Thermodynamics of the complexation of uranium(VI) with oxalate in aqueous solution at 10–70 °C†

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The protonation reactions of oxalate (ox) and the complex formation of uranium(VI) with oxalate in 1.05 mol kg^{-1} NaClO$_4$ were studied at variable temperatures (10–70 °C). Three U(VI)/ox complexes ($UO_2ox_j^{(2-2j)+}$ with $j = 1, 2, 3$) were identified in this temperature range. The formation constants and the molar enthalpies of complexation were determined by spectrophotometry and calorimetry. The complexation of uranium(VI) with oxalate ion is exothermic at lower temperatures (10–40 °C) and becomes endothermic at higher temperatures (55–70 °C). In spite of this, the free energy of complexation becomes more negative at higher temperatures due to increasingly more positive entropy of complexation that exceeds the increase of the enthalpy of complexation. The thermodynamic parameters at different temperatures, in conjunction with the literature data for other dicarboxylic acids, provide insight into the relative strength of U(VI) complexes with a series of dicarboxylic acids (oxalic, malonic and oxydiacetic) and rationalization for the highest stability of U(VI)/oxalate complexes in the series. The data reported in this study are of importance in predicting the migration of uranium(VI) in geological environments in the case of failure of the engineering barriers, which protect waste repositories.

Introduction

Nuclear wastes can contact ground waters if the engineering barriers of waste repositories fail. Therefore, the migration of actinides into the environment is of great concern in the long-term performance assessment of the waste repositories. Safe management of nuclear wastes requires correct models of radionuclide migration toward the surrounding environment. In particular, such models should predict the behaviour and evolution of repository sites for thousands of years. To achieve these results, a deep knowledge of the various parameters on which metal ion mobility depends (oxidation state, temperature, pH, presence of several inorganic or organic complexing agents, nature of the solid stationary phases, *etc.*), must be acquired. In this context, studies on the complexation of actinides by organic materials at elevated temperatures raise significant scientific interest, because the temperature in nuclear waste storage tanks and waste forms in repositories is significantly higher than the ambient temperature, due to the radioactive decay energy.[1] At present, most of the thermodynamic data on actinide complexation are obtained at or near 25 °C.[2] The lack of data at elevated temperatures makes it difficult to predict the behaviour of actinides in waste processing and disposal, where those temperatures are expected. Moreover, while providing data to support the safe management of nuclear wastes, studies of actinide complexation at elevated temperatures can also provide fundamental information on actinide chemistry,

such as the effect of temperature on the structure and dielectric properties of the solvent, the solvation of both the actinide ion and the ligand, and the energetics of the complexation. The composition of liquid nuclear wastes in the storage tanks is extremely diverse, where a number of carboxylic acids (acetic acid, citric acid, EDTA, etc.) exist in large amounts. Among these, oxalic acid is one of the most important. For example, in the Waste Isolation Pilot Plant repository (WIPP, located near Carlsbad, New Mexico), the total amount of sodium oxalate and oxalic acid is expected to be close to 50 tons, more than the total amounts of acetate/acetic acid and citrate/citric acid.[3] In addition, oxalate ions are present in relatively high concentrations in several natural environments such as soil solutions, oil field sedimentary basin brines, and deposits originated from thermal degradation of more complex organic matter.[4]

Three well-established mononuclear complexes between U(VI) (as UO_2^{2+} cation) and oxalate have been reported in the literature. The stability constants of the complexes have been critically reviewed[5] and integrated[6] in recent publications. These data indicate that the thermodynamic properties of U(VI) oxalate complexes are quite well defined at temperatures near the ambient, but very scarce at higher temperatures. Therefore, we have conducted the present work to fill this gap of knowledge and help to predict the chemical behaviour of actinide complexation at elevated temperatures. Stability constants and enthalpies of formation of oxalate complexes of U(VI) were determined in aqueous solution at $I = 1.05$ mol kg^{-1} NaClO$_4$ and in the temperature range 10–70 °C.

Because oxalate is a moderately weak base that forms very strong chelate complexes with U(VI), ordinary potentiometry using proton competition is not applicable to the measurements of the stability constants of U(VI)/oxalate complexes. Consequently, the complexation of U(VI) by oxalate was studied in this work by

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Table 1 Protonation of oxalate at $I = 1.05$ mol kg^{-1} NaClO$_4$, $j = 1$–2, the error limits represent 3σ. To allow comparison at different temperatures, the protonation constants in molarity were converted into the constants in molality according to eqn (4)

Reaction		$T/^\circ C$	$\log\beta_{j,M}^{H}$	$\log\beta_{j,M}^{H}$	$\log\beta_{j}^{H,o}$	$-\Delta G_{j}^{H}/$kJ mol^{-1}	$\Delta H_{j}^{H}/$kJ mol^{-1}	$\Delta S_{j}^{H}/$J K^{-1} mol^{-1}
(1) H$^+$ + ox^{2-} = Hox$^-$	$j = 1$	10	3.52 ± 0.01	3.50 ± 0.01	4.17 ± 0.04	−18.97 ± 0.06	1.66 ± 0.02	72.9 ± 0.3
		25	3.54 ± 0.01	3.52 ± 0.01	4.21 ± 0.04	−20.09 ± 0.06	4.13 ± 0.02	81.2 ± 0.3
		40	3.59 ± 0.01	3.57 ± 0.01	4.28 ± 0.04	−21.40 ± 0.06	6.37 ± 0.03	88.7 ± 0.3
		55	3.65 ± 0.01	3.63 ± 0.01	4.36 ± 0.04	−22.80 ± 0.06	9.52 ± 0.12	98.5 ± 0.6
		70	3.72 ± 0.01	3.70 ± 0.01	4.46 ± 0.04	−24.31 ± 0.06	11.54 ± 0.25	104.5 ± 0.9
(2) 2H$^+$ + ox^{2-} = H$_2$ox	$j = 2$	10	4.47 ± 0.03	4.43 ± 0.03	5.43 ± 0.05	−24.01 ± 0.17	2.10 ± 0.05	92.2 ± 0.8
		25	4.58 ± 0.03	4.54 ± 0.03	5.56 ± 0.05	−25.91 ± 0.17	5.64 ± 0.07	105.8 ± 0.8
		40	4.64 ± 0.02	4.60 ± 0.02	5.66 ± 0.04	−27.58 ± 0.11	8.92 ± 0.07	116.6 ± 0.6
		55	4.70 ± 0.02	4.66 ± 0.02	5.76 ± 0.04	−29.28 ± 0.11	16.9 ± 1.1	141 ± 4
		70	4.81 ± 0.03	4.77 ± 0.03	5.91 ± 0.05	−31.34 ± 0.17	25.7 ± 2.7	166 ± 9

spectrophotometry, in conjunction with microcalorimetric titrations to obtain the heats of complexation at variable temperatures.

Experimental measurements were carried out at both University of Padova (UP) in Italy and Lawrence Berkeley National Laboratory (LBNL) in the United States of America. In particular, all the potentiometric titrations, most spectrophotometric measurements, and the microcalorimetric titrations at 10–40 °C were conducted at UP, while some of the spectrophotometric measurements and the microcalorimetric titrations at 25–70 °C were conducted at LBNL. Overlapping calorimetric measurements at 25–40 °C were carried out at both UP and LBNL in order to check the mutual consistency of the measurements.

Results and discussion

Protonation of oxalate at 10–70 °C

The protonation constants and enthalpy of oxalate at different temperatures are summarized in Table 1. The values of the protonation constants ($\log\beta_{1,M}^{H}$ and $\log\beta_{2,M}^{H}$) obtained at 25 °C (3.54 ± 0.01 and 4.58 ± 0.03) are in good agreement with those measured by Vasca *et al.*[7] in the same ionic medium (3.57 ± 0.02 and 4.57 ± 0.03). The second stepwise protonation stability constants at 40 °C (1.05 ± 0.02) and 55 °C (1.05 ± 0.02) from the present study also agree well with those reported by Kallen[8] (1.027 ± 0.008 for 40 °C and 1.063 ± 0.043 for 55 °C). The enthalpy of the first protonation of oxalate at 25 °C obtained in this study is also fairly consistent with those reported in the recent NEA database.[5] To our knowledge, no enthalpy data concerning temperatures higher than 35 °C have been reported to date for both protonation reactions of oxalate in the literature.

As already observed for other carboxylic acids (acetate,[9] malonate (mal),[10] oxydiacetate (oda),[11] thiodiacetate[12]) the enthalpies of protonation of the carboxylic groups of oxalate are small (a few kJ mol^{-1}) and become more endothermic when the temperature is increased (Table 1 and Fig. 2). Though the enthalpy becomes more unfavourable to the protonation at higher temperatures, the protonation constants increase slightly with temperature because the increase in the positive entropy terms ($T\Delta S$) favouring protonation exceeds the increase of unfavourable enthalpies.

Fig. 1A shows that, between 10 °C and 70 °C, $\log\beta_{1,m}^{H}$ does not increase linearly with temperature. The full line in Fig. 1B represents the best fit obtained with a second-order polynomial from which the enthalpies of protonation can be calculated by the
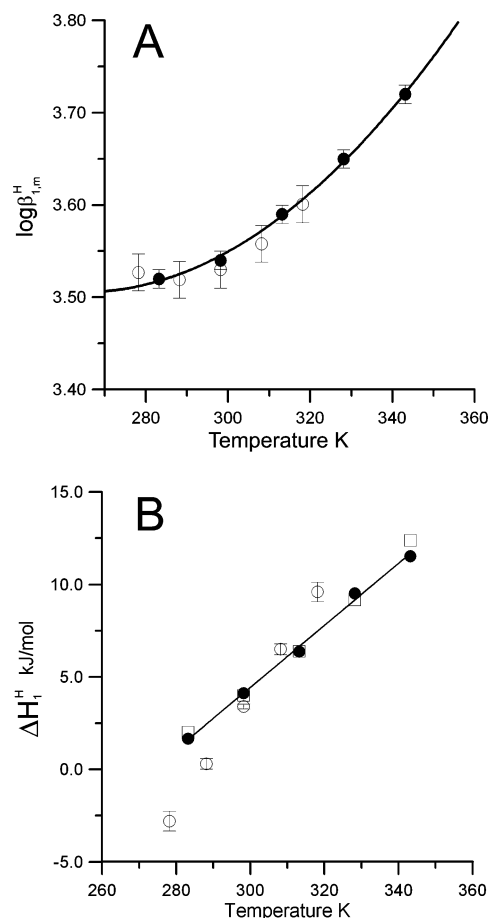

Fig. 1 A. (●) The changes of the first protonation constant of oxalate as a function of the temperature in 1.05 mol kg^{-1} NaClO$_4$. The full line represents the best fit of the experimental data obtained with a second-order polynomial. Error bars, 3σ of $\log\beta_{1,m}^{H}$ given by the minimization program. B (●) observed enthalpy changes, ΔH_1^{H}; (□) enthalpy changes calculated with the van't Hoff equation and the derivative at each selected temperature of the best-fit line in Fig. 1A. The slope of the full line, the best-fit line of the experimental results, is 0.168 kJ K^{-1} mol^{-1}, which indicates that ΔC_p for the protonation reaction is 168 J K^{-1} mol^{-1}. (○) Values for $\log\beta_{1,m}^{H}$ and ΔH_1^{H} recommended by Sammartano *et al.* in ref. 13.

van't Hoff equation. As shown in the figure, the enthalpies of the first protonation (ΔH_1^{H}) calculated by the van't Hoff equation compare very well with the experimental enthalpies obtained

from calorimetric titrations. However, the comparison between the values of ΔH_2^{H} from the van't Hoff equation and calorimetry is less satisfactory. For example, the calculated ΔH_2^{H} at 25 °C and 55 °C by van't Hoff (9.56 and 11.7 kJ mol^{-1}) are quite far from the experimental values (calorimetry) (5.64 and 16.9 kJ mol^{-1}).

The specific ion interaction approach (SIT) and ion interaction parameters reported in the NEA database (ref. 5, pp. 99, 144) were used to estimate the standard enthalpy changes at infinite dilution for the stepwise protonation reactions of oxalate at 25 °C. The values are: $\Delta H_1^{\mathrm{H,o}} = 9.10 \pm 0.02$ kJ mol^{-1} and $\Delta H_2^{\mathrm{H,o}} = 4.50 \pm 0.07$ kJ mol^{-1}, different, even if not very far, from the recommended values given in the NEA database (ref. 5: $\Delta H_1^{\mathrm{H,o}} = 7.3 \pm 0.1$ kJ mol^{-1}; $\Delta H_2^{\mathrm{H,o}} = 3.3 \pm 0.5$ kJ mol^{-1}).

A comparison of thermodynamic parameters (ΔG, ΔH, and $T\Delta S$) at all temperatures between oxalic and malonic acids is informative. Data in Fig. 2 indicate that oxalate is more acidic than malonate ($\Delta G_{\mathrm{ox}} > \Delta G_{\mathrm{mal}}$) at all temperatures (10–70 °C), principally because the protonation entropy of oxalate is much smaller (less positive) than that of malonate ($T\Delta S_{\mathrm{ox}} < T\Delta S_{\mathrm{mal}}$). The difference in the entropy of protonation between oxalate and malonate depends on several factors including: (1) the repulsion of negative charges in the dianions; (2) the increase of the conformational entropy, which follows dianion protonations; (3) the ability of the dianions and acids to form hydrogen bonding; and (4) the solvation/desolvation effects that depend on a delicate balance among a number of interactions between water and the carboxylates, including the hydrophilic electrostatic interactions between water and the $-\mathrm{CO_2}^-/-\mathrm{CO_2H}$ groups, and the hydrophobic interactions between water and the aliphatic carbon backbone of the dicarboxylates.[14] Recent studies of molecular dynamics show that, in small anions where the carboxylic groups are separated by an aliphatic chain, the hydrophilic interactions of the charged carboxylates prevail over the hydrophobic forces due to the aliphatic chain. As a consequence, the water molecules encompass the whole dianion in which the two carboxylate groups are co-linear due to the strong Coulombic repulsion and each of them is solvated roughly by seven water molecules.[14] In contrast, similar studies concerning oxalate show that the degree of solvation of this ion, in which the two carboxylate groups are not separated by an aliphatic chain, is lower: only six water molecules are necessary to complete its first solvation shell.[15] These last findings suggest that the entropy of protonation of oxalate, smaller than that of malonate as observed in Fig. 2, may reflect the significant role of the desolvation of dicarboxylates on the overall entropy changes, which follow ligand protonations.

The difference in the enthalpy of protonation between oxalate and malonate also contributes, even if less significantly, to the difference in the acidity between the two acids. Though the solvation shell of oxalate is smaller than that of malonate, electrostatic considerations suggest that the water molecules in the solvated oxalate are more tightly held around this smaller dianion and more energy is required for its desolvation. This may explain the slightly more positive enthalpy of protonation of oxalate in Fig. 2.

Complexation of U(VI) with oxalate

Stability constants. Fig. 3 shows the results of a representative spectrophotometric titration at 25 °C. For clarity, only one half of the experimental spectra used in the minimization procedure are shown in the figure. As the $C_{\mathrm{ox}}/C_{\mathrm{U}}$ ratio was increased, the absorption bands of U(VI) became more intense and were slightly shifted toward longer wavelengths. The data were best fitted with the formation of three U(VI)/ox complexes. The stability constants thus calculated are shown in Table 2. The uncertainties of stability constants, except those of $\log\beta_1$, were directly obtained by the minimization program. In the case of $\log\beta_1$, a value of ± 0.01 was assigned when the uncertainties given by the minimization program were less than 0.01.
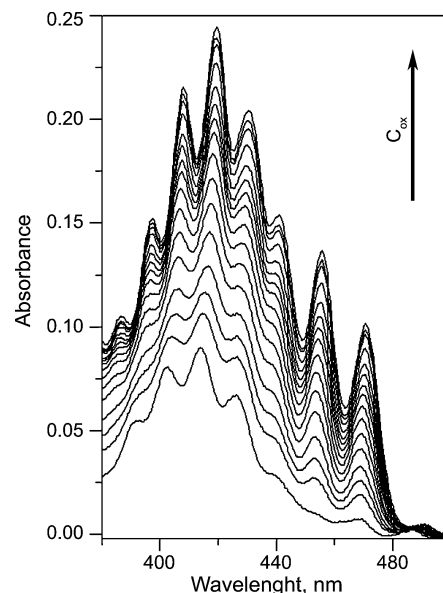

Fig. 3 Absorption spectra of U(VI) solutions at 25 °C. $C_{\mathrm{U}} \sim 12$ mmol dm^{-3}, $0.0 \leq C_{\mathrm{ox}} \leq 56$ mmol dm^{-3}, $1.7 < -\log[\mathrm{H}^+] < 2.7$. The species distribution and analytical details for the titration are given in Fig. S1a of electronic supplementary information (ESI).†

Fig. 2 Comparison of the thermodynamic parameters for the first protonation reaction of oxalate (◆) and malonate (△).

Enthalpy of complexation. The results of calorimetric experiments are shown in Fig. 4, in the form of $\Delta h_{\mathrm{v,obs}}$ vs. $\bar{n}$, the average number of ligands per mole of metal. The quantity $\Delta h_{\mathrm{v,obs}}$ represents the observed total complexation heat per mole of U(VI)
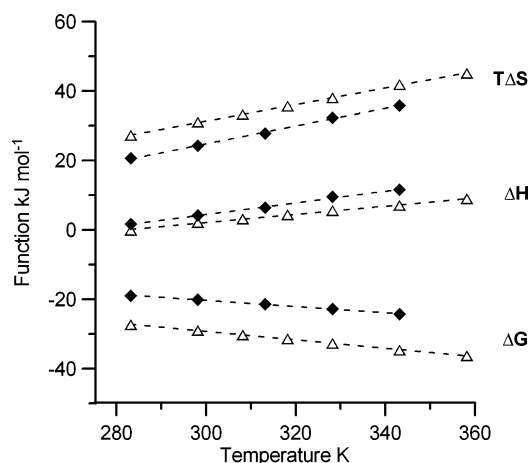
Table 2 Complexation of dioxouranium(VI) with oxalate at different temperatures. $I = 1.05$ mol kg^{-1} NaClO$_4$, $j = 1$–3, the error limits represent 3σ. To allow comparison at different temperatures, the overall stability constants in molarity were converted into the constants in molality according to eqn (4)

Reaction (n)	T/°C	log $\beta_{j,m}$	log $\beta_{j,m}$	logβ^0_j	$-\Delta G_j$/kJ mol^{-1}	ΔH_j/kJ mol^{-1}	ΔS_j/J K^{-1} mol^{-1}
(3) UO$_2$$^{2+}$ + ox^{2-} = UO$_2$ox	10	6.36 ± 0.03	6.34 ± 0.03	7.71 ± 0.08	−34.37 ± 0.16	−4.90 ± 0.05	104.1 ± 0.6
	25	6.06 ± 0.01	6.04 ± 0.01	7.44 ± 0.07	−34.48 ± 0.06	−2.77 ± 0.03	106.3 ± 0.6
	40	6.08 ± 0.01	6.06 ± 0.01	7.52 ± 0.07	−36.33 ± 0.06	−1.03 ± 0.03	112.7 ± 0.6
	55	5.87 ± 0.01	5.85 ± 0.01	7.35 ± 0.07	−36.75 ± 0.06	0.66 ± 0.09	114.0 ± 0.7
	70	6.24 ± 0.01	6.22 ± 0.01	7.78 ± 0.07	−40.86 ± 0.07	2.36 ± 0.10	126.0 ± 0.7
(4) UO$_2$$^{2+}$ + 2ox^{2-} = UO$_2$ox$_2$$^{2-}$	10	11.08 ± 0.03	11.04 ± 0.03	12.35 ± 0.10	−59.85 ± 0.16	−9.20 ± 0.09	178.9 ± 0.7
	25	10.76 ± 0.02	10.72 ± 0.03	12.07 ± 0.10	−61.19 ± 0.11	−5.43 ± 0.09	187.0 ± 0.5
	40	10.80 ± 0.02	10.76 ± 0.02	12.16 ± 0.09	−64.51 ± 0.12	−2.36 ± 0.15	198.5 ± 0.6
	55	10.46 ± 0.02	10.42 ± 0.02	11.87 ± 0.09	−65.34 ± 0.13	0.81 ± 0.12	201.6 ± 0.5
	70	11.10 ± 0.03	11.06 ± 0.03	12.57 ± 0.10	−72.66 ± 0.20	4.43 ± 0.13	224.7 ± 0.7
(5) UO$_2$$^{2+}$ + 3ox^{2-} = UO$_2$ox$_3$$^{4-}$	10	13.46 ± 0.20	13.40 ± 0.20	13.59 ± 0.23	−72.6 ± 1.1	−9.68 ± 0.65	222 ± 4
	25	13.27 ± 0.22	13.21 ± 0.22	13.40 ± 0.25	−75.4 ± 1.3	−5.68 ± 0.45	234 ± 4
	40	13.74 ± 0.16	13.68 ± 0.16	13.87 ± 0.19	−82.0 ± 1.0	−2.36 ± 0.50	254 ± 3
	55	13.25 ± 0.22	13.19 ± 0.22	13.38 ± 0.25	−82.9 ± 1.4	2.20 ± 0.60	259 ± 5
	70	14.06 ± 0.19	14.00 ± 0.19	14.19 ± 0.22	−92.0 ± 1.2	5.7 ± 2.7	285 ± 9

[a] Values from ref. 5 UO$_2$$^{2+}$ + ox^{2-} = UO$_2$ox

and is obtained from the stepwise complexation heat ($Q_{cplx,j}$).‡ The quantity $\Delta h_{v,calc}$ was calculated from the protonation constants (obtained by potentiometry), the stability constants (obtained by spectrophotometry) and the enthalpy of protonation in Tables 1 and 2. The value of n̄ was calculated with the protonation and stability constants in the above mentioned tables and the total concentrations of U(VI), proton and oxalate given in Table S1 (ESI)† for each step of the titration. The number of experimental data points in Fig. 4 is reduced for clarity; experimental details for the calorimetric titrations are given in Table S1.† The good agreement between the calculated and experimental values confirms the mutual consistency of the calorimetric and spectrophotometric data on complexation, as well as the reliability of the results obtained separately for the protonation of oxalate.
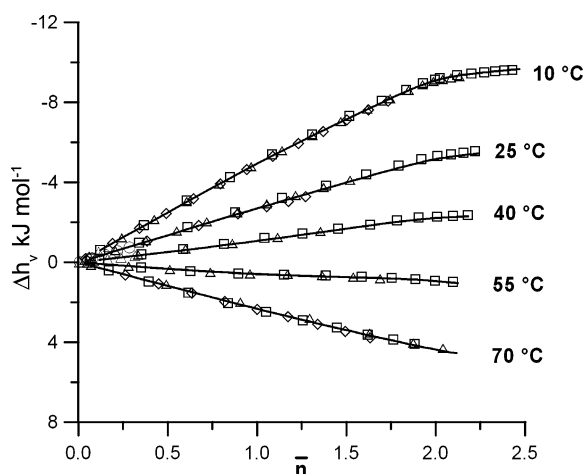

Fig. 4 The $\Delta h_{v,obs}$ *vs.* n̄, for the calorimetric titrations of U(VI) oxalate systems at the different temperatures, $I = 1.05$ mol kg^{-1} NaClO$_4$. Symbols ○, □, △, ◇: experimental data; lines: calculated with the constants and enthalpy values reported in Tables 1 and 2.

‡ $Q_{cplx,j} = Q_{ex,j} - Q_{dil,j} - Q_{p,j}$, where: $Q_{ex,j}$ = total stepwise reaction heat, $Q_{dil,j}$ = dilution heat, $Q_{p,j}$ = heat due to the protonation/deprotonation reactions of the ligand.

As shown in Fig. 4, at each temperature, values of $\Delta h_{v,obs}$ correlate very well with the values of n̄ for multiple titrations where the concentrations of U(VI), oxalate and H$^+$ are varied. This correlation suggests that, under the experimental conditions, the formation of acidic and polynuclear U(VI)/oxalate species that have been reported in the literature[5,16] can be neglected.

The effect of temperature on U(VI) complexation

Fig. 5 shows the thermodynamic parameters for U(VI)/oxalate complexation at 10–70 °C. The trends can be summarized as follows: (1) The magnitude of ΔH_j at all temperatures is quite small (less than 10 kJ mol^{-1}), and ΔG_j, $j = 1$–3, are close to $-T\Delta S_j$ at all temperatures, indicating that entropic stabilization is the main driving force for the complexation reactions at all temperatures. This is characteristic of the interaction between "type A" cations and anions. (2) As the temperature increases, the enthalpies of complexation change from being exothermic at lower
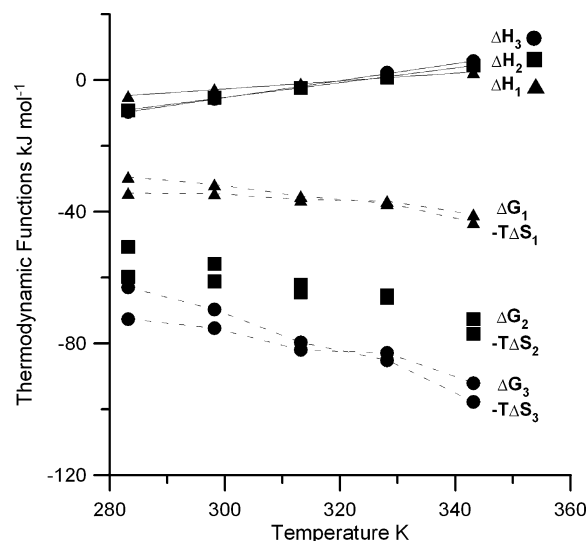

Fig. 5 Overall thermodynamic parameters for the complexation of U(VI) with oxalate in the temperature range 10–70 °C. $I = 1.05$ mol kg^{-1} NaClO$_4$.

temperatures to being slightly endothermic at higher temperatures, thus becoming more unfavourable to the complexation as the temperature is elevated. (3) The entropies of complexation are larger and more positive at higher temperatures, becoming more favourable to the complexation. It is because the entropy term ($T\Delta S_j$) increases more significantly than the enthalpy of complexation (ΔH_j) as the temperature is elevated, that the free energy of complexation of U(VI) with oxalate is more negative at higher temperatures. The increase in entropy with temperature may be the consequence of a more disordered bulk water structure at higher temperatures, due to the increase in thermal movements. During complexation, water molecules are released from the highly-ordered solvation shells of the reacting ions to an expanded and more disordered bulk solvent. As a result, the gain in complexation entropy is larger at higher temperatures.[11,17]

Fig. 5 shows that the values of ΔH_j of all three complexes increase linearly with temperature. From the best linear fit, the heat capacity of complexation (ΔC_p, J mol^{-1}K^{-1}) was calculated to be 120 ± 3, 223 ± 5, and 258 ± 6 for [UO$_2$(ox)], [UO$_2$(ox)$_2$]$^{2-}$ and [UO$_2$(ox)$_3$]$^{4-}$, respectively.

Comparison of U(VI) dicarboxylate complexes at different temperatures

Thermodynamic parameters of the 1 : 1 U(VI) complexes with three dicarboxylates at 10–70 °C are compared in Fig. 6, including oxalate, malonate[10] and oxydiacetate.[11] The effect of temperature on the enthalpy and entropy of complexation is very similar for all three dicarboxylates: the enthalpy and entropy of complexation become more positive as the temperature is increased. Because the increase in the entropy term ($T\Delta S$) exceeds that in the enthalpy (ΔH), the free energy of complexation becomes more negative at higher temperatures for all three dicarboxylates.
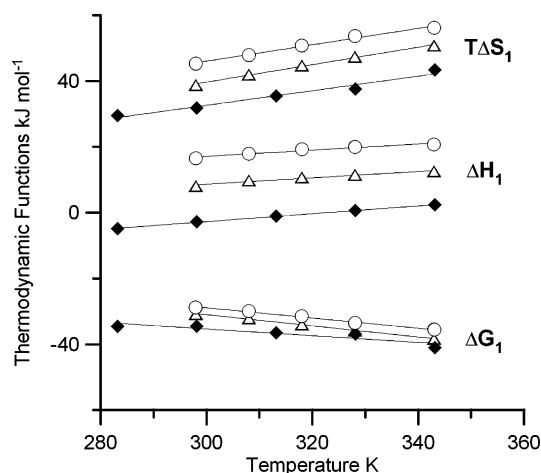

Fig. 6 Comparison of the thermodynamic data for the complexation of U(VI) by oxalate (◆), malonate (△, ref. 10) and oxydiacetate (○, ref. 11) at $I = 1.05$ mol kg^{-1} and different temperatures.

Fig. 6 also shows that the enthalpy and the entropy term for the three carboxylates differ significantly from each other, but the difference in the free energy between the three ligands is much smaller because the enthalpy and entropy terms contribute to the free energy in opposite directions and "compensate" each other. Taking the thermodynamic parameters at 25 °C as an example, the

Table 3 Thermodynamic parameters for the formation of dioxouranium(VI)-oxalate, -malonate, -oxydiacetate complexes at 25 °C and $I = 1.05$ mol kg^{-1} NaClO$_4$

	ΔG/kJ mol^{-1}	ΔH/kJ mol^{-1}	$T\Delta S$/kJ mol^{-1}
UO$_2^{2+}$ + ox^{2-} ⇌ UO$_2$ox	−34.6	−2.8	31.8
UO$_2^{2+}$ + mal^{2-} ⇌ UO$_2$mal	−30.8	8.0	38.9
UO$_2^{2+}$ + oda^{2-} ⇌ UO$_2$oda	−28.8	16.5	45.3

differences ($\Delta(\Delta H_1)_{oda-ox}$ and $\Delta(T\Delta S_1)_{oda-ox}$ are about 19 kJ mol^{-1} and 14 kJ mol^{-1}, respectively, while $\Delta(\Delta G_1)_{oda-ox}$ is only about −6 kJ mol^{-1} (Table 3). It is of interest to note that, in spite of the enthalpy/entropy "compensation", a smaller but clear trend in the free energy for the three ligands is observed at all temperatures: $\Delta G_{1,ox} < \Delta G_{1,mal} < \Delta G_{1,oda}$. In other words, the stability of the 1 : 1 complexes follows this order at all temperatures: $\log\beta_{1,ox} > \log\beta_{1,mal} > \log\beta_{1,oda}$. Seemingly, the order of the relative stabilities of the complexes with different carboxylates depends on the enthalpy: the thermodynamic function that apparently has minor contribution to the free energy (Fig. 5).

The difference in $T\Delta S$ and ΔH between different carboxylates could be rationalized by taking into consideration of the molecular complexities of the ligands and associated changes in the solvation of the metal ion, ligand as well as the complexes. From oxalate to malonate and oxydiacetate, the ligand bulkiness and molecular complexities increase (in fact, oxydiacetate is a tri-dentate ligand to UO$_2^{2+}$). We could hypothesize that, complexation of bulkier and more complex ligands with UO$_2^{2+}$ would probably require a higher degree of desolvation of the reacting ions and cause a larger structure perturbation in the bulk solvent, thus resulting in more disorder and higher energy demand. The observed trends ($T\Delta S_{1,oda} > T\Delta S_{1,mal} > T\Delta S_{1,ox}$ and $\Delta H_{1,oda} > \Delta H_{1,mal} > \Delta H_{1,ox}$) are consistent with the above hypothesis.

Calculation of protonation and complexation constants at infinite dilution and variable temperatures by SIT

The experimental stability constants in molality scale, $\log\beta_{j,m}$, were used to calculate, by eqn (1), the constants at infinite dilution, $\log\beta_j^\circ$, by applying the specific ion interaction theory (SIT), originated from the Brønsted–Guggenheim–Scatchard model.[18]

$$\log\beta_{j,m} - \Delta Z^2 D = \log\beta_j^\circ - \Delta\varepsilon_j I_m \qquad (1)$$

In eqn (1), ΔZ^2 is the difference between the sum of the squares of product and reactant ionic charges, D is the Debye–Hückel term used in the SIT method ($D = AI_m^{1/2}/(1 + 1.5AI_m^{1/2})$), and I_m is the ionic strength in molality. Parameter A in D is temperature-dependent and available in the literature.[5] The specific ion interaction term, $\Delta\varepsilon_j$, at 25 °C, for the reactions in Tables 1 and 2, was calculated from the specific interaction parameters, ε_j, suggested by the NEA review.[5] In particular, for reaction (1), $\Delta\varepsilon = \varepsilon(\text{Hox}^-, \text{Na}^+) - \varepsilon(\text{ClO}_4^-, \text{H}^+) - \varepsilon(\text{ox}^{2-}, \text{Na}^+) = -(0.13 \pm 0.04)$ kg mol^{-1}; for reaction (2), $\Delta\varepsilon = \varepsilon(\text{H}_2\text{ox}, \text{Na}^+ + \text{ClO}_4^-) - 2\varepsilon(\text{ClO}_4^-, \text{H}^+) - \varepsilon(\text{ox}^{2-}, \text{Na}^+) = -(0.20 \pm 0.04)$ kg mol^{-1}; for reaction (3), $\Delta\varepsilon = \varepsilon(\text{UO}_2\text{ox}, \text{Na}^+ + \text{ClO}_4^-) - \varepsilon(\text{ClO}_4^-, \text{UO}_2^{2+}) - \varepsilon(\text{ox}^{2-}, \text{Na}^+) = -(0.43 \pm 0.06)$ kg mol^{-1}, for reaction (4), $\Delta\varepsilon = \varepsilon(\text{UO}_2\text{ox}_2^{2-}, \text{Na}^+) - \varepsilon(\text{ClO}_4^-, \text{UO}_2^{2+}) - 2\varepsilon(\text{ox}^{2-}, \text{Na}^+) = -(0.48 \pm 0.09)$ kg mol^{-1}; and for reaction (5), $\Delta\varepsilon = \varepsilon(\text{UO}_2\text{ox}_3^{4-}, \text{Na}^+) - \varepsilon(\text{ClO}_4^-, \text{UO}_2^{2+}) - 3\varepsilon(\text{ox}^{2-}, \text{Na}^+) = -(0.23 \pm 0.11)$ kg mol^{-1}. The calculated protonation and

complexation constants at infinite dilution and at 25 °C are in very good agreement with those in the literature.[5]

For the calculation of the protonation and complexation constants at temperatures other than 25 °C the guidelines suggested by NEA review[5] have been followed. In particular, the tabulated[5] values of the Debye–Hückel term A at the different temperatures and a constant value of $\Delta\varepsilon$ (25 °C) were used. As discussed in the literature,[19] the effect of temperature on $\Delta\varepsilon$ is expected to be insignificant for many reactions. Therefore, the uncertainties introduced by using $\Delta\varepsilon$ at 25 °C for all temperatures are negligible.

Conclusions

In the temperature range 10–70 °C three successive mononuclear uranium(VI) oxalate complexes have been identified by spectrophotometry and calorimetry in aqueous solutions where $C_{ox}/C_U < 6$ and p[H$^+$] < 3.5. Oxalate forms with U(VI) very strong complexes that are mainly stabilized by the large entropies of complexation. In contrast, the enthalpies of complexation are small and become more positive as the temperature is increased, changing from being slightly exothermic at lower temperatures (10–40 °C) to being slightly endothermic at higher temperatures (> 40 °C). The complexes become stronger at higher temperatures, due to the increasingly more positive entropies of complexation, which exceed the increase in the unfavourable enthalpy of complexation.

A comparison of the thermodynamic functions for the formation of the ML complexes of oxalate, malonate and oxydiacetate with U(VI) shows that the oxalate complex is the strongest, notwithstanding its less favourable formation entropy, because of the most favorable formation enthalpy. Thus, though entropy is the driving force for the complexation of U(VI) with dicarboxylates, the relative stability of the U(VI) complexes of oxalate, malonate and oxydiacetate depends on the enthalpy: the thermodynamic function with minor weight in these systems.

Experimental

Chemicals

Disodium oxalate [Aldrich, 99.5+%] was used as received. Oxalic acid dihydrate [Aldrich, reagent grade] was recrystallized twice following ref. 20. Stock solutions of disodium oxalate and of oxalic acid were prepared by weight. The stock solutions of U(VI) were prepared in two different ways. At LBNL, a weighed amount of uranium trioxide was dissolved in water with about 1.4 excess of perchloric acid with respect to the stoichiometric quantity. At UP, a known amount of $UO_2(ClO_4)_2 \cdot xH_2O$ (Johnson Matthey) was dissolved in water containing an equimolar quantity of perchloric acid. The acidity of the stock solutions was determined by the Gran's potentiometric method[21] while the content of U(VI) was obtained by gravimetric determination after ignition to U_3O_8 at UP or by absorption spectrophotometry and fluorimetry at LBNL,[22] respectively. Deionized water, passed through a Millipore Milli-Q Academic filtration apparatus, was used in preparations of all solutions. Perchloric acid stock solutions were obtained by dilution of a concentrated solution [Aldrich, re-distilled 70%] and standardized with the usual analytical methods. Aldrich standard sodium hydroxide solutions, free from carbonate, were used as supplied. Sodium perchlorate [Aldrich 99%] was purified

by repeated (usually twice or three times) re-crystallizations from water.

The ionic strength of all the working solutions was adjusted to 1.00 mol dm^{-3} at 25 °C, equivalent to 1.05 mol kg^{-1}, by adding appropriate amounts of sodium perchlorate.

Potentiometry

The protonation constants of oxalate (ox) were determined by potentiometric titrations in the temperature range 10–70 °C. A specially designed titration vessel was used to avoid the problem of water-vapour condensation during the titrations at temperatures above the ambient. Detailed description of the potentiometric setup is given in ref. 23. The electromotive force (emf) was measured with an Amel Model 338 pH-meter equipped with an Unitrode Metrohm combination pH electrode (Model 6.0259.100). The original 3.0 M KCl electrode salt bridge solution was replaced with a 1.0 M sodium chloride solution to avoid formation of insoluble KClO$_4$ in the electrode joint sleeve that is in contact with the working solution. The experimental data were collected by means of a home-made PC-controlled automatic data acquisition system.

Prior to each potentiometric titration, the electrode was standardized in order to measure the hydrogen ion concentration. Eqn (2) was employed at any temperature to obtain $E°$ and the electrode junction potential for the hydrogen ion, $E_{j,H}$. These two parameters allowed determination of the hydrogen ion concentrations in the subsequent titration. Correction for the junction potential of hydroxide was not necessary because all measurements were carried out in the acidic region. Detailed conditions of the titrations are provided in Table S1 of ESI.†

$$E = E° + RT/F\ln[H^+] + E_{j,H}[H^+] \qquad (2)$$

Three titrations of solutions containing different oxalate concentration (C_{ox}) were conducted at each temperature. 40–60 points were collected for each titration. The overall protonation constants in molarity scale ($\log\beta_{1,M}^H$, $j = 1,2$) were calculated with the program Hyperquad.[24]

Spectrophotometry

Different conditions were used in the spectrophotometric titrations at LBNL and UP. At LBNL, 2.5 cm^3 of a solution containing the metal ion and an excess of perchloric acid were loaded into a quartz cell (1.0 cm path length, ~3.5 cm^3 in volume) and titrated with a solution of oxalate (~100 mmol dm^{-3}). After each titrant addition, the quartz cell was introduced in the measuring compartment of a Varian Cary-5G spectrophotometer equipped with a Peltier automatic temperature controller and let to reach thermal equilibrium before spectrum acquisition. At UP, the spectra were collected on a Cary 50 spectrophotometer equipped with a thin optic fiber probe (0.5 cm external diameter and 1 cm path length). The probe was dipped in the cup solution that was maintained at the selected temperature by an external thermostat. Three titrations were carried out at each temperature with an initial cup solution of a constant U(VI) concentration (12 mmol dm^{-3}) and three increasing proton concentrations: 20, 120 and 220 mmol dm^{-3}, respectively. During the titration, known volumes of a buffer solution (Hox$^-$/ox^{2-} = 30/60;

UO_2^{2+} = 12 mmol dm^{-3}) were added to the cup solution, until the C_{ox}/C_U ratio was ~6. To avoid photo-oxidation, the U/ox solution employed as titrant was kept in the dark by wrapping its container in aluminum foils and similarly the titration vessel was protected from the sun light. Use of high and varying proton concentrations in the cup allowed us to accurately determine the stability constants of very strong U(VI)/oxalate complexes by exploiting the competition between the protonation and complexation reactions. Detailed information on the titration conditions and the speciation changes during the titration are provided in ESI (Table S2, Fig. S1a–S1c).†

The stability constants of the U(VI) oxalate complexes were calculated, from the spectrophotometric data in the range 380–480 nm, with the Hyperquad 2000 program.[24] Because there is good correspondence between the results of the minimization processes applied singularly to the data obtained in the two laboratories, all spectrophotometric data were treated as an *unicum*. Protonated U(VI)/oxalate complexes, such as $UO_2(Hox)^+$ described in the literature,[5] were included in the minimization calculation using Hyperquad 2000 at all temperatures. However, such species were always rejected by the program, suggesting that they are insignificant under the experimental conditions.

To allow the comparison of stability constants at different temperatures, the constants in molarity were converted into the constants in molality according to eqn (3)[5]

$$\log_{10}\beta_{j,m} = \log_{10}\beta_{j,M} + \sum_r \nu_r \log_{10}\vartheta \qquad (3)$$

where $\beta_{j,m}$ and $\beta_{j,M}$ are the equilibrium constants of a reaction in molality and molarity, respectively, $\sum_r \nu_r$ is the sum of stoichiometric coefficients of the reaction (ν_r is positive for products and negative for reactants), ϑ is the ratio of the values of molality to molarity for the specific ionic medium. For 1.00 mol dm^{-3} NaClO$_4$ used in this study, ϑ equals 1.05 dm^3 of solution per kg of water. Therefore, the correction of logβ from molarity to molality follows eqn (4), where $j = 1$–2 for oxalate protonation and $j = 1$–3 for U(VI) oxalate complexation:

$$\log_{10}\beta_{j,m} = \log_{10}\beta_{j,M} - 0.02\,j \qquad (4)$$

Calorimetry

Calorimetric titrations were carried out at 10, 25, 40, 55 and 70 °C to determine the enthalpies of oxalate protonation and complexation with U(VI), using the isothermal microcalorimeters at both UP (Thermometric 2277 Thermal Activity Monitor, nanoWatt model) and LBNL (ITC 4200, Calorimetry Sciences Corp.).

The microcalorimeter at LBNL can operate at high temperatures (up to 70 °C) but is not suitable for titrations below the room temperature due to the lack of a dry nitrogen purging system that is necessary to prevent condensation inside the calorimeter. As a result, the titrations above 40 °C were exclusively conducted with the microcalorimeter at LBNL, whereas the titrations at 10 °C were exclusively conducted at UP. The titrations at 25 °C and 40 °C were conducted at both laboratories so that the results were compared in order to check the mutual reliability.

At least three titrations with different C_M and C_H (1 < C_M < 25 mmol dm^{-3}; 1 < C_H < 10 mmol dm^{-3}) were carried out for each U(VI)-oxalate system at each temperature. The calorimetric

titrations were designed so that the highest p[H$^+$] reached in the titration vessel was below 3.5 in order to avoid the hydrolysis of U(VI) and the formation of mixed U(VI)/oxalate/hydroxide complexes and favour the formation of binary species.

Details concerning the treatment of the experimental data from calorimetric measurements are provided in ref. 12. The enthalpies of protonation of oxalate and complexation of U(VI) were calculated by a computer program, which basically uses the Letagrop approach,[25] with some changes in the original routines, to minimize the error squares sum of the error-carrying variable.

The agreement between the enthalpy changes obtained by fitting the individual sets of data at 25 and 40 °C from the two laboratories was very good (see ESI).† Therefore, the enthalpies at 25 °C and 40 °C were obtained by processing all the experimental data together, while the enthalpies at 10 °C and those at 55 and 70 °C were obtained from the data from UP and LBNL, respectively (Table 2). The standard deviations for the reaction enthalpies at the defined temperatures reflect the data reliability.

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