

Supplementary Information

Formation of $\text{CaUO}_2(\text{CO}_3)_3^{2-}$ and $\text{Ca}_2\text{UO}_2(\text{CO}_3)_3(\text{aq.})$ Complexes at Variable Temperatures (10 – 70 °C)

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Table S1. The stoichiometric number of calcium in complexation with $\text{UO}_2(\text{CO}_3)_3^{4-}$ obtained from the TRLFS slope analysis in triplicate.

Temperature (°C)	Slope	
	x_1	x_2
10	0.92 ± 0.09	2.39 ± 0.21
25	0.83 ± 0.04	2.06 ± 0.15
40	0.94 ± 0.08	2.23 ± 0.10
55	0.84 ± 0.15	2.10 ± 0.19
70	-	2.27 ± 0.16

Table S2. Ion interaction parameter ϵ (j,k) (j: ion, k: medium) for SIT correction.

Ion	Background electrolyte medium			Ref.
	Na ⁺	Cl ⁻	ClO ₄ ⁻	
Ca ²⁺	-	0.14 ± 0.01	0.27 ± 0.03	NEA-TDB ¹
UO ₂ (CO ₃) ₃ ⁴⁻	-0.01 ± 0.11	-	-	NEA-TDB ¹
CaUO ₂ (CO ₃) ₃ ²⁻	-0.1 ± 0.1	-	-	PSI/Nagra TDB ²
Ca ₂ UO ₂ (CO ₃) ₃ (aq)	-0.06 ± 0.0	-	-	NEA-TDB ¹ , This work

Note that no change in ion interaction parameter in the temperature range of interest (10 – 70 °C) in this work was assumed as discussed in database¹.

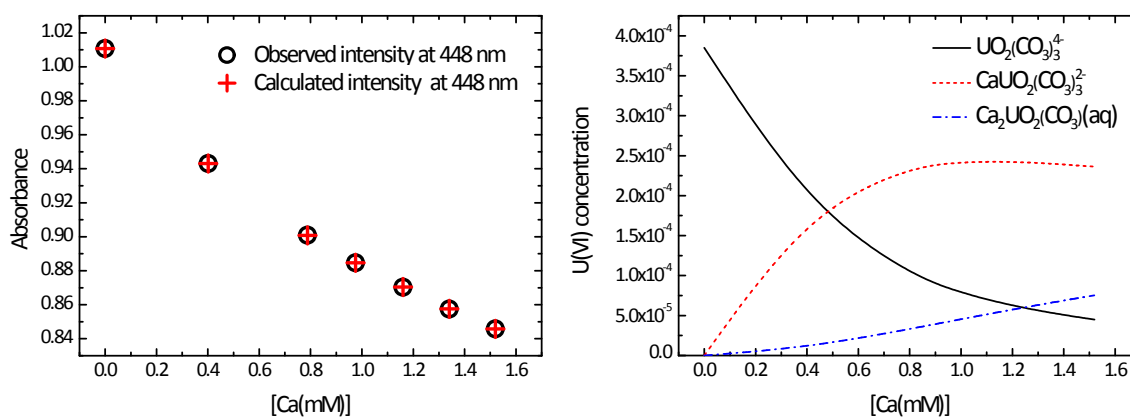
Table S3. Debye-Hückel constant A and Debye-Hückel term for SIT at 10, 25, 40, 55, and 70 °C.

Temperature (°C)	A (kg·mol ⁻¹) ^{1/2}	D	Ref.
10	0.498	0.107	NEA-TDB ¹
25	0.509	0.109	NEA-TDB ¹
40	0.525	0.113	NEA-TDB ¹
55	0.540	0.116	Obtained from interpolation of data ¹
70	0.558	0.120	Obtained from interpolation of data ¹

Note that $Ba_j = 1.5 \text{ kg}^{1/2}\cdot\text{mol}^{-1/2}$ was assumed to be identical in the temperature range of interest (10 – 70 °C) in this work as discussed in database¹.

Table S4. Thermodynamic data of relevant reactions used in TRFS and calorimetry analysis.

Reactions	log K°	$\Delta_r H_m^\circ$ (kJ/mol)	Ref.
$\text{H}_2\text{O}(\text{l}) \rightleftharpoons \text{H}^+ + \text{OH}^-$	-13.997	55.81	NIST 46.7
$\text{H}^+ + \text{CO}_3^{2-} \rightleftharpoons \text{HCO}_3^-$	10.33	-14.7	[PAT/MES84] ³
$2\text{H}^+ + \text{CO}_3^{2-} \rightleftharpoons \text{CO}_2(\text{aq}) + \text{H}_2\text{O}(\text{l})$	16.68	-23.8	[PAT/MES84] ³ [PAT/MES82] ⁴
$\text{Ca}^{2+} + \text{CO}_3^{2-} \rightleftharpoons \text{CaCO}_3(\text{aq})$	3.22	15	[PLU/BUS82] ⁵ , SUPCRT ⁶ ,
$\text{Ca}^{2+} + \text{H}^+ + \text{CO}_3^{2-} \rightleftharpoons \text{CaHCO}_3^+$	1.11	-3.66	[PLU/BUS82] ⁵ , SUPCRT ⁶ ,
$\text{Ca}^{2+} + \text{OH}^- \rightleftharpoons \text{CaOH}^+$	-12.70	Not used	NIST 46.7
$\text{UO}_2^{2+} + 2\text{CO}_3^{2-} \rightleftharpoons \text{UO}_2(\text{CO}_3)_2^{2-}$	16.61	18.5	NEA-TDB ¹
$\text{UO}_2^{2+} + 3\text{CO}_3^{2-} \rightleftharpoons \text{UO}_2(\text{CO}_3)_3^{4-}$	21.84	-39.2	NEA-TDB ¹

**Figure S1.** Representative UV/Vis spectrophotometry obtained from experiment with LWCC. Comparison of observed and calculated intensities at 448 nm (left) and U(VI) speciation during titration (right).

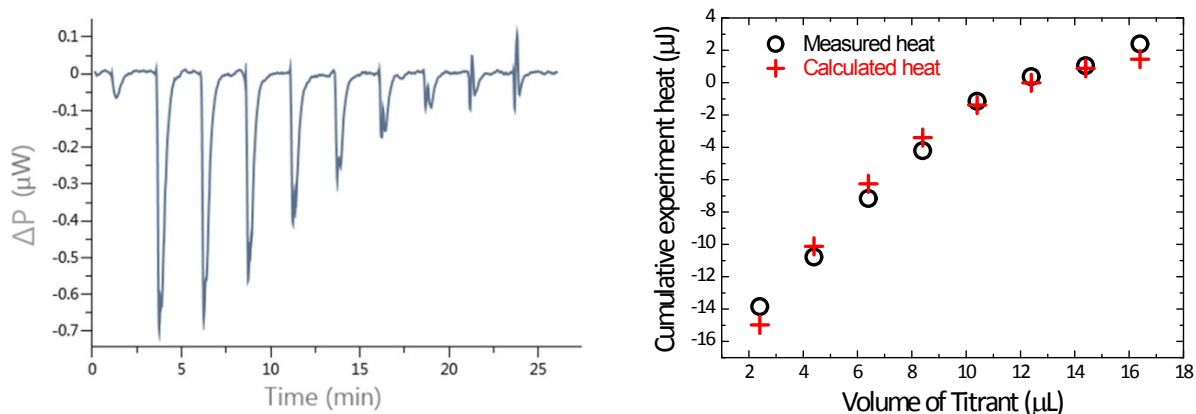


Figure S2. Representative calorimetric titration at 25 °C (PEAQ-ITC). Thermogram of a calorimetric titration (left) and measured and calculated cumulative heats (right).

Table S5. Comparison of reaction enthalpies measured by TAM-III (TA instrument) and PEAQ-ITC (Malvern)

Reactions	$\Delta_r H^\circ_m$ (kJ/mol)	
	TAM-III	PEAQ-ITC
$\text{Ca}^{2+} + \text{UO}_2(\text{CO}_3)_3^{4-} \rightleftharpoons \text{CaUO}_2(\text{CO}_3)_3^{2-}$	-1.2 ± 0.3	-1.2 ± 0.3
$\text{Ca}^{2+} + \text{CaUO}_2(\text{CO}_3)_3^{2-} \rightleftharpoons \text{Ca}_2\text{UO}_2(\text{CO}_3)_3(\text{aq})$	-3.5 ± 1.4	-0.2 ± 1.3

Calculation of reaction enthalpy

In this work, reaction enthalpy was calculated by the error minimization between the measured heat and the calculated heat. The method of least square was used for the error minimization. The measured heat in i th addition ($Q_{\text{ex},i}$) from the main titration was corrected by the dilution heat in i th addition ($Q_{\text{dil},i}$) from a separated titration run to obtain the net heat from reactions of interest ($Q_{\text{net},i} = Q_{\text{ex},i} - Q_{\text{dil},i}$). The calculated heat in i th addition ($Q_{\text{cal},i}$) was obtained by the formation constants corrected by SIT and enthalpies of relevant chemical reaction (Table S5) as shown in eq S1:

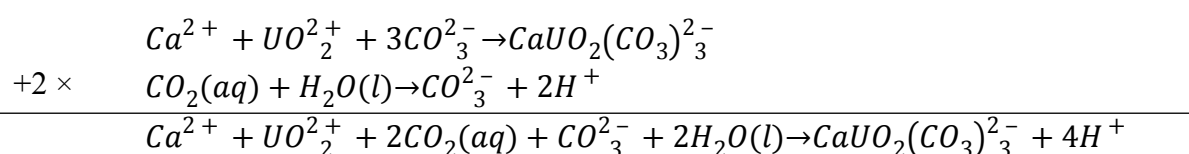
$$Q_i(\text{cal.})$$

$$= \Delta H_{013}(v_i^{013} - v_{i-1}^{013}) + \Delta H_{113}(v_i^{113} - v_{i-1}^{113}) + \Delta H_{213}(v_i^{213} - v_{i-1}^{213})$$

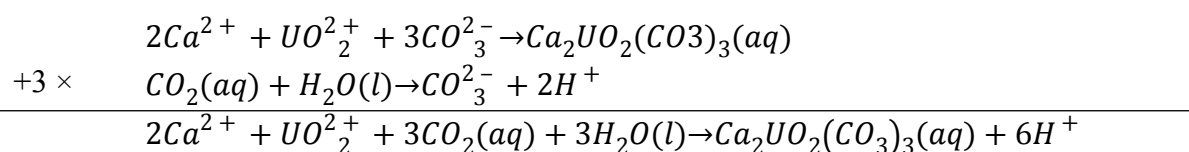
(S1)

Modification to isoelectric reaction

For the constant reaction enthalpy approximation, the original reactions of (i) and (ii) were modified to the isoelectric reactions, in which the total amount of positive charges among the reactants is equal to that among the products and the same condition is applied to the negative charge. In case of the isoelectric reaction, the electrostatic contribution to the temperature can be canceled out and the change in heat capacity of reaction can be assumed to be negligible¹. For the modification, the subtraction or/and addition of relevant reaction equations are required as follows:



Likewise,



Thermodynamic data for the modification are presented in Table S6.

Table S6. Thermodynamic data of relevant reactions used in the modification to isoelectric reaction.

Reactions	log K°	$\Delta_r H_m^\circ$ (kJ/mol)	Ref.
$H^+ + CO_3^{2-} \rightleftharpoons HCO_3^-$	10.33	-14.7	[PAT/MES84] ³
$2H^+ + CO_3^{2-} \rightleftharpoons CO_2(aq) + H_2O(l)$	16.68	-23.8	[PAT/MES84] ³ [PAT/MES82] ⁴
$UO_2^{2+} + 3CO_3^{2-} \rightleftharpoons UO_2(CO_3)_3^{4-}$	21.84	-39.2	NEA-TDB ¹
$Ca^{2+} + UO_2(CO_3)_3^{4-} \rightleftharpoons CaUO_2(CO_3)_3^{2-}$	5.18	-1.2	This work
$Ca^{2+} + CaUO_2(CO_3)_3^{2-} \rightleftharpoons Ca_2UO_2(CO_3)_3(aq)$	3.52	-0.5	This work

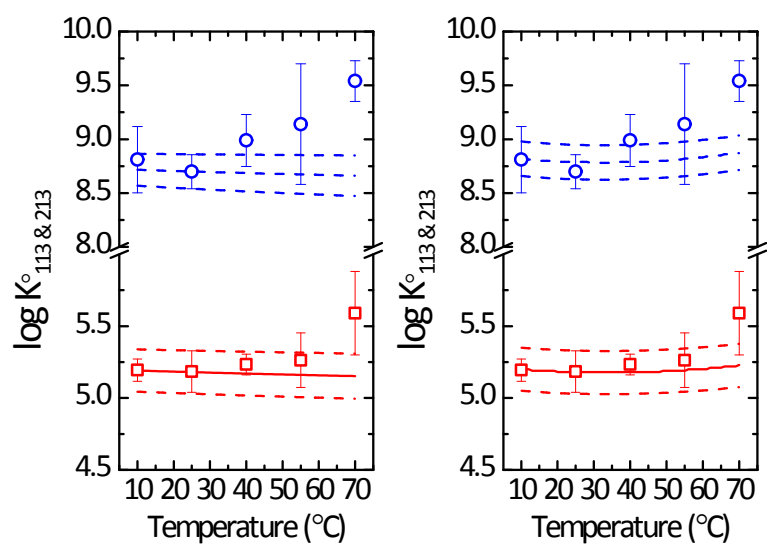


Figure S3. Van't Hoff equation (left) and DQUANT⁷ (right) approximations.

Uranium(VI) speciation at 70 °C

The U(VI) speciation was carried out using PHREEQC⁸. The formation constants ($\log K^\circ$) and the molar reaction enthalpies ($\Delta_r H^\circ_m$) for U(VI) hydrolysis and $\text{UO}_2(\text{CO}_3)_x^{2-2x}$ ($x = 1, 2$, and 3) at 25 °C were obtained from NEATDB¹. $\log K^\circ$ and $\Delta_r H^\circ_m$ of $\text{CaUO}_2(\text{CO}_3)_3^{2-}$ and $\text{Ca}_2\text{UO}_2(\text{CO}_3)_3(\text{aq})$ at 25 °C determined in this work were used. $\log K^\circ$ and $\Delta_r H^\circ_m$ of other relevant reactions were obtained at 25 °C from the database 'sit.dat' of PHREEQC⁸.

Hydrolysis constants were corrected to the values at 70 °C based on the van't Hoff equation. Approximation of the van't Hoff equation for U(VI) hydrolysis showed an excellent agreement in previous work⁹. $\log K^\circ$ of $\text{UO}_2(\text{CO}_3)_x^{2-2x}$ ($x = 1, 2$ and 3) and $\text{Ca}_y\text{UO}_2(\text{CO}_3)_3^{2-2y}$ ($y = 1$ and 2) were corrected to the values at 70 °C based on the constant reaction enthalpy approximation via the modification to isoelectric reactions (as described above) and introduced to database in expressions as follows:

$$\log K(T) = \frac{p_1}{T} + p_2 \cdot \log(T) + p_3 \cdot T + \frac{p_4}{T^2} + p_5$$

Table S7. Expressions for $\log K^\circ(T)$ based on the constant enthalpy approximation

	$\text{Ca}^{2+} + \text{UO}_2(\text{CO}_3)_3^{4-} \rightleftharpoons \text{CaUO}_2(\text{CO}_3)_3^{2-}$	$2\text{Ca}^{2+} + \text{UO}_2(\text{CO}_3)_3^{4-} \rightleftharpoons \text{Ca}_2\text{UO}_2(\text{CO}_3)_3(\text{aq})$
p_1	- 27723	- 55483
p_2	- 157.79	- 315.59
p_3	0.08394	0.16788
p_4	2.2087×10^6	4.4174×10^6
p_5	4.3874×10^2	8.7593×10^2

$\log K^\circ$ of other relevant reactions were corrected to the values at 70 °C based on the van't Hoff equation.

References

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