonate from 10 to 70 °C. The formation constants of three complexes and the enthalpies of complexation are determined by potentiometry and calorimetry. The effect of temperature on the complexation and the trends in thermodynamic parameters are discussed in terms of an electrostatic model.

2. Experimental

2.1. Chemicals

In this study, all the concentrations in molarity refer to 25 °C. All chemicals were reagent grade or higher. Distilled/deionized water was used in preparations of all solutions. A standard sodium hydroxide solution (Aldrich, ACS volumetric standard) was used to determine the concentrations of perchloric acid by potentiometry. Sodium malonate (Aldrich) was used without further purification. Buffer solutions of sodium malonate/malonic acid were prepared by adding calculated amounts of perchloric acid into solutions of sodium malonate. The stock solution of Th(IV) perchlorate was prepared from Th(IV) nitrate as follows. $Th(NO_3)_4{\cdot}4H_2O$ was dissolved in water. $Th(OH)_4(s)$ was precipitated by adding NaOH. The precipitate was centrifuged, washed with water and re-dissolved with an excess of perchloric acid. The precipitation and dissolution were repeated three times. The concentrations of thorium and free perchloric acid in the stock solution were determined by complexometry [17] and Gran's potentiometric method [18]. The ionic strength of all the solutions in potentiometry and calorimetry was adjusted to $1.0\,\mathrm{mol\,dm^{-3}}$ at 25 °C, equivalent to $1.05\,\mathrm{mol\,kg^{-1}}$, by adding appropriate amounts of sodium perchlorate.

2.2. Potentiometry

Potentiometric experiments were carried out at 10 and 85 °C for the protonation of malonate and at 10, 25, 40, 55 and 70 °C for the complexation of malonate with Th(IV) with a variable-temperature titration setup. Detailed description of the apparatus and the procedures are provided elsewhere [5,11,19]. Electromotive force (EMF, in millivolts) was measured with a Metrohm pH meter (model 713) equipped with a Ross combination pH electrode (Orion model 8102). The electrode is workable up to 100 °C. However, it was found that the electrode frit glass septum could rapidly become damaged at 85 °C in the Th(IV)/malonate titrations, probably due to thermal expansion and contraction during prolonged vigorous washing with cold water between titrations. As a result, the complexation titrations were conducted up to 70 °C.

The original electrode filling solution ($3.0\,\mathrm{mol\,dm^{-3}}$ KCl) was replaced with $1.0\,\mathrm{mol\,dm^{-3}}$ NaCl to avoid clogging of the electrode frit septum by precipitation of $KClO_4$. The EMF of the glass electrode in the acidic region can be expressed by Eq. (1).

$$E = E^0 + \frac{RT}{F}\ln[\mathrm{H^+}] + \gamma_{\mathrm{H}}[\mathrm{H^+}] \tag{1}$$

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 ($\Delta E_{j,\mathrm{H+}}$), 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 EMFs in the subsequent titration. Corrections for the electrode junction potential of the hydroxide ion were not necessary in these experiments.

Detailed experimental conditions of potentiometry are provided in Table A.1 of Appendix A. The EMF data were collected at time intervals determined by the data collection criterion, i.e., the drift of EMF (ΔE) was less than 0.1 mV for 180 s. Fifty to seventy data points were collected in each titration. Multiple titrations were conducted at each temperature with solutions of different concentrations of thorium ($C^0_{\mathrm{Th}} = 2.4$–$15\,\mathrm{mmol\,dm^{-3}}$) and perchloric acid ($C^0_{\mathrm{H}} = 3.5$–$61\,\mathrm{mmol\,dm^{-3}}$). The initial volume of the test solutions ranged from 30 to 50 $\mathrm{cm^3}$ at 25 °C. The protonation and complexation constants on the molarity scale were calculated with the program Hyperquad [20]. To allow comparison at different temperatures, the constants in molarity were converted to the constants in molality according to the method in the literature [21]. The equilibrium constant of a reaction in molality (K_{m}) is related to that in molarity (K_{M}) by Eq. (2).

$$\log_{10} K_{\mathrm{m}} = \log_{10} K_{\mathrm{M}} + \sum\nolimits_{\mathrm{r}} \nu_{\mathrm{r}} \log_{10} \vartheta \tag{2}$$

where ϑ is the ratio of the values of molality to molarity for the specific ionic medium and equals 1.05 $\mathrm{dm^3}$ of solution per kg of water for $1.0\,\mathrm{mol\,dm^{-3}}$ $NaClO_4$ at 25 °C. $\Sigma_{\mathrm{r}}\nu_{\mathrm{r}}$ is the sum of the stoichiometric coefficients of the reaction (ν_{r} is positive for products and negative for reactants) and is equal to $-j$ for malonate protonation ($j\mathrm{H^+} + \mathrm{L^{2-}} = \mathrm{H}_j\mathrm{L}^{(j-2)+}$) and for Th(IV) malonate complexation ($\mathrm{Th^{4+}} + j\mathrm{L^{2-}} = \mathrm{ThL}_j^{(4-2j)+}$). Therefore, the correction of log β from molarity to molality follows Eq. (3), where j = 1–2 for malonate protonation and j = 1–3 for Th(IV) malonate complexation.

$$\log_{10} \beta_{\mathrm{m},j} = \log_{10} \beta_{\mathrm{M},j} - 0.02j \tag{3}$$

2.3. Calorimetry

Calorimetric titrations were conducted with a solution calorimeter (model ISC-4285, Calorimetry Sciences Corp.). Details of the calorimeter have been given elsewhere [11]. Its performance was tested by measuring the enthalpy of protonation of 2-bis(2-hydroxyethyl)amino-2-hydroxymethyl-propan-1,3-diol. The results are $-29.1 \pm 0.3\,\mathrm{kJ\,mol^{-1}}$ at 45 °C and $-29.3 \pm 0.3\,\mathrm{kJ\,mol^{-1}}$ at 70 °C and compare well with those in the literature ($-28.4 \pm 0.3\,\mathrm{kJ\,mol^{-1}}$ at 45 °C and $-29.3 \pm 0.2\,\mathrm{kJ\,mol^{-1}}$ at 70 °C) [22].

Detailed titration conditions are provided in Table A.2 of Appendix A. For each titration run, n values of the total heat generated in the reaction vessel ($Q_{\mathrm{ex},j}$, $j = 1$ to n) were obtained as a function of the volume of the added titrant. These values were corrected for the heat of dilution of the titrant ($Q_{\mathrm{dil},j}$), determined in separate runs. The net reaction heat at the j-th point ($Q_{\mathrm{r},j}$) was obtained from the difference: $Q_{\mathrm{r},j} = Q_{\mathrm{ex},j} - Q_{\mathrm{dil},j}$. The quantities $\Delta h_{\nu,\mathrm{H}}$ and $\Delta h_{\nu,\mathrm{M}}$, the total heat/mol of malonate (in protonation titrations) or thorium (in complexation titrations), were then calculated by

$$\Delta h_{\nu,\mathrm{H}} = \sum \frac{Q_{\mathrm{r},j}}{n} \tag{4}$$

$$\Delta h_{\nu,M} = \sum \frac{(Q_{\mathrm{r},j} - Q_{\mathrm{p},j})}{n} \tag{5}$$

where n was the number of moles of malonate (in protonation titrations) or Th(IV) (in complexation titrations) in the calorimetric cell and $Q_{\mathrm{p},j}$ was the heat due to the protonation reactions of the ligand. The enthalpy of protonation or complexation was calculated by the computer program Letagrop [23]. The original version of Letagrop was appropriately modified in order to use $\Delta h_{\nu,\mathrm{H}}$ or $\Delta h_{\nu,\mathrm{M}}$ as the error–carrying variable.

3. Results

3.1. Protonation of malonate at variable temperatures

The protonation constants and enthalpies from 25 to 70 °C were previously reported [13,24]. The present work has extended the temperature range to 10–85 °C. As shown in Table 1, the protonation constants and enthalpies at 10 and 85 °C fit very well with previous values. As is typical of many carboxylic acids, the enthalpies of protonation of malonate are small (from 0 to a few $\mathrm{kJ\,mol^{-1}}$) and more endothermic at higher temperatures. Despite that the enthalpy becomes more unfavorable to the protonation at higher temperatures, the protonation constants increase slightly when the temperature is increased, largely due to the increasingly more positive entropy of protonation at higher temperatures (Table 1).

The protonation constants and enthalpies in Table 1 were used in the calculation of the formation constants and enthalpies of complexation between Th(IV) and malonate.

3.2. Formation constants of Th(IV)/malonate complexes at variable temperatures

Results of two representative potentiometric titrations are shown in Fig. 1. The best fit of the data indicates that three successive complexes form during the titration. The overall complexation reactions are represented by equilibrium (6), where L stands for malonate and $j = 1, 2, 3$.

$$\mathrm{Th}^{4+} + j\mathrm{L}^{2-} \leftrightarrows \mathrm{ThL}_j^{(4-2j)+} \tag{6}$$

Table 1
Protonation of malonate, $I = 1.05\,\mathrm{mol\,kg^{-1}}$ ($\mathrm{NaClO_4}$), the error limits represent 3σ

T (°C)	$\log \beta_{\mathrm{H,M}}$	$\log \beta_{\mathrm{H,m}}$	$-\Delta G$ ($\mathrm{kJ\,mol^{-1}}$)	ΔH ($\mathrm{kJ\,mol^{-1}}$)	ΔS ($\mathrm{J\,K^{-1}\,mol^{-1}}$)	Reference
$\mathrm{H^+ + L^{2-} = HL^-}$						
10	5.06 ± 0.01	5.04 ± 0.01	27.3 ± 0.1	−0.1 ± 0.2	96 ± 1	This work
25	5.10 ± 0.01	5.08 ± 0.01	29.0 ± 0.1	2.07 ± 0.03	104 ± 1	[13]
	5.09 ± 0.02		28.9	2.0	104 ± 1	[24]
35	5.15 ± 0.01	5.13 ± 0.01	30.3 ± 0.1	3.12 ± 0.03	108 ± 1	[13]
40	5.16			3.73		[a]
45	5.17 ± 0.01	5.15 ± 0.01	31.4 ± 0.1	4.34 ± 0.03	112 ± 1	[13]
55	5.22 ± 0.01	5.20 ± 0.01	32.7 ± 0.1	5.55 ± 0.04	116 ± 1	[13]
70	5.29 ± 0.02	5.27 ± 0.02	34.6 ± 0.1	7.08 ± 0.08	122 ± 1	[13]
85	5.32 ± 0.02	5.30 ± 0.02	36.3 ± 0.1	8.94 ± 0.05	126 ± 1	This work
$\mathrm{2H^+ + L^{2-} = H_2L}$						
10	7.66 ± 0.01	7.62 ± 0.01	41.3 ± 0.1	−2.9 ± 0.2	136 ± 1	This work
25	7.69 ± 0.01	7.65 ± 0.01	43.7 ± 0.1	0.43 ± 0.03	148 ± 1	[13]
	7.68 ± 0.03		43.6 ± 0.1	0.5	148 ± 1	[24]
35	7.82 ± 0.01	7.78 ± 0.01	45.9 ± 0.1	2.58 ± 0.03	157 ± 1	[13]
40	7.82			3.65		[a]
45	7.83 ± 0.02	7.79 ± 0.02	47.4 ± 0.1	4.72 ± 0.03	157 ± 1	[13]
55	7.91 ± 0.02	7.87 ± 0.02	49.4 ± 0.1	6.84 ± 0.03	165 ± 1	[13]
70	8.00 ± 0.02	7.96 ± 0.02	52.3 ± 0.1	10.06 ± 0.08	172 ± 1	[13]
85	8.05 ± 0.03	8.01 ± 0.03	54.9 ± 0.1	12.24 ± 0.06	181 ± 1	This work

[a] The values of $\log \beta_{\mathrm{H,M}}$ and ΔH at 40 °C were obtained by interpolation using the values at other temperatures (10–85 °C).

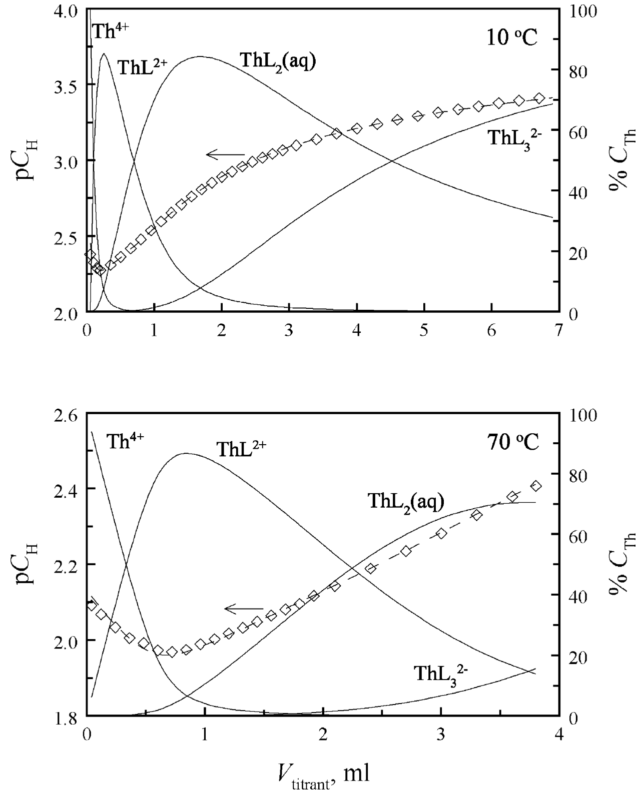

Fig. 1. Potentiometric titration of the thorium-malonate system, $I = 1.05\ \mathrm{mol\ kg^{-1}}$ $NaClO_4$. Titrant: $C_H = 0.400\ \mathrm{mol\ dm^{-3}}$, $C_{malonate} = 0.400\ \mathrm{mol\ dm^{-3}}$. Initial cup solution ($V^0$) in ml: 30.2 (10 °C), 50.7 (70 °C). Initial cup concentrations (C_H/C_{Th}, $\mathrm{mmol\ dm^{-3}}$): 3.530/2.387 (10 °C), 7.359/4.978 (70 °C). Symbols: (◊) experimental data (pC_H); dashed line – fit (pC_H); solid lines—percentage of Th(IV) species (right y-axis).

$$\beta_j = \frac{[\mathrm{ThL}_j^{(4-2j)+}]}{([\mathrm{Th}^{4+}][\mathrm{L}^{2-}]^j)} \tag{7}$$

The calculated equilibrium constants and Gibbs free energy of the reactions are given in Table 2. The data indicate that the complexation between Th(IV) and malonate is enhanced as the temperature increases. The stabilities of ThL^{2+}, $ThL_2{}^0$ and $ThL_3{}^{2-}$ are about 4, 9 and 50 times higher at 70 °C than those at 25 °C, respectively.

3.3. Enthalpy of complexation at variable temperatures

The experimental data of the calorimetric titrations are shown in Fig. 2, in the form of $\Delta h_{\nu,\mathrm{M}}$ versus $\bar{n}$, where $\bar{n}$ is the average number of ligands coordinated to each Th(IV) and defined as

$$\bar{n} = \frac{\sum(j \times [\mathrm{ML}_j])}{C_\mathrm{M}} \tag{8}$$

Values of $\bar{n}$ were calculated using the formation constants in Table 2 and the total concentrations of Th(IV), proton and malonate at each step of the titration. The enthalpies of complexation were calculated from the calorimetric data and summarized in Table 2.

Using the enthalpies and formation constants in Table 2, curves simulating the calorimetric titrations were calculated and shown in Fig. 2. The good agreement between the curves and the experimental points confirms the mutual consistency of the calorimetric and potentiometric data on the complexation as well as the reliability of the data on protonation. It should be noted that no Th(IV) malonate complexes higher

Table 2
Complexation of Th(IV) with malonate, $I = 1.05\ \mathrm{mol\ kg^{-1}}$ ($NaClO_4$), the error limits represent 3σ

T (°C)	$\log \beta_\mathrm{M}$	$\log \beta_\mathrm{m}$	$-\Delta G$ ($\mathrm{kJ\ mol^{-1}}$)	ΔH ($\mathrm{kJ\ mol^{-1}}$)	ΔS ($\mathrm{J\ K^{-1}\ mol^{-1}}$)
$Th^{4+} + L^{2-} = ThL^{2+}$					
10	7.41 ± 0.06	7.39 ± 0.06	40.1 ± 0.3	7.1 ± 0.3	167 ± 2
25	7.47 ± 0.04	7.45 ± 0.04	42.5 ± 0.2	11.3 ± 0.1	180 ± 1
	7.47 ± 0.01[a]	7.45 ± 0.01	42.5 ± 0.1	11.9 ± 0.1[a]	182 ± 1
40	7.65 ± 0.07	7.63 ± 0.07	45.7 ± 0.4	14.3 ± 0.1	192 ± 1
55	7.84 ± 0.08	7.82 ± 0.08	49.1 ± 0.5	15.8 ± 0.2	198 ± 2
70	8.03 ± 0.15	8.01 ± 0.15	52.6 ± 1.0	17.1 ± 0.2	203 ± 3
$Th^{4+} + 2L^{2-} = ThL_2$					
10	12.69 ± 0.07	12.65 ± 0.07	68.6 ± 0.4	12.1 ± 0.4	285 ± 2
25	12.84 ± 0.04	12.80 ± 0.04	73.1 ± 0.2	19.1 ± 0.1	309 ± 1
	12.79 ± 0.03[a]	12.75 ± 0.03	72.8 ± 0.2	20.4 ± 0.4[a]	313 ± 2
40	13.17 ± 0.09	13.13 ± 0.09	78.7 ± 0.5	23.4 ± 0.5	326 ± 2
55	13.55 ± 0.08	13.51 ± 0.08	84.9 ± 0.5	27.2 ± 0.2	342 ± 2
70	13.81 ± 0.15	13.77 ± 0.15	90.5 ± 1.0	29.9 ± 0.4	351 ± 3
$Th^{4+} + 3L^{2-} = ThL_3{}^{2-}$					
10	15.91 ± 0.07	15.85 ± 0.07	85.9 ± 0.4	15.0 ± 0.5	356 ± 2
25	16.54 ± 0.06	16.48 ± 0.06	94.1 ± 0.4	23.1 ± 0.2	393 ± 2
	16.28 ± 0.12[a]	16.22 ± 0.12	92.6 ± 0.7	25.0 ± 1.2[a]	394 ± 5
40	17.30 ± 0.12	17.24 ± 0.12	103.4 ± 0.7	30.2 ± 1.2	427 ± 4
55	17.88 ± 0.09	17.82 ± 0.09	111.9 ± 0.6	34.7 ± 0.3	447 ± 2
70	18.24 ± 0.15	18.18 ± 0.15	119.4 ± 1.0	39.2 ± 0.6	462 ± 4

[a] Values from [24].

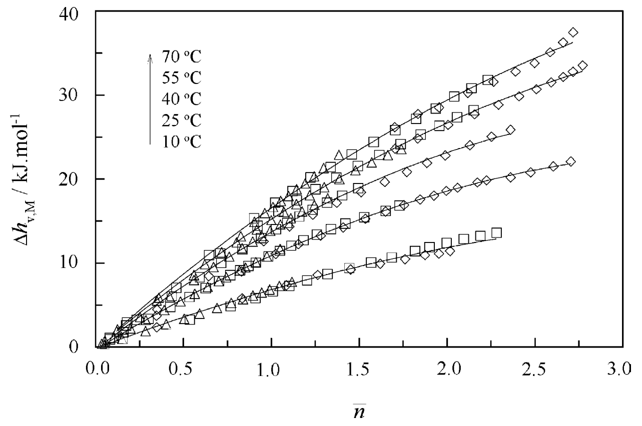

Fig. 2. Calorimetric titrations of Th(IV) malonate complexation: $\Delta h_{v,M}$ vs. $\bar{n}$ at different temperatures, $I = 1.05$ mol kg^{-1} $NaClO_4$. Symbols: experimental data; line: calculated. Three titrations are represented at each temperature. The number of data points is reduced for clarity. Detailed titration conditions are provided in Table A.2 of Appendix A.

than ML_3 are identified in the potentiometric and calorimetric experiments in this work, though a solid compound of bis(ethylenediammonium)tetrakis(malonato)thorium(IV), $(C_2H_{10}N_2)_2[Th(C_3H_2O_4)_4(H_2O)]$, has been prepared from a water/methanol solution [25].

4. Discussion

4.1. Effect of temperature on the stability of complexes

Based on the modified Born-equation that describes the Gibbs free energy for a complexation reaction of electrostatic nature [5,11], the temperature effect on the complexation can be expressed as

$$\frac{\partial(\log\beta)}{\partial T} = \frac{Ne^2 Z_1 Z_2 (1/T - 1/\theta)}{0.2303\varepsilon T R d_{12}} \qquad (9)$$

where β is the stability constant of the complex and ε is the dielectric constant of water at temperature T [26,27]. Z_1 and Z_2 are the charges of the two species that form complexes. Other parameters in Eq. (9) are explained elsewhere [28]. Since T is always higher than θ (= 219 K) in the whole accessible temperature range for liquid water, the electrostatic model predicts that $(\partial \log\beta)/\partial T > 0$ if $Z_1Z_2 < 0$. In other words, the complexation between species of opposite charges is strengthened by the increase in temperature. This prediction has been found consistent with many data for the complexation of lanthanide and actinide cations with carboxylate ligands, including Nd(III) acetate [5], U(VI) acetate [11], Th(IV) acetate [12], U(VI) malonate [13], and Sm(III) and U(VI) oxydiacetate [14]. The data for Th(IV) malonate complexation from this work also agree with this prediction (Table 2).

In addition, the electrostatic model predicts that the magnitude of the temperature coefficient $(\partial \log\beta)/\partial T$, is proportional to $|Z_1Z_2|$. In other words, the complexation between species with higher charges is more sensitive to the change in temperature. This appears to agree with many data on the 1:1 complexes (ML) of lanthanides/actinides with simple carboxylates, particularly when compared between the systems with one common species (either M or L). As shown in Table 3, the temperature coefficient of acetate complexation with Nd(III), U(VI) and Th(IV) follows the order of $|Z_1Z_2|$: Nd(III) < U(VI) < Th(IV). For the complexes of U(VI) or Th(IV), the temperature effect (K_{70}/K_{25}) is always higher for the malonate complex than the acetate complex. However, it should be emphasized that the discussions based on the electrostatic model are mostly qualitative. Some experimental data do not agree with the predictions. For example, The electrostatic model predicts that the complexation with a neutral species should be insensitive to the change in temperature ($(\partial \log\beta)/\partial T = 0$ if $|Z_1Z_2| = 0$). Some systems seem to agree with this prediction. For example, the stepwise formation of $UO_2(Ac)_3^-$ and $Th(Ac)_5^-$, $UO_2(Ac)_2^0 + Ac^- = UO_2(Ac)_3^-$ and $Th(Ac)_4^0 + Ac^- = Th(Ac)_5^-$, involves neutral species ($|Z_1Z_2| = 0$) and the formation constants were found to be insensitive to the temperature change [11,12]. On the contrary, the stepwise formation of $UO_2(Mal)_2^{2-}$ and $Th(Mal)_3^{2-}$, $UO_2(Mal)^0 + Mal^{2-} = UO_2(Mal)_2^{2-}$ [13] and $Th(Mal)_2^0 + Mal^{2-} = Th(Mal)_3^{2-}$, has significant temperature effects even though $|Z_1Z_2| = 0$. Such disagreements may reflect that electrostatic interactions should not be completely ignored in the complexation with neutral species because of the inductive effect and charge distribution due to polarization. More detailed and quantitative discussions on this subject will become feasible when data on more diverse complex systems are available.

Table 3
Temperature effect on the formation constants of 1:1 metal/carboxylate complexes

System (M + L → ML)		Z_1Z_2	K_{70}/K_{25}	Reference
M	L			
Nd^{3+}	Ac^-	−3	2	[5]
UO_2^{2+}		−3.2[a]	2.5	[11]
Th^{4+}		−4	2.8	[12]
UO_2^{2+}	Ac^-	−3.2[a]	2.5	[11]
	Mal^{2-}	−6.4[a]	2.8	[13]
Th^{4+}	Ac^-	−4	2.8	[12]
	Mal^{2-}	−8	3.9	This work

[a] Based on the effective charge on UO_2^{2+} in the literature [28,29].

4.2. Effect of temperature on the enthalpy and entropy of complexation

Data in Table 2 show that, in the temperature range from 10 to 70 °C, both the enthalpy and entropy of complexation for all three Th(IV) malonate complexes are positive. The complexation is entropy-driven, characteristic of the interaction between the “A-character” cations and anions [30]. As the temperature is increased, the entropy term ($T\Delta S$) increases more significantly than the enthalpy, resulting in even larger contributions from the entropy to the Gibbs free energy (ΔG) and more stable complexes at higher temperatures. The increase of entropy with the temperature could be the consequence of a more disordered bulk water structure at higher temperatures due to the perturbation by thermal movements. In the process of complexation, the highly ordered solvating water molecules are released to an expanded and more disordered bulk solvent [31]. As a result, the net gain in the complexation entropy is larger at higher temperatures.

For most of the actinide/carboxylate complexation systems previously studied, the enthalpies of complexation increase linearly as the temperature is increased. Thus, the heat capacities of complexation can be considered constant in the temperature region [5,11–14]. However, as Fig. 3 shows, the enthalpies of complexation between Th(IV) and malonate cannot be fitted with linear functions of temperature, suggesting that the heat capacities of complexation are dependent on the temperature. The curves in Fig. 3 represent second-order polynomial fits, from which the heat capacities of complexation, ΔC_p, are calculated to be $(1614.8 - 4.6 \times T)$, $(2100.6 - 5.8 \times T)$ and $(2348.5 - 6.2 \times T)\ \mathrm{J\,K^{-1}\,mol^{-1}}$ for $\mathrm{ThL^{2+}}$, $\mathrm{ThL_2^{0}}$ and $\mathrm{ThL_3^{2-}}$, respectively (where T is in Kelvin).

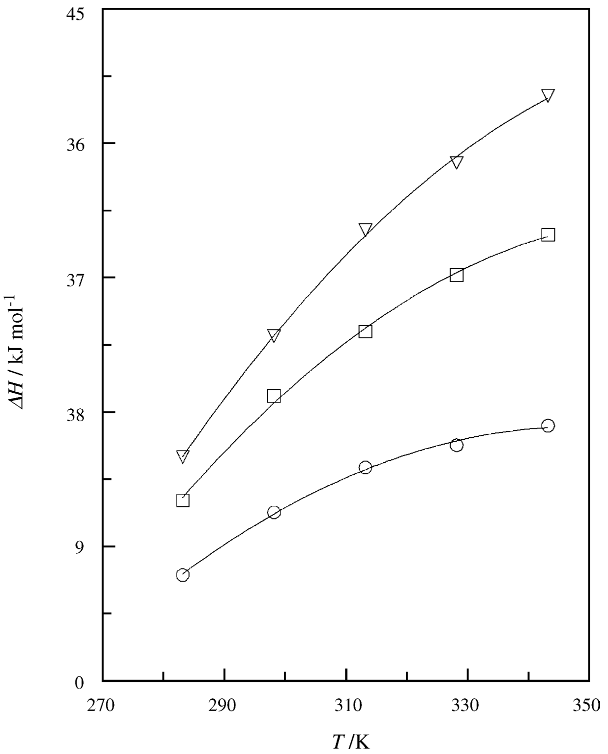

Fig. 3. Enthalpy of complexation between Th(IV) and malonate as a function of temperature. $I = 1.05\ \mathrm{mol\,kg^{-1}}$ $\mathrm{NaClO_4}$. Symbols: (○) $\mathrm{ThL^{2+}}$; (□) $\mathrm{ThL_2}$; (▽) $\mathrm{ThL_3^{2-}}$; curves: second-order polynomial fits.

4.3. *Comparison between Th(mal)$^{2+}$ and UO$_2$(mal) at variable temperatures*

The thermodynamic parameters of the 1:1 U(VI)/malonate and Th(IV)/malonate complexes are compared in Fig. 4. The data can be summarized as follows. (1) The stability of both $\mathrm{Th(mal)^{2+}}$ and $\mathrm{UO_2(mal)}$ is enhanced by increasing temperature, but the former is affected more significantly than the latter, suggested by the larger slope for $\mathrm{Th(mal)^{2+}}$ in Fig. 4a. (2) The enthalpies of complexation for both $\mathrm{Th(mal)^{2+}}$ and $\mathrm{UO_2(mal)}$ are positive and become more positive as the temperature is increased (Fig. 4b). These trends provide interesting insight into the energetics of the complexation. The enthalpy of complexation consists of the energy required for dehydration of both the metal ion and the ligand, the energy released when the metal ion and the ligand forms the

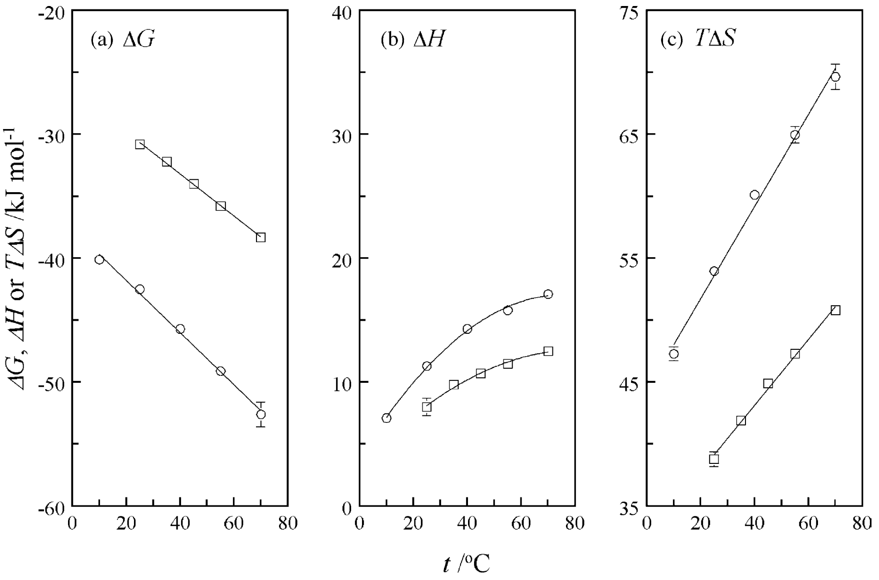

Fig. 4. Comparison of the thermodynamic parameters for the formation of $\mathrm{UO_2(mal)}$ (□) and $\mathrm{Th(mal)^{2+}}$ (○). $I = 1.05\ \mathrm{mol\,kg^{-1}}$ $\mathrm{NaClO_4}$. Data for $\mathrm{UO_2(mal)}$ are from [13].

complex, and the energy released when the dehydrated water molecules form hydrogen bonding with the bulk water. The positive enthalpies of Th(mal)$^{2+}$ and UO_2(mal) indicate that the dehydration energy dominates, which is consistent with the energetics of interactions between a "hard acid" and a "hard base". The trend of ΔH becoming more positive with the increase of temperature probably reflects that less energy is gained from hydrogen bonding between the released water and the bulk at higher temperatures, because the bulk water has a higher degree of disorder due to more thermal perturbations at higher temperatures. (3) Entropy is the driving force of the complexation and is responsible for the enhancement of complexation at higher temperatures for both Th(IV) and U(VI) complexes. As shown in Fig. 4c, the $T\Delta S$ term is much larger in magnitude and more sensitive to the temperature change than ΔH. The $T\Delta S$ term dominates the trends in ΔG. As a result, both complexes become stronger at higher temperatures and, the Th(IV) complex is stronger and has a larger temperature effect than the U(VI) complex.

Acknowledgments

This work was supported by the Director, Office of Science, Office of Basic Energy Sciences and Office of Biological and Environmental Research under U.S.A. Department of Energy Contract no. DE-AC03-76SF0098 at Lawrence Berkeley National Laboratory (LBNL) and by the Ministero dell'Università e della Ricerca Scientifica e Tecnologica (MURST, Roma) within the program COFIN02.

Appendix A

See Tables A.1 and A.2.

Table A.1
Experimental conditions of potentiometry

T (°C)	Cup solution				Titrant	
	V^0 (ml)	C_{Th} (mmol dm^{-3})	C_H (mmol dm^{-3})	C_L (mmol dm^{-3})	C_H (mol dm^{-3})[a]	C_L (mol dm^{-3})
10	30.4	4.743	7.013	0.0	0.400	0.400
	30.9	10.50	15.52	0.0	0.400	0.400
	30.2	2.387	3.530	0.0	0.400	0.400
25	30.4	4.743	47.27	20.07	−1.002	0.0
	30.9	10.50	54.95	19.75	−1.002	0.0
	31.3	14.97	61.12	19.50	−1.002	0.0
	51.3	9.13	53.16	19.82	−1.002	0.0
	30.4	4.743	7.013	0.0	0.400	0.400
	30.4	10.50	15.52	0.0	0.400	0.400
	31.3	14.97	22.14	0.0	0.400	0.400
40	30.4	4.743	7.013	0.0	0.400	0.400
	30.9	10.50	15.52	0.0	0.400	0.400
	31.3	14.97	22.14	0.0	0.400	0.400
55	50.7	4.978	7.359	0.0	0.400	0.400
	30.9	10.50	15.52	0.0	0.400	0.400
	30.2	2.387	3.530	0.0	0.400	0.400
	30.2	4.743	7.013	0.0	0.400	0.400
70	50.4	2.506	3.706	0.0	0.400	0.400
	50.7	4.978	7.359	0.0	0.400	0.400
	51.0	7.414	10.96	0.0	0.400	0.400

I = 1.05 mol kg^{-1} ($NaClO_4$). C_{Th}, C_H and C_L represent the stoichiometric concentrations of thorium, proton and malonic acid.

[a] Negative values of C_H stands for the concentration of hydroxide: $-C_H = C_{OH}$.

Table A.2
Experimental conditions of calorimetry

T (°C)	Symbol[a]	Cup solution			Titrant, Na_2L/H_2L	
		V^0 (ml)	C_{Th} (mmol dm^{-3})	C_H (mmol dm^{-3})	C_H (mol dm^{-3})	C_L (mol dm^{-3})
10	◊	20.0	4.097	10.677	0.400	0.400
		20.0	9.186	23.940	0.400	0.400
		20.0	18.372	47.880	0.400	0.400
	△	20.0	27.558	71.820	0.400	0.400
		20.18	4.096	10.677	0.800	0.800
		20.0	8.038	20.948	0.800	0.800
	□	20.0	16.037	41.896	0.800	0.800
		20.0	32.074	83.982	0.800	0.800

Table A.2 (*Continued*)

T (°C)	Symbol[a]	Cup solution			Titrant, Na_2L/H_2L	
		V^0 (ml)	C_{Th} (mmol dm^{-3})	C_H (mmol dm^{-3})	C_H (mol dm^{-3})	C_L (mol dm^{-3})
25	◊	20.0	4.097	10.677	0.400	0.400
	□	20.0	16.075	41.895	0.400	0.400
		20.0	22.965	59.85	0.400	0.400
	△	20.0	32.151	83.79	0.400	0.400
40	◊	20.0	4.134	10.773	0.400	0.400
	□	20.0	16.075	41.895	0.400	0.400
	△	20.0	22.965	59.85	0.400	0.400
		20.0	8.038	20.948	0.400	0.400
55	◊	20.0	4.134	10.773	0.400	0.400
	□	20.0	8.038	20.948	0.400	0.400
	△	20.0	11.485	29.925	0.400	0.400
70	◊	20.0	4.134	10.773	0.400	0.400
	□	20.0	8.038	20.948	0.400	0.400
	△	20.0	11.485	29.925	0.400	0.400

$I = 1.05$ mol kg^{-1} ($NaClO_4$). C_{Th}, C_H and C_L represent the stoichiometric concentrations of thorium, proton and malonic acid.

[a] Symbols used to show the titrations at different temperatures in Fig. 2 of the article.

References

[1] DOE, Estimating the Cold War Mortgage: The 1995 Baseline Environmental Management Report, DOE/EM-0232, USA Department of Energy, Washington, DC, 1995.

[2] J.M. Cruse, R.L. Gilchrist, developing waste disposal options in the underground storage tank-integrated demonstration program, in: Global 93, Future Nuclear Systems: Emerging Fuel Cycles and Waste Disposal Options, American Nuclear Society, La Grange Park, IL, 1993, p. 1376.

[3] A.E. Martell, R.M. Smith, Critical Stability Constants, vol. 6, Plenum Press, New York, 1989.

[4] P.W. Atkins, Physical Chemistry, sixth edition, W.H. Freeman & Co., New York, 1997.

[5] P. Zanonato, P. Di Bernardo, A. Bismondo, L. Rao, G.R. Choppin, J. Solution Chem. 30 (2001) 1.

[6] H.C. Helgeson, D.H. Kirkham, G.C. Flowers, Am. J. Sci. 281 (1981) 1249.

[7] J.C. Tanger, H.C. Helgeson, Am. J. Sci. 288 (1988) 19.

[8] E.L. Shock, E.H. Oelker, J.W. Johanson, D.A. Sverjensky, H.C. Helgeson, J. Chem. Soc., Faraday Trans. I 88 (1992) 803.

[9] D.P. Fernandez, A.R.H. Goodwin, E.W. Lemmon, J.M.H.L. Sengers, R.C. Williams, J. Phys. Chem. Ref. Data 26 (4) (1997) 1125.

[10] W.L. Marshall, E.U. Franck, J. Phys. Chem. Ref. Data 10 (1981) 295.

[11] J. Jiang, L. Rao, P. Di Bernardo, P. Zanonato, A. Bismondo, J. Chem. Soc., Dalton Trans. (2002) 1832.

[12] L. Rao, Z. Zhang, P. Zanonato, P. Di Bernardo, A. Bismondo, S. B. Clark, J. Chem. Soc., Dalton Trans. (2004) 2867.

[13] L. Rao, J. Jiang, P. Zanonato, P. Di Bernardo, A. Bismondo, A.Yu. Garnov, Radiochim. Acta 90 (2002) 581.

[14] L. Rao, A.Yu. Garnov, J. Jiang, P. Di Bernardo, P. Zanonato, A. Bismondo, Inorg. Chem. 42 (2003) 3685.

[15] P. Zanonato, P. Di Bernardo, A. Bismondo, G. Liu, X. Chen, L. Rao, J. Am. Chem. Soc. 126 (2004) 5515.

[16] L. Rao, T.G. Srinivasan, A. Yu. Garnov, P. Zanonato, P. Di Bernardo, A. Bismondo, Geochim. Cosmochim. Acta 68 (2004) 4821.

[17] J.A. Dean, Analytical Chemistry Handbook, McGraw-Hill Inc., New York, 1995, pp. 3–108.

[18] G. Gran, Analyst 77 (1952) 661.

[19] P. Di Bernardo, A. Cassol, G. Tomat, A. Bismondo, L. Magon, J. Chem. Soc., Dalton Trans. (1983) 733.

[20] P. Gans, A. Sabatini, A. Vacca, Talanta 43 (1996) 1739.

[21] I. Grenthe, I. Puigdomenech, Symbols, Standards, and Conventions, in: I. Grenthe, I. Puigdomenech (Eds.), Modeling in Aquatic Chemistry, NEA/OECD, Paris, 1997 (Chapter II).

[22] R. Smith, P. Zanonato, G.R. Choppin, J. Chem. Thermodyn. 24 (1992) 99.

[23] R. Arnek, Arkiv Kemi 32 (1970) 81.

[24] A. Cassol, L. Magon, G. Tomat, R. Portanova, Inorg. Chim. Acta 3 (1969) 639.

[25] Y.J. Zhang, D. Collison, F.R. Livens, A.K. Powell, S. Wocadlo, H. Eccles, Polyhedron 19 (2000) 1757.

[26] D.G. Archer, P. Wang, J. Phys. Chem. Ref. Data 19 (1990) 371.

[27] R.W. Gurney, Ionic Processes in Solution, McGraw-Hill, New York, 1953.

[28] G.R. Choppin, P.J. Unrein, Thermodynamic study of actinide fluoride complexation, in: W. Muller, R. Lindner (Eds.), Transplutonium Elements, North-Holland Publishing Company, Amsterdam, 1976.

[29] G.R. Choppin, L. Rao, Radiochim. Acta 37 (1984) 143.

[30] G. Schwarzenbach, Interpretation of solution stabilities of metal complexes, in: P. Paoletti, R. Barbucci, L. Fabbrizzi (Eds.), Proceeding of the Summ. Sch. Stability Constants, Scient. University of Florence, Italy, 1977, pp.151–181.

[31] T.M. Seward, Chemistry and geochemistry of solutions at high temperatures and pressures, physics and chemistry of the earth, in: D.T. Rickard, F.E. Wickman (Eds.), Pergamon Press, vols. 13–14, 1981, p. 113.