Thermodynamics of actinide complexation in solution at elevated temperatures: application of variable-temperature titration calorimetry

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Studies of actinide complexation in solution at elevated temperatures provide insight into the effect of solvation and the energetics of complexation, and help to predict the chemical behavior of actinides in nuclear waste processing and disposal where temperatures are high. This *tutorial review* summarizes the data on the complexation of actinides at elevated temperatures and describes the methodology for thermodynamic measurements, with the emphasis on variable-temperature titration calorimetry, a highly valuable technique to determine the enthalpy and, under appropriate conditions, the equilibrium constants of complexation as well.

1 Introduction

Complexation of actinides with a variety of organic and inorganic ligands in solution has been studied since the beginning of the development of nuclear energy in the 1940s. However, the majority of the studies were conducted at or near 25 °C and limited to the measurements of only equilibrium constants. As a result, few thermodynamic data of actinide complexation in solution at elevated temperatures are available. Even for 25 °C, other thermodynamic parameters (enthalpy, heat capacity, *etc.*) are very scarce. The scarcity of important thermodynamic parameters at 25 °C and the absence of data at elevated temperatures make it extremely difficult to predict the chemical behavior of actinides in the processing and disposal of nuclear wastes, because these activities involve systems with temperatures significantly higher than the ambient. For example, the temperature in the liquid nuclear waste storage tanks has been found to be up to 90 °C due to the radioactive decay energy. Besides, it is predicted that the temperature of the waste forms disposed of in the geological repository could still be significantly higher than the ambient temperature thousands of years after the closure of the repository. If the engineering barriers of the waste packages were breached, groundwater could come into contact with the wastes and dissolve the radioactive materials including actinides. To accurately predict the transport of actinides in the repository, thermodynamic data on the interactions of actinides with various organic and inorganic ligands at elevated temperatures must be known.

One could argue that, in the absence of thermodynamic data at elevated temperatures, a few approximation approaches could be used to estimate the equilibrium constants at elevated temperatures, such as the constant enthalpy approach, the constant heat capacity approach, the DQUANT equation, the Ryzhenko–Bryzgalin model, and the Helgeson–Kirkham–Flowers (HKF) equations.[1] However, there are limitations in the application of the approximation approaches in the actinide systems. For example, all approaches require the values of enthalpy, entropy and/or heat capacity of complexation that are rarely available for actinide systems. Even if the enthalpy at 25 °C is known, extrapolation of the data to elevated temperatures may result in large errors if the enthalpy of complexation is strongly temperature-dependent and/or the temperature range of interest is wide. More recent theoretical models developed by Helgeson and co-workers have considerably improved the accuracy in predicting the thermodynamic properties of aqueous species at high temperatures, but the model parameters for many actinide species do not exist at present and need to be determined by regression procedures with experimental data.[1] As a result, reliable experimental data on the complexation of actinides in solution at elevated temperatures are needed to develop and test the approximation approaches.

In addition to providing support to the safe management of nuclear wastes at the practical level, the study of the temperature effect on actinide complexation in solution is of significance at the fundamental level as well. The change in temperature perturbs the structure of water in the bulk and in

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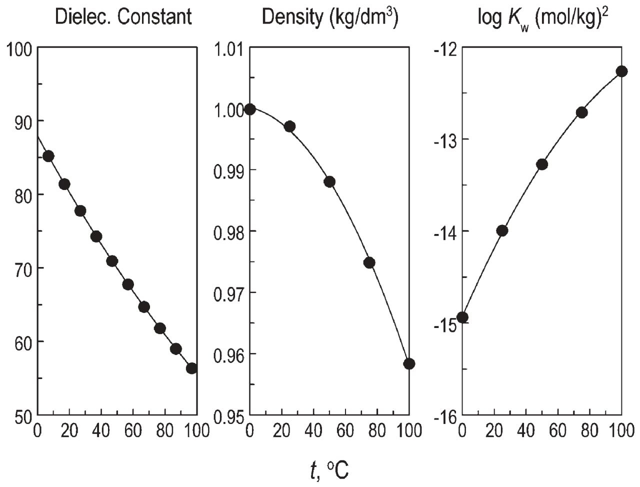

Fig. 1 Properties of water as a function of temperature.[2]

the vicinity of the ions, alters its ionization and dielectric properties, and thus affects the energetics of the complexation and hydrolysis reactions. For example, the ionic product of water ($K_w = [H^+][OH^-]$) increases by almost three orders of magnitude and the dielectric constant decreases by about 35% from 0 to 100 °C (Fig. 1). The increase in K_w affects the hydrolysis of actinides because the concentration of the hydroxide ion at the same concentration of the hydrogen ion becomes much higher at higher temperatures. On the other hand, the change in the dielectric constant is expected to have a great impact on the interaction of actinides with ligands if the interaction is dominantly electrostatic in nature. Therefore, the study of the complexation of actinides in solution at elevated temperatures could help to improve the fundamental understanding of the nature of actinide complexes.

2 Techniques for thermodynamic measurements

Two important thermodynamic parameters that are directly measured by experiments are the stability constant (K) and the enthalpy of complexation (ΔH) at variable temperatures. Other parameters, including Gibbs free energy (ΔG), entropy (ΔS) and heat capacity (ΔC_p), are derived from the stability constant and enthalpy of complexation as follows.

$$\Delta G = -RT \ln K \qquad (1)$$

$$\Delta S = (\Delta H - \Delta G)/T \qquad (2)$$

$$\Delta C_p = d(\Delta H)/dT \qquad (3)$$

A number of techniques can be used to determine the stability constants, including potentiometry, distribution methods (*e.g.*, solvent extraction and ion exchange), solubility measurements, and spectroscopy (*e.g.*, optical absorption, fluorescence, photoacoustic and NMR spectroscopy). Application of some of the techniques to the studies of actinide complexation in solution at elevated temperatures is briefly described in section 3, along with the review of thermodynamic data. Detailed discussions on these techniques are not included in this review, but are available in the corresponding publications cited in section 3.

Though the enthalpy of complexation can be calculated from the temperature dependency of stability constants: $d(\ln K)/d(1/T) = -(\Delta H)/R$, titration calorimetry is the technique that can be used to directly measure the enthalpy of complexation at variable temperatures. Moreover, both the enthalpy and stability constants can be determined by titration calorimetry, provided that the concentrations of components and the magnitude of stability constants are in appropriate ranges. Despite that titration calorimetry is a technique of particular importance in thermodynamic measurements, its application to the studies of actinide complexation in solution at elevated temperatures has been very limited, probably due to the unfamiliarity of calorimetry as well as the sophistication in the instrumentation and data reduction. To help the readers to design calorimetric titration experiments, a brief introduction of titration calorimetry is given below.

2.1 Measurement of reaction heat by titration calorimetry

The principles of measuring the reaction heat by a calorimeter vary according to the types of calorimeters (*e.g.*, the isothermal, isoperibol, or adiabatic calorimeters). These principles are not discussed in this review, but are available in the literature.[3,4] Instead, the following discussions are focused on the methodology of calculating enthalpy from the observed heat of a titration, using the data obtained with an isothermal microcalorimeter as an example.

A titration thermogram obtained with an isothermal microcalorimeter is shown in Fig. 2. This is a titration for the complexation of hexavalent uranium ion (UO_2^{2+}) with fluoride.[5] At certain time intervals (*e.g.*, every 400 s), a small volume (*e.g.*, 5 μL) of the titrant (NaF) is added into the cell that contains UO_2^{2+}. The heat effect is observed as a "peak" in the thermogram (in μJ s^{-1}). Negative peaks indicate heat being absorbed. A total of n additions are made (usually n = 40–70), corresponding to the n peaks in the thermogram. Integration of the peaks over time results in n experimental values of the

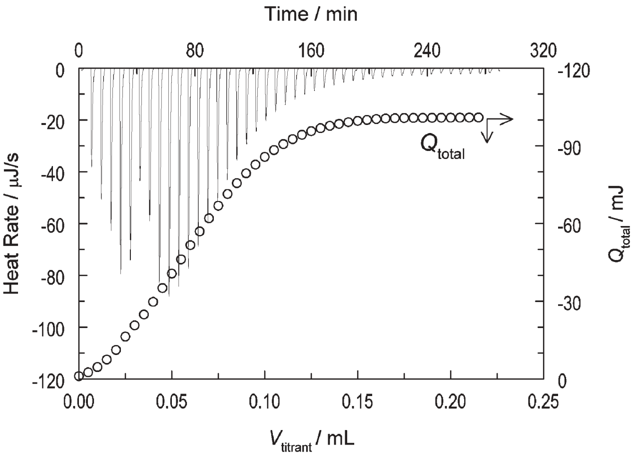

Fig. 2 Thermogram (thin line, using top x-axis and left y-axis) and total heat (circle, using bottom x-axis and right y-axis) of a calorimetric titration. Cell solution: V° = 0.900 mL $C_U{}^\circ = 7.87 \times 10^{-3}$ mol dm^{-3}, $C_H{}^\circ = 9.42 \times 10^{-3}$ mol dm^{-3}; titrant: 0.300 mol dm^{-3} NaF/0.0333 mol dm^{-3} $HClO_4$, 5 μL/addition, 45 additions; t = 25 °C, I = 1.0 mol dm^{-3} $NaClO_4$.[5]

heat generated during the titration ($Q_{ex,j}$, where $j = 1$ to n). These values are then corrected for the heat of dilution of the titrant ($Q_{dil,j}$), which is determined in a separate "blank" titration where the titrant is the same but the cell contains only the background ionic medium (*e.g.*, 1 mol dm^{-3} $NaClO_4$) without UO_2^{2+}. The net reaction heat at the *j*th point ($Q_{r,j}$) was obtained from the difference: $Q_{r,j} = Q_{ex,j} - Q_{dil,j}$. In Fig. 2, the accumulated reaction heat is also plotted as a function of the volume of titrant added into the cell.

2.2 Calculation of enthalpy of complexation from reaction heat

The net reaction heat at the *j*th point is in turn a function of $\Delta n_{i,j}$, the change of moles of the *i*th species at the *j*th point, and ΔH_i, the enthalpy of reaction corresponding to the *i*th species:

$$Q_{r,j} = \sum_i \left(\Delta n_{i,j} \Delta H_i\right) \tag{4}$$

$\Delta n_{i,j}$ is a function of the concentrations of the components and the equilibrium constants of all reactions involved in the titration. For the titration shown in Fig. 2, a number of reactions need to be considered:

$$H^+ + OH^- = H_2O\ (l);\ K_w,\ \Delta H_{H_2O} \tag{5}$$

$$H^+ + F^- = HF\ (aq);\ K_{HF},\ \Delta H_{HF} \tag{6}$$

$$UO_2^{2+} + F^- = UO_2F^+;\ K_1,\ \Delta H_1 \tag{7}$$

$$UO_2F^+ + F^- = UO_2F_2\ (aq);\ K_2,\ \Delta H_2 \tag{8}$$

$$UO_2F_2\ (aq) + F^- = UO_2F_3^-;\ K_3,\ \Delta H_3 \tag{9}$$

$$UO_2F_3^- + F^- = UO_2F_4^{2-};\ K_4,\ \Delta H_4 \tag{10}$$

Reaction (5) is included because the pH varies during the titration. Usually the K_w and ΔH_{H_2O} for the ionic medium (*e.g.*, 1 mol dm^{-3} $NaClO_4$ in this example) are available in the literature or can be determined by separate acid/base potentiometric and calorimetric titrations. Similarly, the equilibrium constant and enthalpy of fluoride protonation (reaction (6)) can be taken from the literature or determined by separate protonation titrations.

The stability constants of U(VI)/fluoride complexes (K_1, K_2, K_3 and K_4) have previously been determined and are available in the literature.[6] Thus, the distribution of U(VI) species in the titration becomes known as shown in Fig. 3 and $\Delta n_{i,j}$ of eqn (4) can be calculated. In this case, calculation of the enthalpy of complexation becomes relatively easy. Usually, the best values of ΔH_i (i = 1–4) are calculated by a least square analysis of eqn (4), minimizing the error square sum over the n data points.

$$U(\Delta H_i) = \sum_j^n \left(Q_{r,j} - \sum_i \left(\Delta n_{i,j} \Delta H_i\right)\right)^2 \tag{11}$$

In general, multiple titrations with varying concentrations are conducted to improve the accuracy and precision of the results. This is particularly important when multiple parameters need to be calculated.

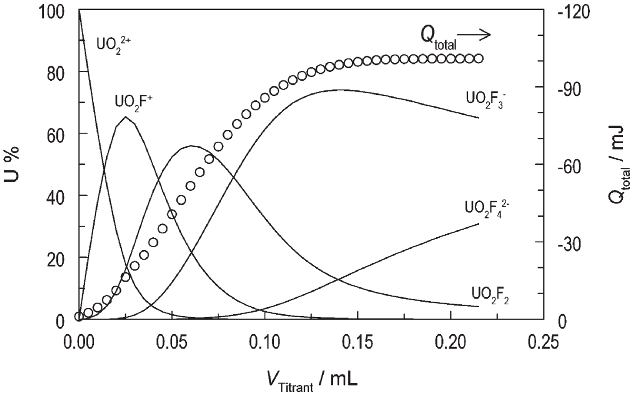

Fig. 3 Calorimetric titration of U(VI) fluoride complexation. Cell solution: $V^\circ = 0.900$ mL $C_U^\circ = 7.87 \times 10^{-3}$ mol dm^{-3}, $C_H^\circ = 9.42 \times 10^{-3}$ mol dm^{-3}; titrant: 0.300 mol dm^{-3} NaF/0.0333 mol dm^{-3} $HClO_4$, 5 μL/addition, 45 additions; t = 25 °C, I = 1.0 mol dm^{-3} $NaClO_4$.

2.3 Calculation of stability constants and enthalpy of complexation from reaction heat

Provided that the magnitudes of equilibrium constant (K) and enthalpy (ΔH) of a reaction are within certain ranges, calorimetric titrations can be applied to simultaneous determination of the equilibrium constant and enthalpy. This application can be illustrated by the following simulation using a hypothetical reaction. Fig. 4a shows the calorimetric data of a hypothetic complexation titration (M + L = ML) with C_M° = 0.01 mol dm^{-3} and ΔH = 20 kJ mol^{-1}. The curvature of the heat data varies as the stability constant (K) changes. For complexation with values of K greater than 10^4, the data do not possess sufficient curvature and the curves differ only slightly from one another. Thus, at C_M° = 0.01 mol dm^{-3}, it is difficult to calculate the stability constants of strong complexes with K greater than 10^4 from the calorimetric data, though the enthalpy of complexation could be accurately measured. On the other hand, for complexation with K smaller than 10, little complexation takes place even at high ratios of C_L/C_M, generating very small amounts of heat. Thus, it is difficult to calculate either the stability constant or the enthalpy of complexation. Under the assumed conditions (C_M° = 0.01 mol dm^{-3} and ΔH = 20 kJ mol^{-1}), the stability constants in the range of 10–10^4 could be calculated simultaneously with the enthalpy from the calorimetric data.

The above discussions hold only for the titration of a solution with C_M° = 0.01 mol dm^{-3}. As Fig. 4b shows, if the C_M° is lowered by two orders of magnitude, the range of K that can be properly measured by calorimetry becomes 10^3–10^6. Thus, very low concentrations are required in order to measure stability constants of very strong complexes. In turn, working with solutions of very low concentrations requires the use of calorimeters with extremely high sensitivity. Therefore, microcalorimeters have been found particularly useful in measuring the enthalpy as well as the stability constants of strong complexes.

Calorimetry can be a highly valuable technique to determine the equilibrium constants in systems where common techniques are not applicable due to various reasons. For example,

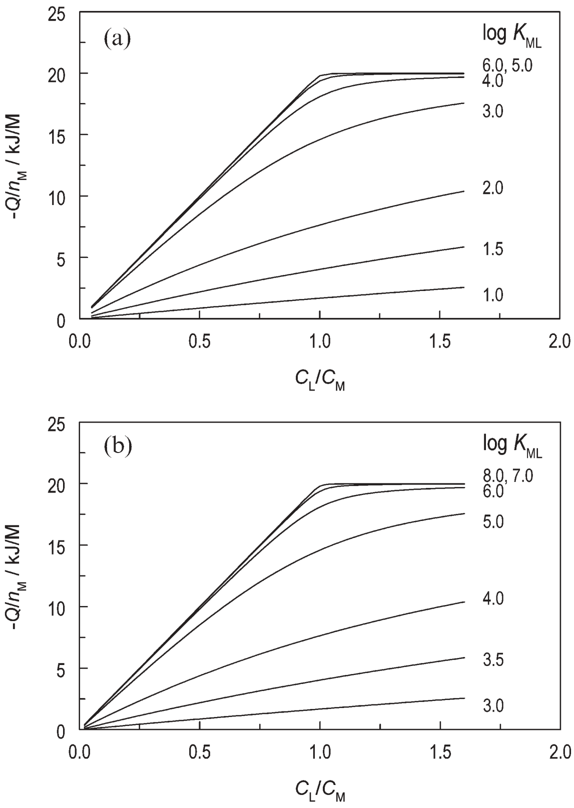

Fig. 4 Dependence of calorimetric data on the equilibrium constant (K_{ML}) of a hypothetic complexation reaction: M + L = ML, with ΔH = 20 kJ mol^{-1} and different concentrations of M: (a) $C_M{}^\circ$ = 0.01 mol dm^{-3}; (b) $C_M{}^\circ$ = 0.0001 mol dm^{-3}. Q is the total heat and n_M is the number of moles of M in the solution.

acid–base potentiometry cannot be directly used to determine the stability constants of metal complexes with ligands without dissociable protons. Also, potentiometry using a glass-electrode is not suitable for studying systems where corrosion or "poisoning" of the electrode could occur. Advantages of using titration calorimetry in these systems are demonstrated by the following two examples.

Example I: Simultaneous determination of the equilibrium constants and enthalpy of Eu(III) complexation with *N*,*N*,*N*′,*N*′-tetramethylmalonamide (TMMA) in organic solvents[7]. Acid–base potentiometry is not applicable to this system because the malonamide ligand does not have dissociable protons and the complexes form in organic solvents. Therefore, titration calorimetry is ideal for this study. Multiple calorimetric titrations with different concentrations of Eu(III) ($C_M{}^\circ$) were performed. Data in Fig. 5 show that the formation of the first complex (in the region $C_L/C_M < 1$) is relatively strong and endothermic, while the second complex is weaker and exothermic (in the region $C_L/C_M > 1$). The trends were satisfactorily explained by the solvation of Eu(III) by dimethyl sulfoxide and the de-solvation energy required to form the Eu(III)/TMMA complexes.[7] The curvature of the data in Fig. 5 allowed simultaneous calculation of the equilibrium constants and the enthalpies of complexation for three Eu(III)/TMMA complexes.[7]

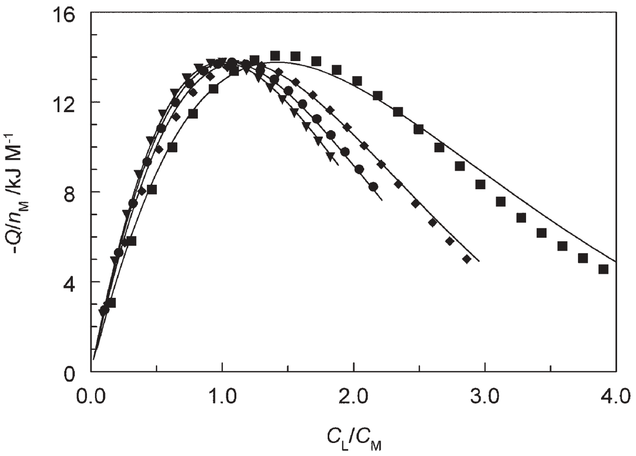

Fig. 5 Calorimetric titrations of the complexation of Eu(III) with *N*,*N*,*N*′,*N*′-tetramethylmalonamide in a mixture of acetonitrile and dimethyl sulfoxide.[7] Points – experimentally observed; curves – simulated with the equilibrium constants and enthalpies of complexation. $C_M{}^\circ$ (mmol dm^{-3}) = 33.8 (▼), 25.3 (●), 16.9 (◆), 8.44 (■).

Example II: Simultaneous determination of the equilibrium constants and enthalpy of fluoride protonation at variable temperatures[8]. Conventional potentiometry with a glass pH-electrode cannot be used to determine the protonation constant of fluoride due to the problem with corrosion, especially at elevated temperatures. Titration calorimetry proves to be highly valuable in this study. Fig. 6 shows the calorimetric data obtained with a microcalorimeter at different temperatures. Multiple titrations at different concentrations were performed at each temperature so that the protonation constant and enthalpy of protonation could be simultaneously calculated.

3 Data on actinide complexation at elevated temperatures

This section reviews the data in the literature on actinide complexation (including hydrolysis) at elevated temperatures. Because the data on actinides are generally scarce and because the trivalent lanthanides are very similar to the trivalent actinides

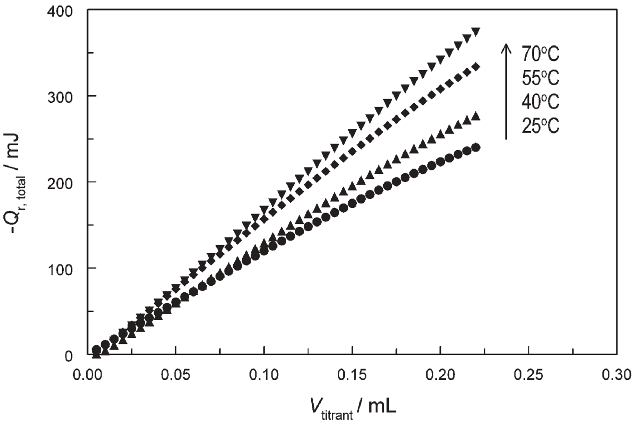

Fig. 6 Calorimetric titrations of the protonation of fluoride at different temperatures. Initial cell solution: 0.90 mL, C_{NaF} = 0.0333 mol dm^{-3}, titrant: 0.1032 mol dm^{-3} $HClO_4$, 5 μL/addition; I = 1 mol dm^{-3} $NaClO_4$.[8]

in complexation, publications on the complexation of trivalent lanthanides at elevated temperatures are also referenced.

Because the emphasis of this review is on the effect of temperature on actinide complexation in solution, only the studies that have generated thermodynamic data at variable temperatures are reviewed. Data from studies performed at only 25 °C are not included in the review. Besides, studies that have determined the enthalpy of complexation at variable temperatures with calorimetry are discussed in more detail, because the application of titration calorimetry is a focal point of this review. Determination of enthalpy at different temperatures allows the calculation of heat capacity, another important thermodynamic parameter of actinide complexation.

The stability constants reported in the literature are either on the molarity scale (mol dm^{-3}) or on the molality scale (mol kg^{-1}). To allow a comparison between data at different temperatures, the constants in molarity should be converted to the constants in molality. According to the method in the literature,[6] the equilibrium constant of a reaction in molality (K_m) is related to that in molarity (K_M) by eqn (12).

$$\log_{10}K_m = \log_{10}K_M + \sum_r \nu_r \log_{10}\vartheta \qquad (12)$$

where ϑ is the ratio of the values of molality to molarity for the specific ionic medium. For example, the value of ϑ for 1.0 mol dm^{-3} NaClO$_4$ equals 1.05 dm^3 of solution per kg of water. $\sum_r \nu_r$ is the sum of the stoichiometric coefficients of the reaction (ν_r is positive for products and negative for reactants). For example, $\sum_r \nu_r$ is equal to $-j$ for the complexation reaction ($M + jL = ML_j$).

3.1 Trivalent actinides

Complexation with inorganic ligands. Data on the complexation of trivalent actinides in solution at variable temperatures are extremely scarce. There are only a few studies on the complexation of Am(III) and Cm(III) with carbonate[9–11] and chloride[12] (Table 1). In none of the studies is calorimetry used to directly measure the enthalpy of complexation. Wruck *et al.* determined the stability constant of AmCO$_3^+$ at three temperatures (25, 50 and 75 °C) by pulsed laser photoacoustic spectroscopy.[9] The high sensitivity of this technique allowed the use of very low concentrations of Am(III) (1 × 10^{-6} mol kg^{-1}). The characteristic absorption band of free Am^{3+} at 503 nm was shifted to 505 nm as the concentration of carbonate increased. The stability constants of AmCO$_3^+$ at 25 and 50 °C were calculated by deconvolution of the spectra. The constant at 75 °C was estimated from the spectra under limiting conditions, because the spectra were not in sufficient detail and there might be a significant amount of second complex, Am(CO$_3$)$_2^-$, present in the solution. The enthalpy of complexation ($Am^{3+} + CO_3^{2-} = AmCO_3^+$) was estimated to be 11 kJ mol^{-1}, from the stability constants at 25 and 50 °C by the van't Hoff equation.

Vercouter *et al.* used time-resolved laser-induced fluorescence spectroscopy (TRLFS) to determine the equilibrium constant of the reaction $Cm(CO_3)_2^- + CO_3^{2-} = Cm(CO_3)_3^{3-}$ in the temperature range 10–70 °C.[10] The features of the fluorescence spectra of Cm(III) were followed as the carbonate concentration was varied. A peak at 607.4 nm was observed for Cm(III) solutions with the concentration of carbonate higher than 0.1 mol dm^{-3} and assigned to the limiting species Cm(CO$_3$)$_3^{3-}$. The peak decreased and shifted to 606.1 nm as the concentration of carbonate was lower than 0.1 mol dm^{-3}. This change was interpreted as being due to the dissociation of Cm(CO$_3$)$_3^{3-}$ into Cm(CO$_3$)$_2^-$ and CO$_3^{2-}$, and the equilibrium constant was accordingly calculated. The complexation became stronger as the temperature was increased from 10 to 70 °C (Table 1). The enthalpy of complexation

Table 1 Complexation of trivalent actinides in solution at variable temperatures. Methods: pa – photoacoustic spectroscopy, fluo – fluorescence spectroscopy, sol – solubility, dis – solvent extraction

Ligand	Reaction	Medium	T/°C	Method	log K	ΔH/kJ mol^{-1}	ΔS/J K^{-1} mol^{-1}	Ref.
Carbonate	$Am^{3+} + CO_3^{2-} = AmCO_3^+$	0.1 mol kg^{-1} NaHCO$_3$/Na$_2$CO$_3$	25	pa	6.53 ± 0.18	11		9
			50		6.68 ± 0.20			
			75		7.54 ± 0.43			
	$Cm(CO_3)_2^- + CO_3^{2-} = Cm(CO_3)_3^{3-}$	3.0 mol dm^{-3} NaClO$_4$	10	fluo	1.86 ± 0.15			10
			25		2.08 ± 0.10	12.2 ± 0.4	79 ± 16	
			37		2.10 ± 0.15			
			50		2.23 ± 0.15			
			70		2.26 ± 0.20			
	$Am(CO_3)_2^- + CO_3^{2-} = Am(CO_3)_3^{3-}$	4.0 mol dm^{-3} NaCl	20	sol	2.3 ± 0.3			11
					2.0 ± 0.2[a]			
			30		2.45 ± 0.17			
					2.0 ± 0.2[a]			
			40		2.94 ± 0.14			
					2.1 ± 0.2[a]			
			45		2.94 ± 0.10			
					2.1 ± 0.2[a]			
			50		2.64 ± 0.14			
					2.1 ± 0.2[a]			
			60		2.98 ± 0.24			
					2.0 ± 0.2[a]			
			70		2.98 ± 0.17			
					2.1 ± 0.2[a]			
Chloride	$Am^{3+} + Cl^- = AmCl^{2+}$	1.0 mol dm^{-3} NaClO$_4$	25	dis	0.11 ± 0.05	19.4 ± 7.4		12
			50		0.38 ± 0.05			

[a] Data obtained from ref. 10 after re-interpreting the solubility data in ref. 11.

($Cm(CO_3)_2^- + CO_3^{2-} = Cm(CO_3)_3^{3-}$) was calculated to be 12.2 ± 0.4 kJ mol^{-1}. Vercouter *et al.* also re-interpreted the solubility data of Am(III) in the literature[11] and showed that the equilibrium constants of Am(III) complexation, $Am(CO_3)_2^- + CO_3^{2-} = Am(CO_3)_3^{3-}$, are quite similar to those for $Cm(CO_3)_3^{3-}$, in the entire temperature range 10–70 °C.

Yeh *et al.* determined the stability constants of $AmCl^{2+}$ (at 25 and 50 °C) and $EuCl^{2+}$ (at 25, 50 and 75 °C) using solvent extraction.[12] The stability constants increased as the temperature was elevated (Table 1). The enthalpies of complexation were calculated by the van't Hoff equation to be about 20 kJ mol^{-1} for both $AmCl^{2+}$ and $EuCl^{2+}$, contradicting some data in the literature that showed the 1 : 1 lanthanide-chloro complexation was exothermic.[12] Such discrepancy might be due to the inherent weakness of metal chloro-complexes in the aqueous solution that results in large scatter in the data and makes it difficult to accurately determine the enthalpy by the temperature dependency of the stability constants. Direct measurements of the reaction enthalpy by microcalorimetry could generate more reliable data and help to resolve the discrepancy.

Trivalent lanthanides as chemical analogs. There have been a number of studies on the complexation of trivalent lanthanides with inorganic and organic ligands in solution at variable temperatures. These data, not discussed in this review, could be used as estimates for the trivalent actinide complexes because of the chemical similarity between the trivalent lanthanides and actinides. The studies include Eu(III) with carbonate (15–35 °C, solvent extraction),[13] Nd(III) with sulfate (30–250 °C, spectrophotometry),[14] Lanthanides (III) with fluoride (5–45 °C, ion exchange),[15] Nd(III)/Sm(III)/Ho(III) with chloride (100–250 °C, spectrophotometry),[16] Pr(III) with acetate (20–95 °C, absorption spectroscopy),[17] Nd(III) with acetate (25–225 °C, potentiometry),[18] (20–70 °C, photoacoustic spectroscopy),[19] (25–70 °C, potentiometry and calorimetry),[20,21] Eu(III) with acetate (25–170 °C, potentiometry),[22] (8–59 °C, fluorescence spectroscopy),[23] Lanthanides (III) with oxydiacetate (5–50 °C, potentiometry and calorimetry),[24] Sm(III) with oxydiacetate (25–70 °C, potentiometry and calorimetry),[25] and Eu(III) with 4-phenylethynyl-2,6-pyridinedicarboxylic acid (25–87.5 °C, fluorescence spectroscopy).[26]

3.2 Tetravalent actinides

Hydrolysis. The hydrolysis of Th(IV) has been studied at 0 and 95 °C by Baes *et al.* using potentiometry and solubility measurements,[27] and 15–35 °C by Ekberg *et al.* using potentiometry and solvent extraction.[28] A number of models including various combinations of hydrolyzed Th(IV) species were tested to fit the experimental data. The best models from the two studies (Table 2) are generally in good agreement, except that Baes *et al.* included a dimer, $Th_2(OH)_2^{6+}$, while Ekberg *et al.* evoked two more monomeric species, $Th(OH)_3^+$ and $Th(OH)_4$ (aq), based on the results of

Table 2 Hydrolysis of Th(IV) at variable temperatures. Methods: pot – potentiometry, sol – solubility measurements, dis – solvent extraction

Reaction	Medium	T/°C	Method	log K	ΔH/kJ mol^{-1}	ΔS/J K^{-1} mol^{-1}	Ref.
$Th^{4+} + H_2O = ThOH^{3+} + H^+$	1.0 mol kg^{-1} $NaClO_4$	0	pot, sol	−4.32 ± 0.02			27
		25		−4.15 ± 0.04[a]	24.7	3.8	
		95		−2.29 ± 0.02			
$Th^{4+} + 2\ H_2O = Th(OH)_2^{2+} + 2\ H^+$		0		−8.48 ± 0.03			
		25		−7.70 ± 0.03[a]	58.1	46.0	
		95		−4.50 ± 0.01			
$2\ Th^{4+} + 2\ H_2O = Th_2(OH)_2^{6+} + 2\ H^+$		0		−5.60 ± 0.02			
		25		−4.61 ± 0.02[a]	61.9	118.7	
		95		−2.55 ± 0.03			
$4\ Th^{4+} + 8\ H_2O = Th_4(OH)_8^{8+} + 8\ H^+$		0		−22.79 ± 0.02			
		25		−19.01 ± 0.02[a]	241.3	445.8	
		95		−10.49 ± 0.03			
$6\ Th^{4+} + 15\ H_2O = Th_6(OH)_{15}^{9+} + 15\ H^+$		0		−43.84 ± 0.02			
		25		−36.76 ± 0.02[a]	453.7	818.4	
		95		−20.63 ± 0.03			
$Th^{4+} + H_2O = ThOH^{3+} + H^+$	1.0 mol dm^{-3} $NaClO_4$	15	pot, dis	−3.6 ± 0.1			28
		25		−3.3 ± 01	38 ± 6	60 ± 20	
		35		−3.2 ± 0.1			
$Th^{4+} + 2\ H_2O = Th(OH)_2^{2+} + 2\ H^+$		15		−8.8 ± 0.1			
		25		−8.6 ± 0.1	36 ± 1	−44 ± 4	
		35		−8.4 ± 0.1			
$Th^{4+} + 3\ H_2O = Th(OH)_3^+ + 3\ H^+$		15		−14.9 ± 2.8			
		25		(−14.2)	190 ± 40	300 ± 100	
		35		−12.7 ± 3.5			
$Th^{4+} + 4\ H_2O = Th(OH)_4 + 4\ H^+$		15		−22.0 ± 0.4			
		25		−19.4 ± 0.5	360 ± 40	800 ± 100	
		35		−17.8 ± 0.4			
$4\ Th^{4+} + 8\ H_2O = Th_4(OH)_8^{8+} + 8\ H^+$		15		−20.2 ± 0.3			
		25		−19.1 ± 0.1	191 ± 3	280 ± 10	
		35		−18.0 ± 0.1			
$6\ Th^{4+} + 15\ H_2O = Th_6(OH)_{15}^{9+} + 15\ H^+$		15		−41.4 ± 0.2			
		25		−39.5 ± 0.2	410 ± 60	600 ± 200	
		35		−36.6 ± 0.2			

[a] Values obtained by re-calculating the data at 25 °C in the literature.[27]

solvent extraction where much lower concentrations of Th(IV) were used.

In both studies, the enthalpy of hydrolysis was calculated from the temperature dependency of the hydrolysis constants, assuming the enthalpy is independent of temperature. As shown in Table 2, large discrepancies exist in the enthalpies for $Th(OH)^{3+}$, $Th(OH)_2{}^{2+}$, $Th_4(OH)_8{}^{8+}$ and $Th_6(OH)_{15}{}^{9+}$ between the two studies, probably because the measurements were performed at only three temperatures and the temperature range was quite narrow in one study (15–35 °C). Future experiments to determine the enthalpy of hydrolysis with calorimetry could help resolve the discrepancy and test the validity of the assumption of constant enthalpy.

Complexation with organic ligands. Complexation of Th(IV) with a few organic ligands at variable temperatures has been studied, including acetate,[29] malonate,[30] and tricine.[31] In the studies of Th(IV)/acetate and Th(IV)/malonate, the enthalpy of complexation at different temperatures was determined by titration calorimetry, in conjunction with the stability constants obtained by potentiometry. Data in Table 3 show that the enthalpies of complexation for Th(IV)/acetate and Th(IV)/malonate are not independent of temperature, but become more endothermic as the temperature is increased. From these data, the heat capacity of complexation was calculated.[29,30]

As shown in Table 3, the enthalpy of complexation of Th(IV) with acetate and malonate is always unfavorable (endothermic) to the complexation and becomes even more unfavorable at higher temperatures. However, the complexes become stronger as the temperature is increased, mainly due to the increasingly larger entropy of complexation at higher temperatures. The increase of entropy with 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 water molecules in the primary hydration sphere are released

Table 3 Complexation of Th(IV) with organic ligands at variable temperatures. Methods: pot – potentiometry, cal – calorimetry

Ligand	Reaction	Medium	T/°C	Method	log K	ΔH/kJ mol^{-1}	ΔS/J K^{-1} mol^{-1}	Ref.
Acetate	$Th^{4+} + Ac^- = ThAc^{3+}$	1.05 mol kg^{-1} NaClO$_4$	10	pot, cal	3.69 ± 0.03	10.2 ± 0.23	107 ± 1	29
			25		3.79 ± 0.02	12.2 ± 0.18	114 ± 1	
			40		3.94 ± 0.02	15.2 ± 0.75	124 ± 2	
			55		4.09 ± 0.05	17.3 ± 0.8	131 ± 3	
			70		4.28 ± 0.02	17.0 ± 0.9	131 ± 3	
	$Th^{4+} + 2\ Ac^- = ThAc_2{}^{2+}$	1.05 mol kg^{-1} NaClO$_4$	10	pot, cal	6.72 ± 0.02	12.7 ± 0.33	174 ± 1	
			25		6.79 ± 0.02	16.9 ± 0.27	187 ± 1	
			40		6.90 ± 0.04	20.7 ± 1.4	198 ± 5	
			55		7.27 ± 0.06	25.5 ± 1.3	217 ± 4	
			70		7.63 ± 0.02	28.3 ± 1.4	229 ± 4	
	$Th^{4+} + 3\ Ac^- = ThAc_3{}^+$	1.05 mol kg^{-1} NaClO$_4$	10	pot, cal	8.52 ± 0.06	17.5 ± 1.1	225 ± 4	
			25		8.71 ± 0.13	30.8 ± 0.7	270 ± 3	
			40		8.99 ± 0.07	35.4 ± 2.6	285 ± 8	
			55		9.35 ± 0.15	39.2 ± 3.7	298 ± 12	
			70		9.69 ± 0.17	38.9 ± 4.7	299 ± 10	
	$Th^{4+} + 4\ Ac^- = ThAc_4$	1.05 mol kg^{-1} NaClO$_4$	10	pot, cal	10.04 ± 0.12	29.1 ± 1.7	295 ± 6	
			25		10.17 ± 0.25	30.7 ± 1.4	298 ± 7	
			40		10.43 ± 0.18	44.8 ± 4.5	343 ± 6	
			55		11.27 ± 0.11	65.9 ± 3.1	417 ± 10	
			70		11.46 ± 0.2	99.5 ± 6.1	509 ± 18	
	$Th^{4+} + 5\ Ac^- = ThAc_5{}^-$	1.05 mol kg^{-1} NaClO$_4$	10	pot, cal	11.27 ± 0.15	34.2 ± 1.2	337 ± 5	
			25		11.41 ± 0.22	38.9 ± 0.8	349 ± 5	
			40		11.59 ± 0.21	39.9 ± 3.5	349 ± 12	
			55		12.38 ± 0.28	34.2 ± 3.2	341 ± 11	
			70		12.84 ± 0.24	40.1 ± 4.2	363 ± 13	
Malonate	$Th^{4+} + L^{2-} = ThL^{2+}$	1.05 mol kg^{-1} NaClO$_4$	10	pot, cal	7.39 ± 0.06	7.1 ± 0.3	167 ± 2	30
			25		7.45 ± 0.04	11.3 ± 0.1	180 ± 1	
			40		7.63 ± 0.07	14.3 ± 0.1	192 ± 1	
			55		7.82 ± 0.08	15.8 ± 0.2	198 ± 2	
			70		8.01 ± 0.15	17.1 ± 0.2	203 ± 3	
	$Th^{4+} + 2\ L^{2-} =ThL_2$	1.05 mol kg^{-1} NaClO$_4$	10		12.65 ± 0.07	12.1 ± 0.4	285 ± 2	
			25		12.80 ± 0.04	19.1 ± 0.1	309 ± 1	
			40		13.13 ± 0.09	23.4 ± 0.5	326 ± 2	
			55		13.51 ± 0.08	27.2 ± 0.2	342 ± 2	
			70		13.77 ± 0.15	29.9 ± 0.4	351 ± 3	
	$Th^{4+} + 3\ L^{2-} = ThL_3{}^{2-}$	1.05 mol kg^{-1} NaClO$_4$	10		15.85 ± 0.07	15.0 ± 0.5	356 ± 2	
			25		16.48 ± 0.06	23.1 ± 0.2	393 ± 2	
			40		17.24 ± 0.12	30.2 ± 1.2	427 ± 4	
			55		17.82 ± 0.09	34.7 ± 0.3	447 ± 2	
			70		18.18 ± 0.15	39.2 ± 0.6	462 ± 4	
Tricine[a]	$Th^{4+} + L^- = ThL^{3+}$	0.1 mol dm^{-3} KNO$_3$ 40% (w/w) dioxane–water	5	pot	8.98 ± 0.06			31
			15		8.75 ± 0.05			
			25		8.60 ± 0.01	−33.0	55.5	
			35		8.36 ± 0.04			
			45		8.13 ± 0.04			

[a] *N*-[Tris(hydroxymethy)methyl]glycine, $(HOCH_2)_3NH_2CH_2COOH$.

to an expanded and more disordered bulk solvent. As a result, the net gain in the complexation entropy is larger at higher temperatures.

The enthalpy of complexation consists of three components: the energy required for dehydration of both the Th^{4+} ion and the carboxylate ligand, the energy released when Th^{4+} and the carboxylate forms the complex, and the energy released when the dehydrated water molecules form hydrogen bonding with the bulk water. The positive enthalpy of complexation of Th(IV) with carboxylates suggests that the dehydration energy dominates, which is consistent with the energetics of interactions between "hard acid" cations and "hard base" anions. 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. Discussions on the temperature effect based on an electrostatic model were provided in more detail in the literature.[25,30]

In contrary to the complexation of Th(IV) with carboxylates in water, the complexation of Th(IV) with tricine in 40% (w/w) dioxane–water seems to be an exothermic reaction and the stability constants decrease as the temperature is increased.[31] This difference could be explained by the difference in the nature of coordination bonds (Th–O *vs.* Th–N) as well as the solvent effects. In general, ligands with nitrogen donor atoms are less hydrated so that less dehydration energy is required in complexation with metal ions and few water molecules are released, resulting in large negative enthalpy and small entropy of complexation.

3.3 Pentavalent actinides. Np(V) is the most stable oxidation state of neptunium in solution and is often studied as the oxidation state analog for other pentavalent state actinides such as plutonium and uranium. The complexation of Np(V) with a few inorganic ligands including hydroxide,[32] phosphate,[33] sulfate,[34,35] and fluoride,[8,34] in the temperature range 10–85 °C has been studied. The data are summarized in Table 4.

Microcalorimetry proves to be highly valuable in the thermodynamic study of the neptunium system. Because of the high sensitivity of microcalorimetry, very small quantities of neptunium are required for one titration (*e.g.*, less than 0.1 mg) so that the radiation hazards are minimized. Moreover, solutions with concentrations of Np(V) as low as

Table 4 Complexation of Np(V) with inorganic ligands in solution at variable temperatures. Methods: pot – potentiometry, cal – calorimetry, dis – solvent extraction

Ligand	Reaction	Medium	T/°C	Method	log K	ΔH/kJ mol^{-1}	ΔS/J K^{-1} mol^{-1}	Ref.
Hydroxide	$NpO_2^+ + H_2O = NpO_2OH + H^+$	1.12 mol kg^{-1} $(CH_3)_4NCl$	10	pot, cal	−9.38 ± 0.08			32
			25		−9.06 ± 0.07	31.6 ± 0.6	−67 ± 3	
			40		−8.89 ± 0.10	29.7 ± 1.5	−74 ± 5	
			55		−8.79 ± 0.11	30.4 ± 0.7	−75 ± 3	
			70		−8.70 ± 0.21	28.6 ± 1.2	−82 ± 5	
			85		−8.62 ± 0.12	27 ± 7	−89 ± 20	
	$NpO_2^+ + 2\ H_2O = NpO_2(OH)_2^- + 2\ H^+$	1.12 mol kg^{-1} $(CH_3)_4NCl$	10		−20.26 ± 0.11			
			25		−19.05 ± 0.07	84.1 ± 0.9	−88 ± 5	
			40		−18.15 ± 0.06	81.3 ± 1.7	−93 ± 6	
			55		−17.62 ± 0.05	78.6 ± 0.5	−103 ± 2	
			70		−17.40 ± 0.12	77.4 ± 0.9	−113 ± 4	
			85		−16.82 ± 0.04	76 ± 4	−116 ± 11	
Phosphate	$NpO_2^+ + H_2PO_4^- = NpO_2H_2PO_4$	1.0 mol dm^{-3} $NaClO_4$	25	dis	1.18 ± 0.10	28.1	117	33
			40		1.39 ± 0.06			
			55		1.63 ± 0.03			
Sulfate	$NpO_2^+ + SO_4^{2-} = NpO_2SO_4^-$	1.0 mol dm^{-3} $NaClO_4$	25	dis	0.49 ± 0.31	17.8	69	34
			40		0.65 ± 0.19			
			50		0.73 ± 0.16			
		1.0 mol dm^{-3} $NaClO_4$	25	dis, cal	0.49 ± 0.31	23.1 ± 2.5		8
			40		0.65 ± 0.19	20.0 ± 1.6		
			55		0.78 ± 0.20	25.1 ± 0.3		
			70		0.93 ± 0.20	30.4 ± 1.3		
		0.52 mol dm^{-3} $NaClO_4$	5	dis	−0.43 ± 0.35			35
			25		−0.10 ± 0.08	28.9 ± 4.6	95 ± 15	
			45		0.25 ± 0.03			
		1.05 mol dm^{-3} $NaClO_4$	5	dis	−0.18 ± 0.09			
			25		0.06 ± 0.04	22.2 ± 2.4	76 ± 8	
			45		0.34 ± 0.03			
		2.2 mol dm^{-3} $NaClO_4$	5	dis	−0.04 ± 0.11			
			25		0.19 ± 0.04	18.6 ± 2.5	66 ± 9	
			45		0.40 ± 0.05			
Fluoride	$NpO_2^+ + F^- = NpO_2F$	1.0 mol dm^{-3} $NaClO_4$	25	dis	1.42 ± 0.10	20.8	97	34
			35		1.63 ± 0.03			
			50		1.77 ± 0.04			
			60		1.80 ± 0.03			
		1.0 mol dm^{-3} $NaClO_4$	25	dis, cal	1.47 ± 0.10	18.0 ± 0.3		8
			40		1.63 ± 0.03	12.2 ± 0.6		
			55		1.78 ± 0.04	9.4 ± 0.8		
			70		1.94 ± 0.03	8.2 ± 1.2		

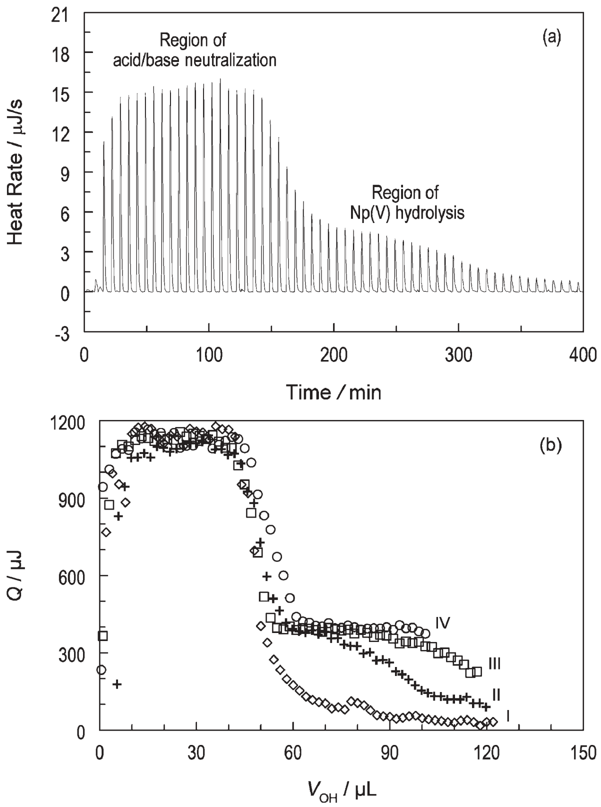

Fig. 7 Calorimetric titrations of Np(V) hydrolysis at 25 °C, I = 1.12 mol kg^{-1} $(CH_3)_4NCl$, titrant: 9.77 mmol dm^{-3} $(CH_3)_4NOH$, cell solution V° = 0.907 ml. (a) – thermogram for titration II, 2 μl of the titrant per addition. (b) $Q_{r,j}$ *vs.* V_{OH}; $C_{Np}{}^\circ$ (mmol dm^{-3}): (I) 0, (II) 0.285, (III) 0.426, (IV) 0.568.[32]

10^{-4} mol dm^{-3} can be studied in the hydrolysis titrations so that the interference with precipitation is reduced. A representative calorimetric titration of Np(V) hydrolysis is shown in Fig. 7. The reaction heat, obtained by integrating the peaks of the thermogram (Fig. 7(a)), consists of the heat of acid–base neutralization and the heat of Np(V) hydrolysis (Fig. 7(b)). The enthalpy of hydrolysis was calculated from the reaction heat, in conjunction with the hydrolysis constants independently determined by potentiometry, based on the least square analysis discussed in a previous section.[32]

Data in Table 4 indicate that the hydrolysis of Np(V) and the complexation of Np(V) with the inorganic ligands (phosphate, sulfate and fluoride) are all enhanced at higher temperatures, which could have a great impact on the transport of neptunium in nuclear waste repositories where the temperature is expected to be significantly higher than the ambient temperature.

3.4 Hexavalent actinides

Hydrolysis. Numerous studies have been conducted on the hydrolysis of U(VI) in aqueous solutions at or near 25 °C,[6] but only a few studies generated thermodynamic data at variable temperatures.[36–39] The data in the temperature range 10–94 °C are in good agreement and summarized in Table 5. The following trends are observed: (1) In the temperature range 10–94 °C, the hydrolysis of U(VI) proceeds as the formation of UO_2OH^+, $(UO_2)_2(OH)_2{}^{2+}$, and $(UO_2)_3(OH)_5{}^+$ in acidic solutions (pC_H or $-\log[H^+] < 6$); (2) all the three hydrolysis constants increase as the temperature is increased, indicating the enhancement of overall hydrolysis at elevated temperatures (Fig. 8).

The hydrolysis constants of UO_2OH^+, $(UO_2)_2(OH)_2{}^{2+}$, and $(UO_2)_3(OH)_5{}^+$ increase with temperature to different extents as shown in Fig. 8. Consequently, the speciation of U(VI) at elevated temperatures differs from that at lower temperatures. In fact, the UO_2OH^+ species becomes more important at higher temperatures and lower concentrations of U(VI) (Fig. 9).

Table 5 Hydrolysis of U(VI) at variable temperatures. Methods: pot – potentiometry, cal – calorimetry

Reaction	Medium	T/°C	Method	log K	ΔH/kJ mol^{-1}	ΔS/J K^{-1} mol^{-1}	Ref.
$UO_2{}^{2+} + H_2O = UO_2OH^+ + H^+$	0.10 mol dm^{-3} $(C_2H_5)_4NClO_4$	10	pot, cal	−6.1 ± 0.3			39
		25		−5.58 ± 0.24	46.5 ± 3.7	53 ± 13	
		40		−5.11 ± 0.11			
		55		−5.07 ± 0.24			
		70		−4.51 ± 0.11			
		85		−4.24 ± 0.15	58 ± 7	85 ± 30	
	0.035 mol dm^{-3} $BaCl_2$	40	pot	−5.09			37
	0.5 mol kg^{-1} KNO_3	94	pot	−4.19			36
$2\ UO_2{}^{2+} + 2\ H_2O = (UO_2)_2(OH)_2{}^{2+} + 2\ H^+$	0.10 mol dm^{-3} $(C_2H_5)_4NClO_4$	10	pot	−6.30 ± 0.02	51.5 ± 0.9	65.3 ± 3.6	39
		25		−5.83 ± 0.02	48.2 ± 1.7	54 ± 6	
		40		−5.43 ± 0.01	50 ± 2	60 ± 6	
		55		−5.06 ± 0.03	53 ± 8	69 ± 24	
		70		−4.73 ± 0.03	58 ± 3	83 ± 7	
		85		−4.49 ± 0.03	61 ± 2	89 ± 6	
	0.15 mol dm^{-3} NaCl	37	pot	−5.693			38
	0.035 mol dm^{-3} $BaCl_2$	40	pot	−5.92			37
	0.5 mol kg^{-1} KNO_3	94	pot	−4.51			36
$3\ UO_2{}^{2+} + 5\ H_2O = (UO_2)_3(OH)_5{}^+ + 5\ H^+$	0.10 mol dm^{-3} $(C_2H_5)_4NClO_4$	10	pot, cal	−17.52 ± 0.01	128.0 ± 0.5	128.5 ± 2.0	39
		25		−16.37 ± 0.02	120.1 ± 1.6	101.5 ± 5.7	
		40		−15.35 ± 0.01	119 ± 2	99 ± 6	
		55		−14.45 ± 0.02	113 ± 7	80 ± 21	
		70		−13.61 ± 0.02	112 ± 3	79 ± 9	
		85		−12.94 ± 0.02	110 ± 2	73 ± 6	
	0.15 mol dm^{-3} NaCl	37	pot	−16.001			38
	0.5 mol kg^{-1} KNO_3	94	pot	−12.74			36

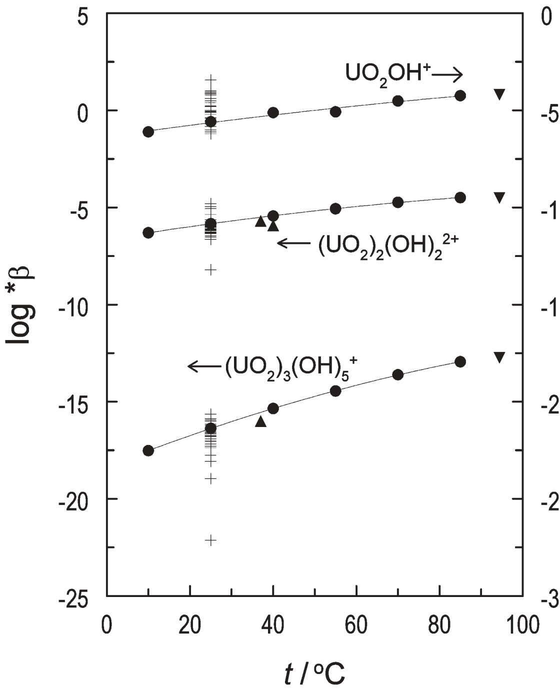

Fig. 8 Hydrolysis constants of U(VI) at variable temperatures. Symbols: (●) [39], (▼) [36], (▲),[37,38] (+).[6]

The enhancement of hydrolysis at elevated temperatures is mainly due to the increase of the degree of ionization of water. As shown in Fig. 1, the ionic product of water increases by 2–3 orders of magnitude from 10 to 90 °C, resulting in higher concentrations of hydroxide ion at the same pC_H. Meanwhile, the increasing importance of UO_2OH^+ at elevated temperatures can be attributed to the decrease in the dielectric constant of water (Fig. 1). Such decrease would increase the electrostatic repulsion of the mononuclear "building blocks" and decrease the formation of polynuclear and highly charged species according to simple electrostatic models.[39]

Zanonato *et al.* used microcalorimetry to determine the enthalpy of U(VI) hydrolysis at different temperatures, which allowed the calculation of the heat capacity and the entropy at different temperatures.[39] With these data, the approximation approaches to predict the temperature effect could be tested with the data on U(VI) hydrolysis. Results show that the approaches, including the constant enthalpy approach, the constant heat capacity approach, the DQUANT equation and the Ryzhenko and Bryzgalin model, provide satisfactory predictions of the hydrolysis constants at temperatures up to 50–60 °C. However, deviations start to increase as the temperature is further increased, reaching 0.1 logarithm unit (about two times larger than the three standard deviations of the experimental data) at 70–80 °C. The revised HKF equation was not tested due to lack of parameters.[39]

Complexation with organic ligands. Results of the studies on the complexation of U(VI) with carboxylates at variable temperatures[25,40–42] are summarized in Table 6. Titration calorimetry was used in all these studies to determine the enthalpy of complexation at variable temperatures, allowing

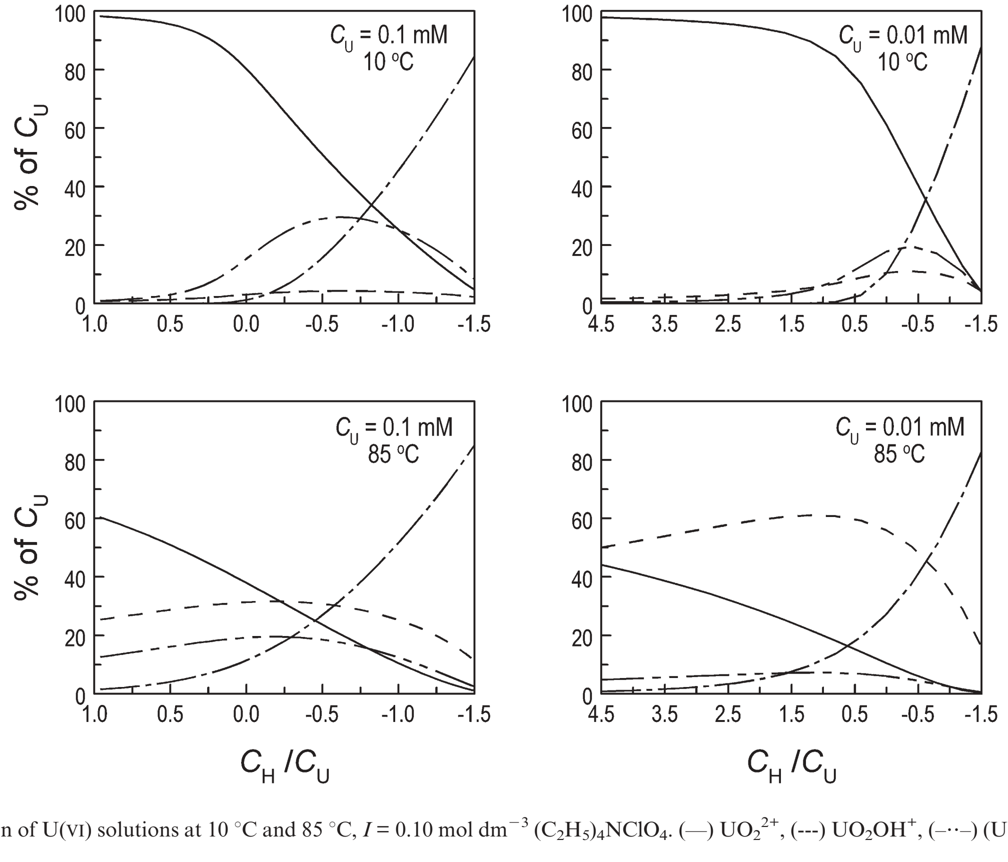

Fig. 9 Speciation of U(VI) solutions at 10 °C and 85 °C, $I = 0.10$ mol dm^{-3} $(C_2H_5)_4NClO_4$. (—) UO_2^{2+}, (---) UO_2OH^+, (–··–) $(UO_2)_2(OH)_2^{2+}$, (-··-) $(UO_2)_3(OH)_5^+$.

an insightful analysis of the energetics of complexation and the calculation of heat capacities of complexation.

Table 6 shows that the complexation of U(VI) with acetate, malonate, oxydiacetate and thiodiacetate is always endothermic and entropy-driven. The enthalpy and entropy of complexation both become more positive at higher temperatures, making opposite contributions to the complexation. The complexes become stronger at higher temperatures because the increase of the entropy term ($T\Delta S$) exceeds that of the enthalpy. Similar thermodynamic trends have been observed

Table 6 Complexation of U(VI) with organic ligands at variable temperatures. Methods: pot – potentiometry, cal – calorimetry

Ligand	Reaction	Medium	T/°C	Method	log K	ΔH/kJ mol^{-1}	ΔS/J K^{-1} mol^{-1}	Ref
Acetate	$UO_2^{2+} + Ac^- = UO_2Ac^+$	1.0 mol dm^{-3} $NaClO_4$	25	pot, cal	2.58 ± 0.03	10.6 ± 0.8	85 ± 3	40
			35		2.67 ± 0.02	11.8 ± 0.5	89 ± 2	
			45		2.74 ± 0.03	13.0 ± 0.6	93 ± 2	
			55		2.85 ± 0.02	14.3 ± 0.5	98 ± 2	
			70		2.98 ± 0.05	15.4 ± 0.7	102 ± 3	
	$UO_2^{2+} + 2\ Ac^- = UO_2Ac_2$	1.0 mol dm^{-3} $NaClO_4$	25	pot, cal	4.37 ± 0.14	20 ± 3	150 ± 13	
			35		4.60 ± 0.08	21 ± 2	155 ± 8	
			45		4.76 ± 0.10	22 ± 2	160 ± 8	
			55		4.94 ± 0.06	24 ± 1	167 ± 4	
			70		5.27 ± 0.09	27 ± 1	179 ± 5	
	$UO_2^{2+} + 3\ Ac^- = UO_2Ac_3^-$	1.0 mol dm^{-3} $NaClO_4$	25	pot, cal	6.86 ± 0.04	17.5 ± 0.6	189 ± 3	
			35		7.11 ± 0.03	18.8 ± 0.3	196 ± 2	
			45		7.23 ± 0.04	20.8 ± 0.3	203 ± 2	
			55		7.38 ± 0.03	22.8 ± 0.3	210 ± 2	
			70		7.62 ± 0.06	24.6 ± 0.4	216 ± 2	
Malonate	$UO_2^{2+} + L^{2-} = UO_2L$	1.0 mol dm^{-3} $NaClO_4$	25	pot, cal	5.36 ± 0.01	8.0 ± 0.7	130 ± 2	41
			35		5.42 ± 0.01	9.8 ± 0.3	136 ± 1	
			45		5.56 ± 0.01	10.7 ± 0.2	141 ± 1	
			55		5.67 ± 0.01	11.5 ± 0.2	144 ± 1	
			70		5.80 ± 0.01	12.5 ± 0.4	148 ± 1	
	$UO_2^{2+} + 2\ L^{2-} = UO_2L_2^{2-}$	1.0 mol dm^{-3} $NaClO_4$	25	pot, cal	9.39 ± 0.01	11 ± 1	218 ± 4	
			35		9.74 ± 0.02	13.4 ± 0.4	231 ± 2	
			45		9.85 ± 0.02	16.0 ± 0.4	240 ± 2	
			55		10.05 ± 0.02	17.4 ± 0.4	246 ± 2	
			70		10.35 ± 0.01	19.8 ± 0.5	257 ± 2	
	$UO_2^{2+} + 3\ L^{2-} = UO_2L_3^{4-}$	1.0 mol dm^{-3} $NaClO_4$	25	pot, cal	11.22 ± 0.06	11.7 ± 4.0	256 ± 14	
			35		12.43 ± 0.06	15.6 ± 0.7	290 ± 3	
			45		12.72 ± 0.08	18.7 ± 0.6	304 ± 3	
			55		13.16 ± 0.12	20.4 ± 0.6	316 ± 4	
			70		13.61 ± 0.02	24.1 ± 0.8	332 ± 3	
Oxy-diacetate	$UO_2^{2+} + L^{2-} = UO_2L$	1.0 mol dm^{-3} $NaClO_4$	25	pot, cal	5.01 ± 0.04	16.4 ± 0.2	152 ± 1	25
			35		5.04 ± 0.05	18.0 ± 0.2	155 ± 2	
			45		5.14 ± 0.09	19.3 ± 0.3	160 ± 3	
			55		5.31 ± 0.04	20.1 ± 0.7	164 ± 3	
			70		5.38 ± 0.10	20.7 ± 0.5	164 ± 3	
	$UO_2^{2+} + 2\ L^{2-} = UO_2L_2^{2-}$	1.0 mol dm^{-3} $NaClO_4$	25	pot, cal	7.64 ± 0.11	23.8 ± 0.1	227 ± 2	
			35		7.67 ± 0.06	27.6 ± 0.1	236 ± 2	
			45		7.84 ± 0.12	31.7 ± 0.2	251 ± 3	
			55		8.10 ± 0.06	34.9 ± 0.4	263 ± 3	
			70		8.12 ± 0.11	36.8 ± 0.3	264 ± 3	
	$UO_2^{2+} + H^+ + 2\ L^{2-} = UO_2HL_2^-$	1.0 mol dm^{-3} $NaClO_4$	25	pot, cal	10.35 ± 0.09	22.4 ± 1.4	275 ± 6	
			35		10.46 ± 0.08	22.6 ± 0.1	275 ± 2	
			45		10.61 ± 0.13	23.4 ± 1.8	278 ± 8	
			55		10.93 ± 0.06	24.4 ± 0.05	285 ± 2	
			70		11.26 ± 0.15	30.0 ± 2.2	305 ± 9	
Thio-diacetate	$UO_2^{2+} + L^{2-} = UO_2L$ (aq)	1.05 mol kg^{-1} $NaClO_4$	10	pot, cal	2.89 ± 0.03	13.4 ± 0.4	102.6 ± 1.5	42
			25		3.02 ± 0.03	15.7 ± 0.7	110.5 ± 2.4	
			40		3.21 ± 0.03	16.3 ± 0.9	113.5 ± 2.9	
			55		3.33 ± 0.05	19.2 ± 1.2	122.3 ± 3.8	
			70		3.60 ± 0.03	20.5 ± 1.8	128.7 ± 5.3	
			85		3.66 ± 0.05	23.0 ± 1.8	134.3 ± 5.1	
	$UO_2^{2+} + H^+ + L^{2-} = UO_2HL^+$	1.05 mol kg^{-1} $NaClO_4$	10	pot, cal	5.62 ± 0.04	7.5 ± 0.6	134.1 ± 2.2	
			25		5.72 ± 0.06	11.9 ± 1.2	149.4 ± 4.2	
			40		5.59 ± 0.07	27 ± 4	193.2 ± 12.8	
			55		5.94 ± 0.07	21.4 ± 2.1	178.9 ± 6.5	
			70		6.06 ± 0.08	25 ± 3	188.9 ± 8.9	
			85		6.30 ± 0.08	30.3 ± 2.7	205.2 ± 7.7	
	$UO_2^{2+} + H^+ + 2\ L^{2-} = UO_2HL_2^-$	1.05 mol kg^{-1} $NaClO_4$	10	pot, cal	8.04 ± 0.08	24.3 ± 0.6	239.7 ± 2.6	
			25		8.42 ± 0.07	30.0 ± 1.2	261.8 ± 4.2	
			40		8.64 ± 0.07	38.6 ± 3.6	288.7 ± 11.6	
			55		8.97 ± 0.07	38.0 ± 1.5	287.5 ± 4.8	
			70		9.30 ± 0.07	39.0 ± 2.5	291.7 ± 7.4	
			85		9.63 ± 0.08	38.2 ± 2.4	291.0 ± 6.9	

for the complexation of carboxylates with other actinide and lanthanide cations, including Th(IV),[29,30] Nd(III)[20,21] and Sm(III).[24,25] The trends in the energetics of complexation are typical of the interactions between "hard acid" cations and "hard base" anions and can be interpreted in terms of the effect of temperature on the dehydration process and the structure of water (see section 3.2). More detailed discussions on the temperature effect based on an electrostatic model were provided in more detail in the literature.[25,30,40,42]

4 Summary

The importance of thermodynamic data on the complexation of actinides in solution at elevated temperatures, the experimental techniques (with an emphasis on titration calorimetry) to determine such data, and the available data in the literature have been reviewed in this paper. In contrast to the large amounts of data at or near 25 °C, data at elevated temperatures are very limited. In particular, the enthalpy data directly measured by calorimetry are still scarce. Recent application of microcalorimetry to the study of actinide complexation at elevated temperatures has generated thermodynamic data that could have significant impact on the prediction of actinide behavior in environmental transport, as well as reveal the energetics and fundamental aspects of actinide complexation.

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