Electronic Supplementary Material (ESI) for Dalton Transactions

Supporting Information to "A Calorimetric Study of the Hydrolysis and Peroxide Complex Formation of the Uranyl(VI) ion."

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Table S1. Titrations carried out to determine the enthaply of formation of water (T1) and HO_2^- (T2 – T6). All concentrations are total concentrations in mM.

Initial concentrations in titration vessel				Concentrations of the titrant	
#	V° mL	$C°_{OH-}$	C_{Na}	$C_{H+,T}$	$C°_{H2O2,T}$
T1	2.208	6.94	0.0	10.07	
T2	2.217	8.75	0.0	0.0	51.75
T3	2.209	17.64	0.0	0.0	51.75
T4	2.190	35.11	0.0	0.0	51.75
T5	2.207	10.08	50.30	0.0	51.75
T6	2.203	35.00	50.43	0.0	51.75

Table S2. Titrations carried out to determine the enthaply of formation of Uranyl(VI) hydroxide complexes in acid (T7 – T10) and in basic (T11 – T18) solution. All concentrations are total concentrations in mM.

	Initial concentrations in titration vessel			Concentrations of the titrant	
#	V° mL	$C°_{H+}$	$C°_{UO2}$	$C_{OH-,T}$	$C_{UO2,T}$
T7	2.501	3.87	10.01	96.74	
T8	2.501	4.99	5.01	74.78	
T9	2.477	0.98	0.99	19.97	
T10	2.486	0.50	0.51	14.90	
#	V° mL	$C°_{OH-}$	$C°_{UO2}$	$C_{H+,T}$	$C_{UO2,T}$
T11	2.197	60.08		10.03	20.05
T12	2.211	59.75		10.04	10.05
T13	2.210	29.96		10.03	20.05
T14	2.199	15.05		10.04	10.05
T15	2.223	14.84		10.03	20.05
T16	2.205	9.99		10.04	10.05
T17	2.208	7.99		10.04	10.05
T18	2.200	6.92		10.04	10.05

Table S3. Titrations carried out to measure the enthalpy changes of the Uranyl(VI)-hydroxide-peroxide complexes in basic solution.

	Initial concentrations in titration vessel			Concentrations of the titrant		
#	V° mL	$C°_{OH^-}$ mM	$C°_{H2O2}$ mM	$C_{H^+,T}$ mM	$C_{UO2,T}$ mM	Tot. V_{add} mL
T19	2.192	9.69	15.06	10.04	10.05	0.30
T20	2.199	24.93	15.02	10.04	10.05	0.30
T21	2.200	6.97	15.00	10.04	10.05	0.42
T22	2.206	5.99	15.0	2.12	9.97	0.36
T23	2.201	5.03	15.00	2.12	9.97	0.32

Table S4. Uranyl(VI) hydroxide complexes in basic solution. Results of the different minimization steps.

Ist minimization step: calorimetric data, titrations T11 – T18

		$\Delta H_{p,q}$
$\log\beta_{3,-7}$ (fixed)	-28.95	205.1 ± 2.2 (refined)
$\log\beta_{3,-8}$ (fixed)	-38.91	227.2 ± 2.3 (refined)
$\log\beta_{1,-3}$ (fixed)	-18.75	104.5 ± 0.9 (refined)
σ = 0.38383 mJ		

2nd minimization step: calorimetric data, titrations T11 – T18

		$\Delta H_{p,q}$
$\log\beta_{3,-7}$ (fixed)	-28.95	201.3 ± 1.3 (refined)
$\log\beta_{3,-8}$ (fixed)	-38.91	230.3 ± 1.6 (refined)
$\log\beta_{1,-3}$ (fixed)	-18.75	95.6 ± 2.1 (refined)
$\log\beta_{1,-4}$ (refined)	-31.10±0.10	170.0 ± 2.1 (refined)
σ = 0.2139 mJ		

IIIrd minimization step: re-analysis of the data of the potentiometric titrations of Ref. 3 with the Hyperquad minimization program (give Reference).

$\log\beta_{0,-1}$ (fixed)	-13.81
$\log\beta_{1,-1}$ (fixed)	-5.19
$\log\beta_{2,-2}$ (fixed)	-5.94
$\log\beta_{3,-4}$ (fixed)	-12.25
$\log\beta_{3,-5}$ (fixed)	-16.43
$\log\beta_{3,-6}$ (refined)	-22.69 ± 0.12
$\log\beta_{3,-7}$ (refined)	-28.97 ± 0.07
$\log\beta_{3,-8}$ (refined)	-38.84 ± 0.18
$\log\beta_{1,-3}$ (refined)	-18.81 ± 0.15
$\log\beta_{1,-4}$ (refined)	-31.25 ± 0.66
σ = 1.798 mV	

IVth final minimization step: calorimetric data (titrations T11 – T18) and stability constants from the IIIrd step

		$\Delta H_{p,q}$
$\log\beta_{3,-7}$ (fixed)	-28.97	200.8 ± 1.4
$\log\beta_{3,-8}$ (fixed)	-38.84	231.1 ± 1.7
$\log\beta_{1,-3}$ (fixed)	-18.81	94.0 ± 1.1
$\log\beta_{1,-4}$ (refined)	-31.25	167.3 ± 1.1
σ = 0.2237 mJ		

Table S5. Comparison of the equilibrium constants from present work and those from Ref. 10.

Complex	Data from p.w.	Data from Ref. 10
$(UO_2)_2(OH)_2^{2+}$	-5.94 ± 0.03	-5.77 ± 0.01
$(UO_2)_3(OH)_5^{+}$	-16.42 ± 0.02	-16.10 ± 0.01
$(UO_2)_3(OH)_7^{-}$	-28.97 ± 0.07	-28.80 ± 0.04
$(UO_2)_3(OH)_8^{2-}$	-38.84 ± 0.14	-37.64 ± 0.07

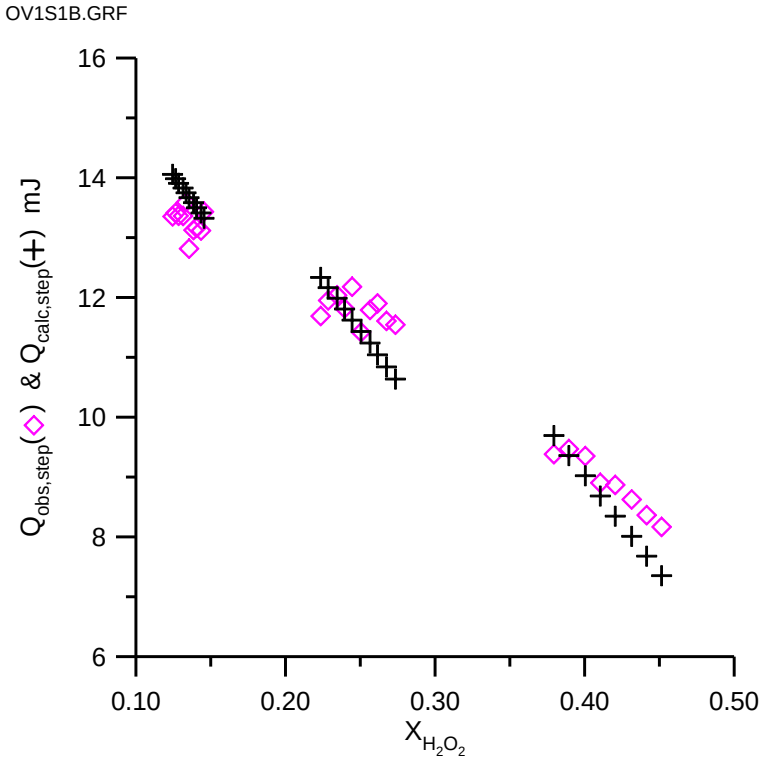

Figure S1A. The observed and calculated heat changes for the deprotonation of hydrogen peroxide. X_{H2O2} is the ratio between the residual and total concentration of hydrogen peroxide in solution. For clarity, only one half of the experimental data are plotted in the Figure.

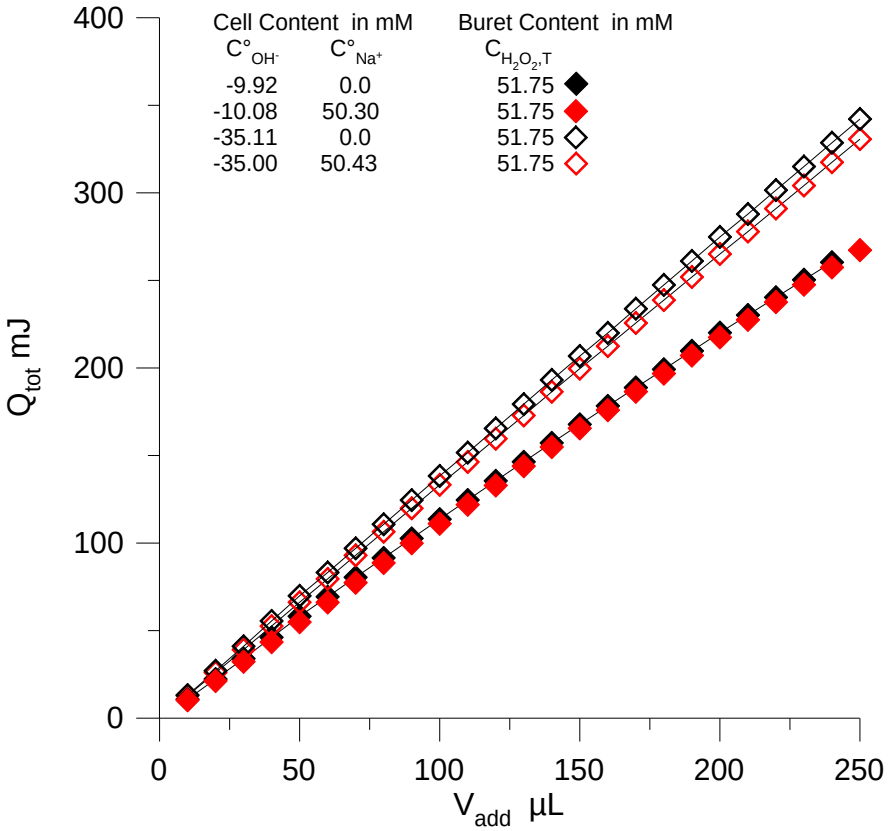

Figure S1B. Titrations carried out by adding the same hydrogen peroxide solution ($C_{H2O2,T}$ = 51.75 mM, 0.100 M $TMANO_3$) to solutions containing the same concentration of TMAOH in 0.100 M $TMANO_3$ and in the mixed $TMANO_3/NaNO_3$ ionic medium.

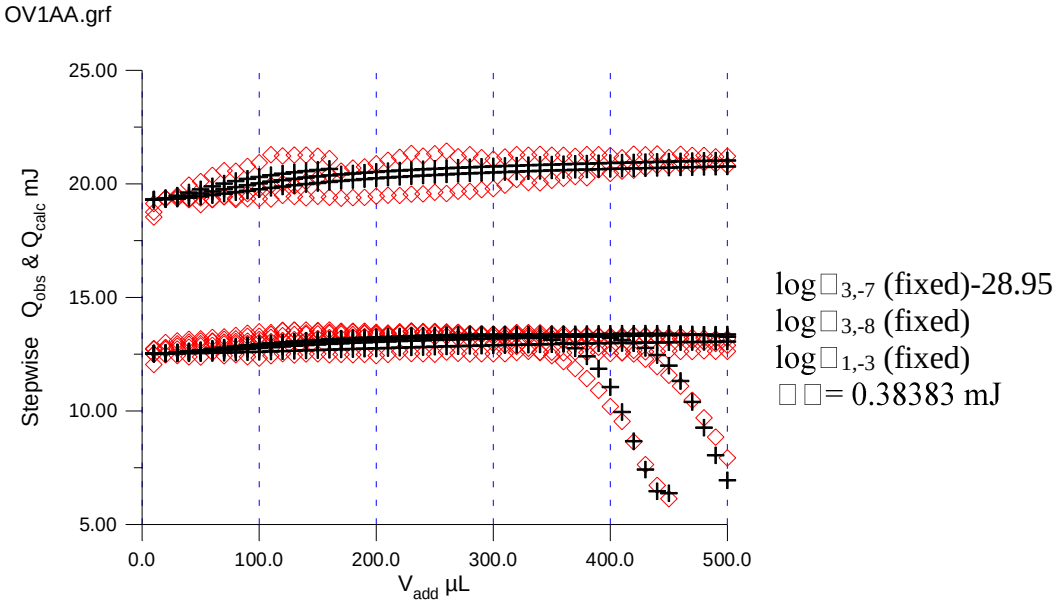

Figure S2. The data fitting (titrations T11 – T18) with the model which comprises only the formation of (3,-7), (3,-8) and (1,-3) complexes. Q_{obs} (◊); Q_{calc} (+). Log□'s fixed at the values given in ref.3 (Table 1).

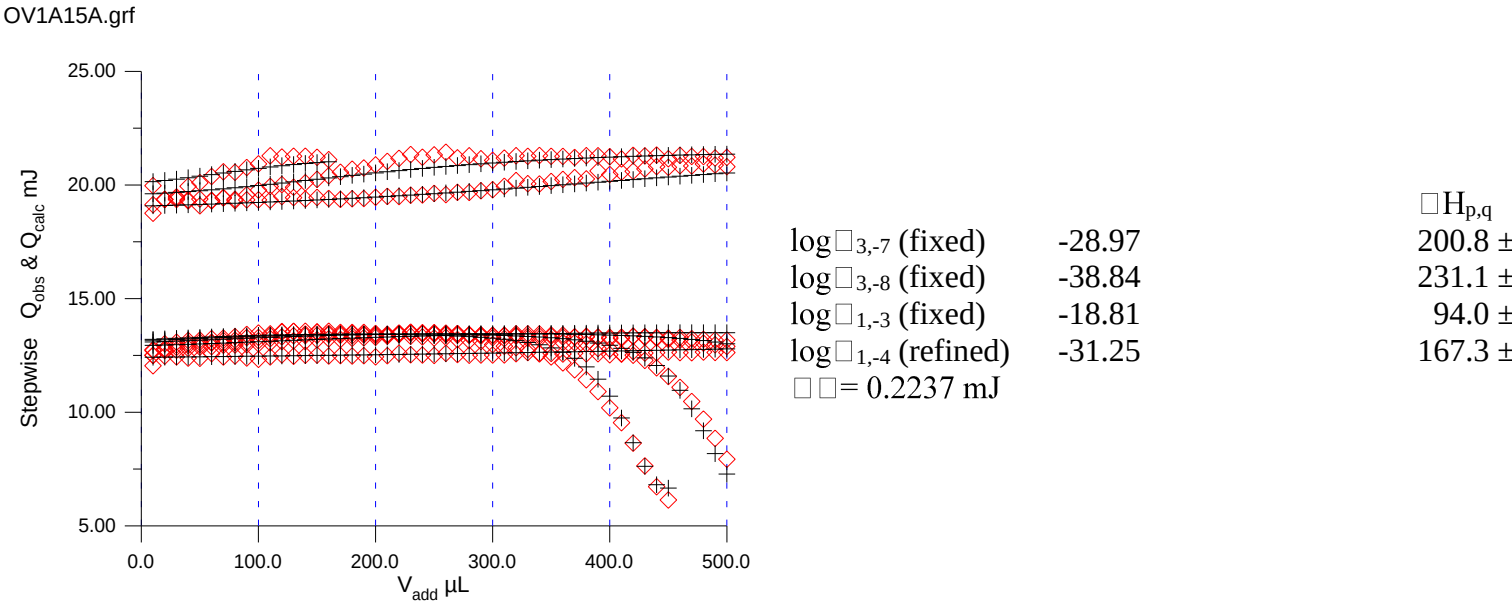

Figure S3. The data fitting with the final model comprising formation of (3,-7), (3,-8), (1,-3), and (1,-4) complexes. . Q_{obs} (◊); Q_{calc} (+).

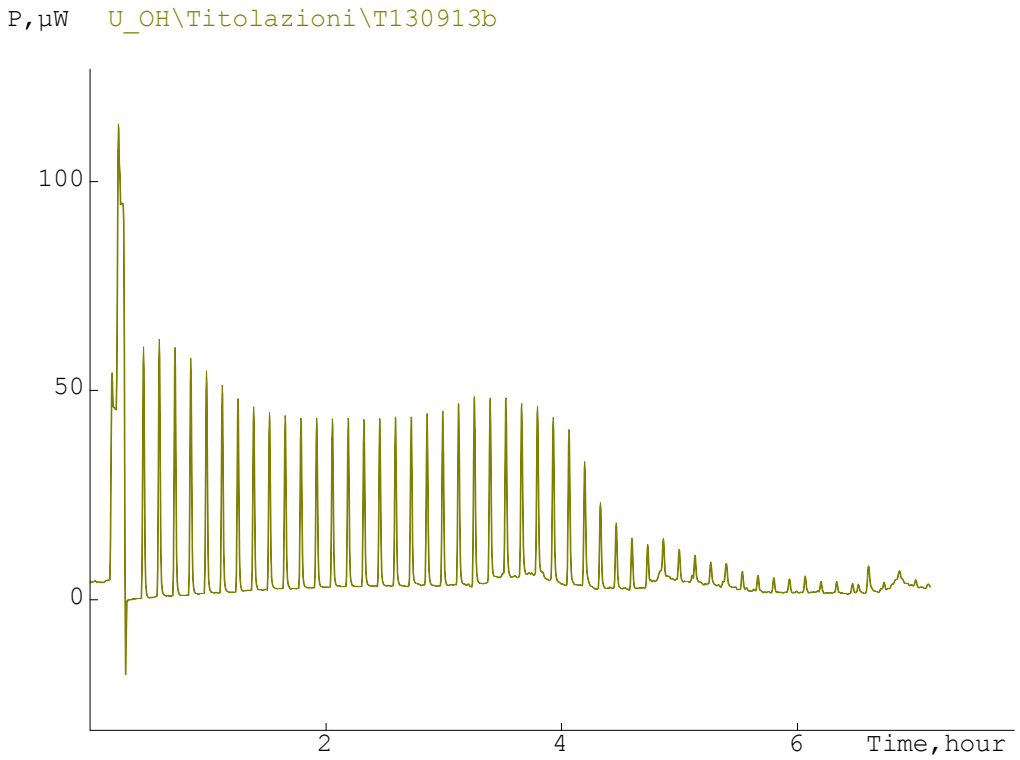

Figure S4. The enthalpigram of the titration T10 in Table S2. The irregular trend of the calorimeter baseline after additions 22 and 32 reflects formation and dissolution of a solid phase, respectively.

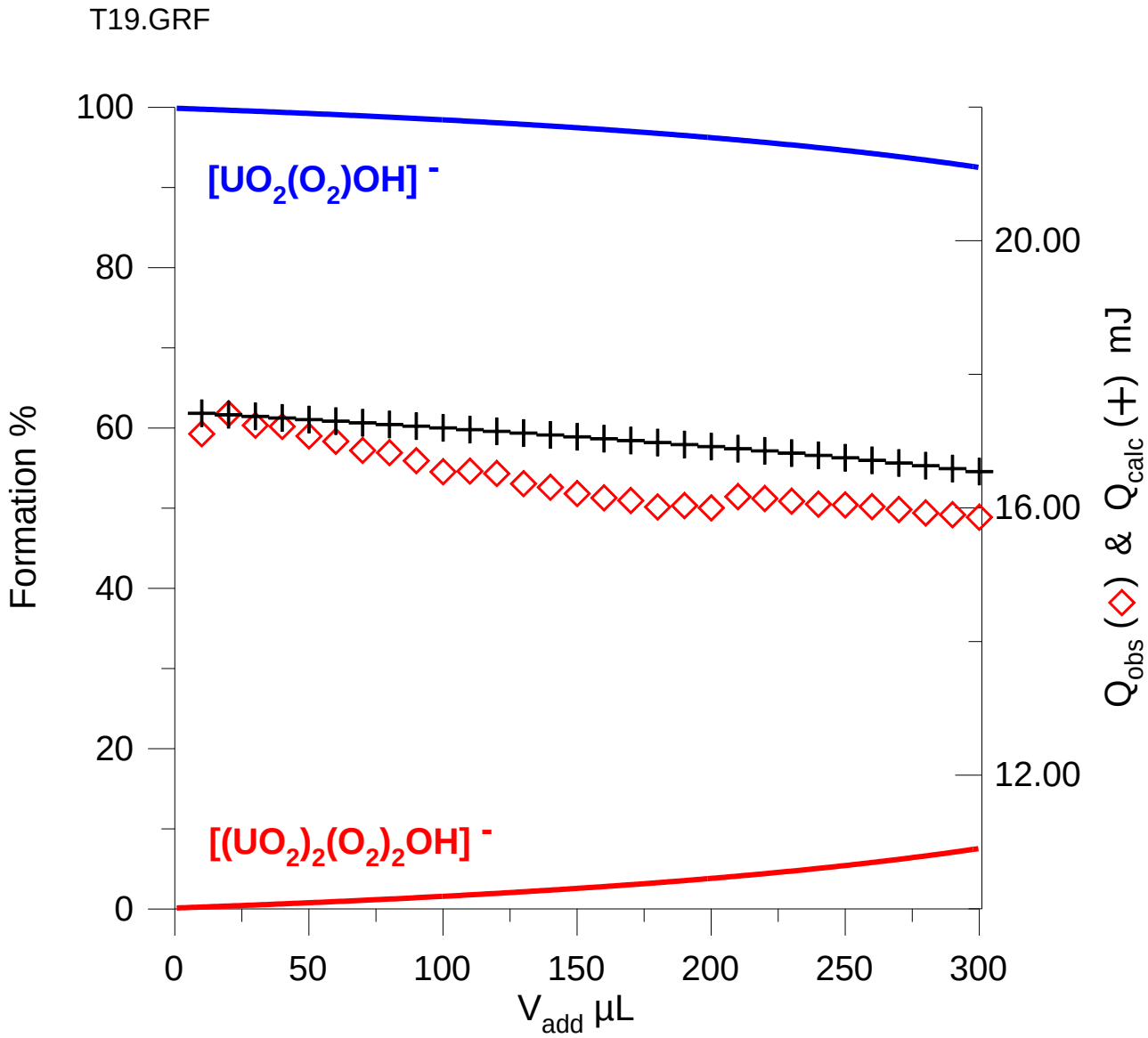

Figure S5

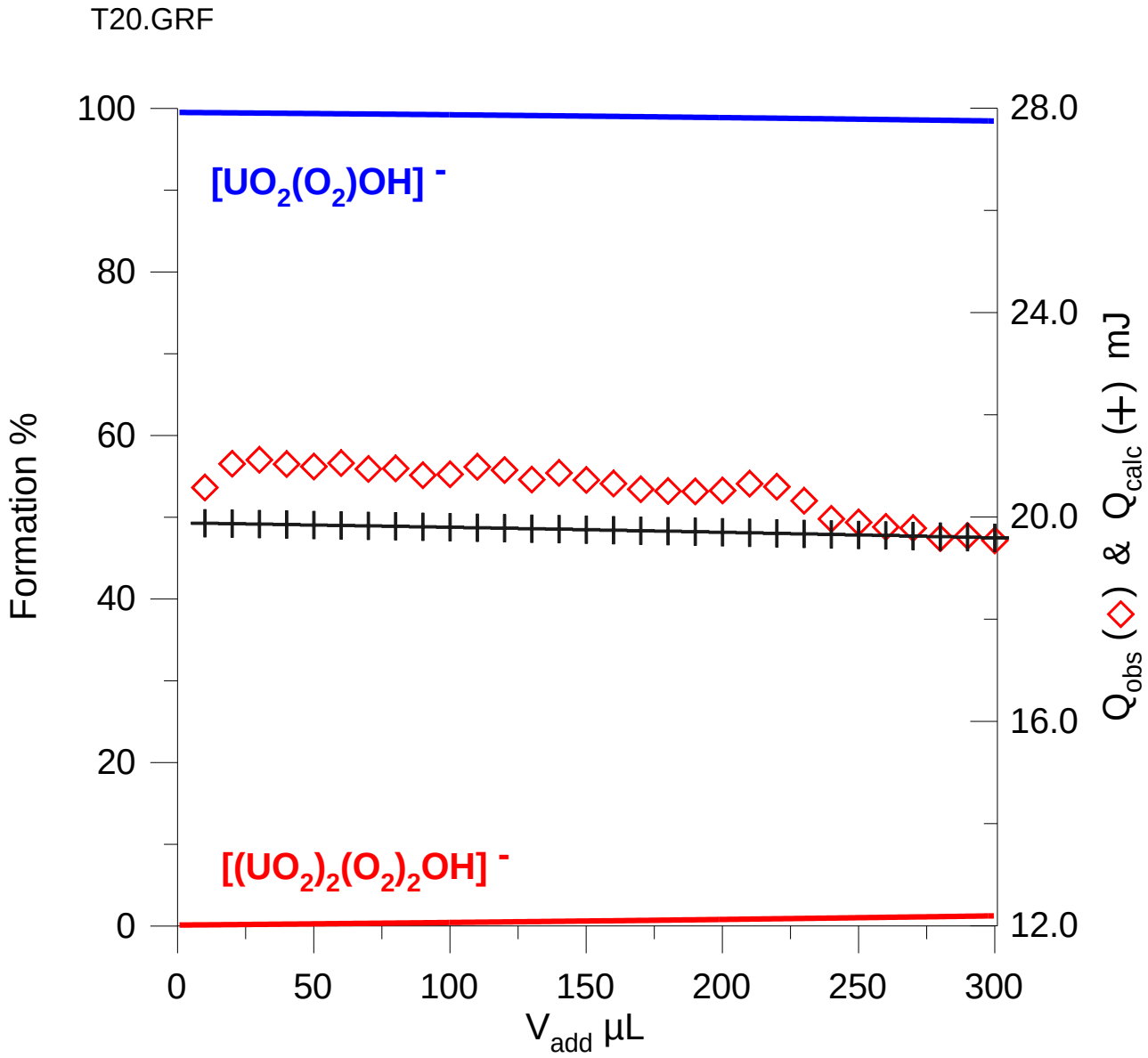

Figure S6

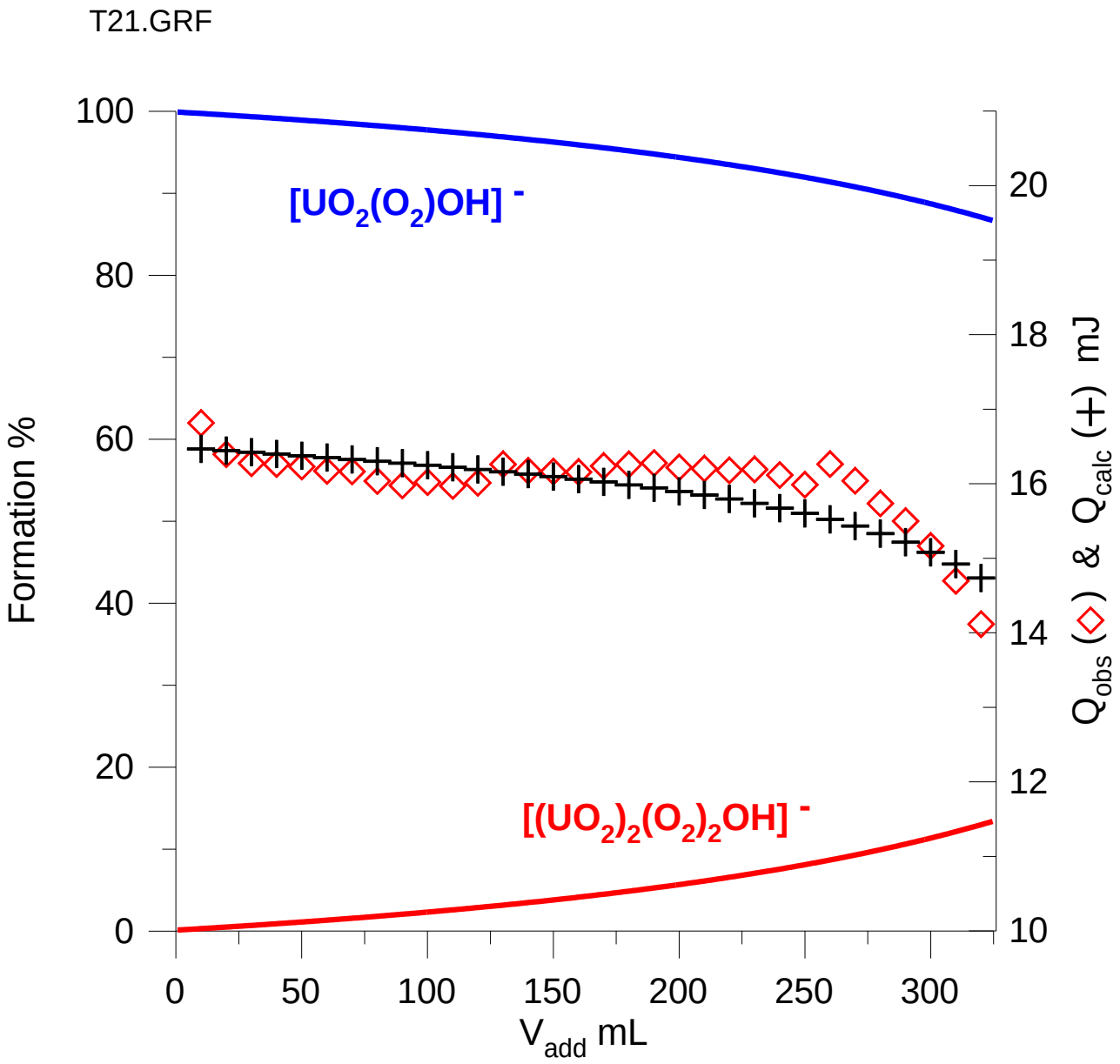

Figure S7

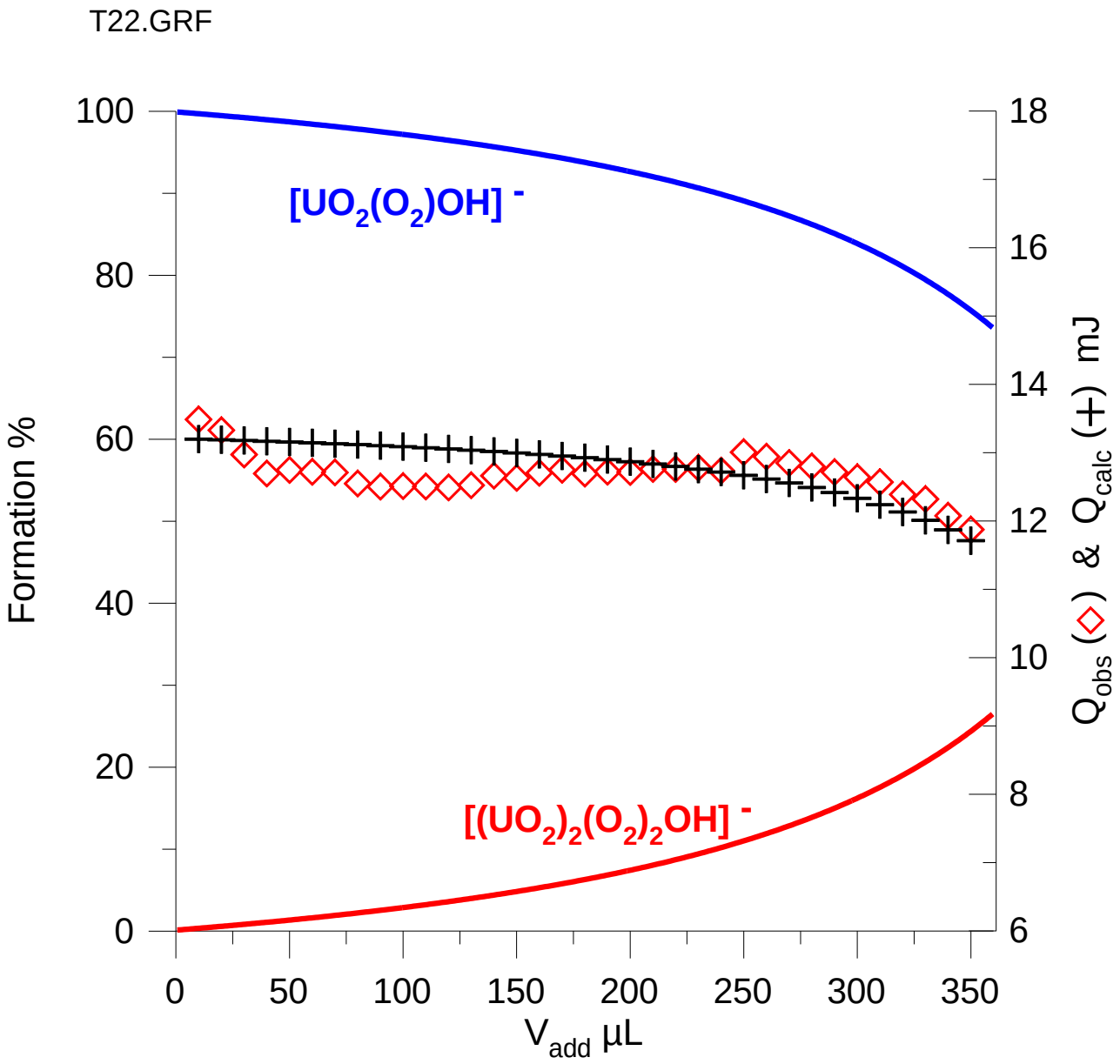

Figure S8

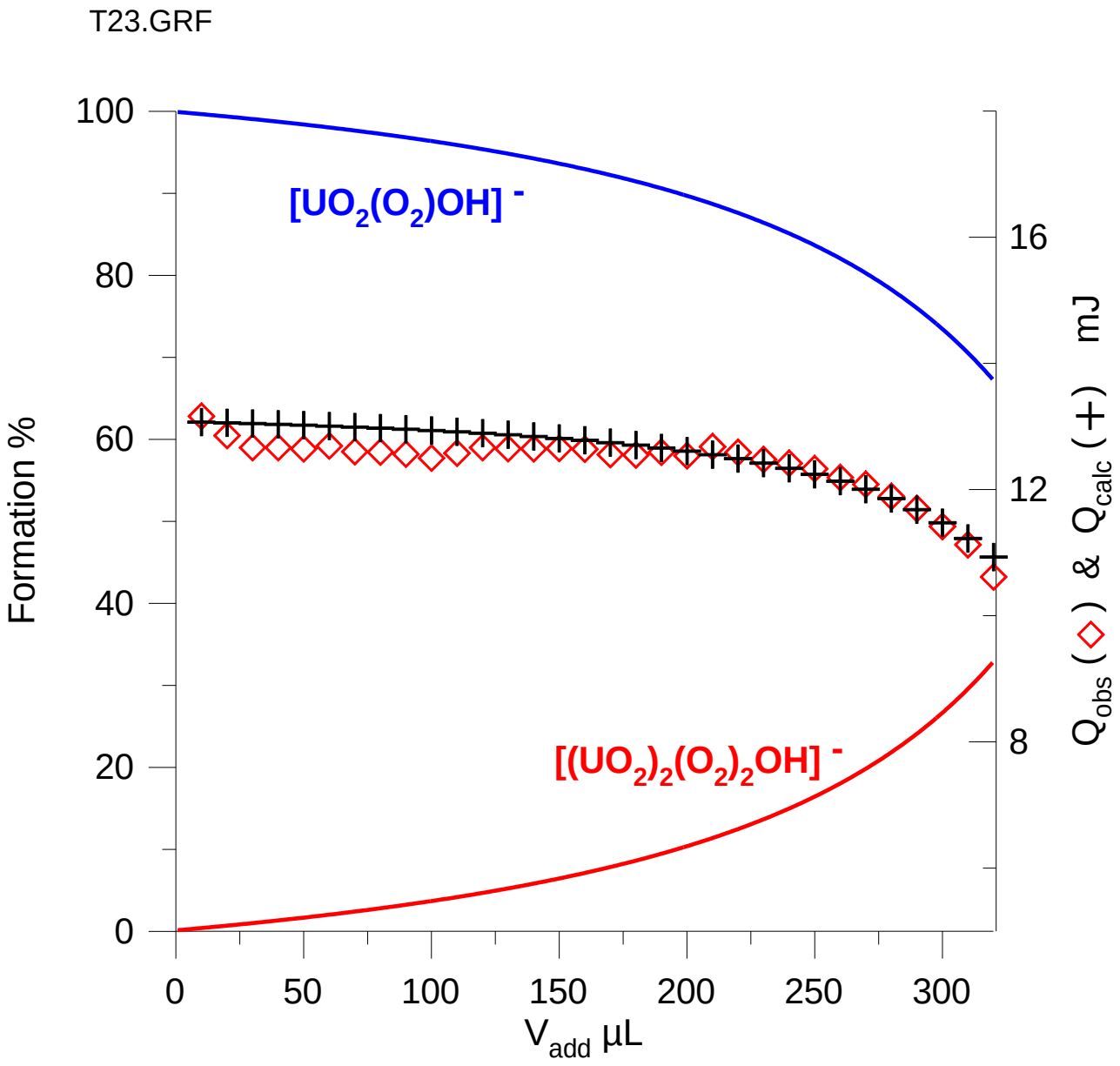

Figure S9

Figures S5-S9. The observed (◇) and calculated (+) stepwise heat changes for the titrations T19 – T23 in Table S3. The plots show also (left axis) the species distribution as a function of the added volume (V_{add}) during titrations.

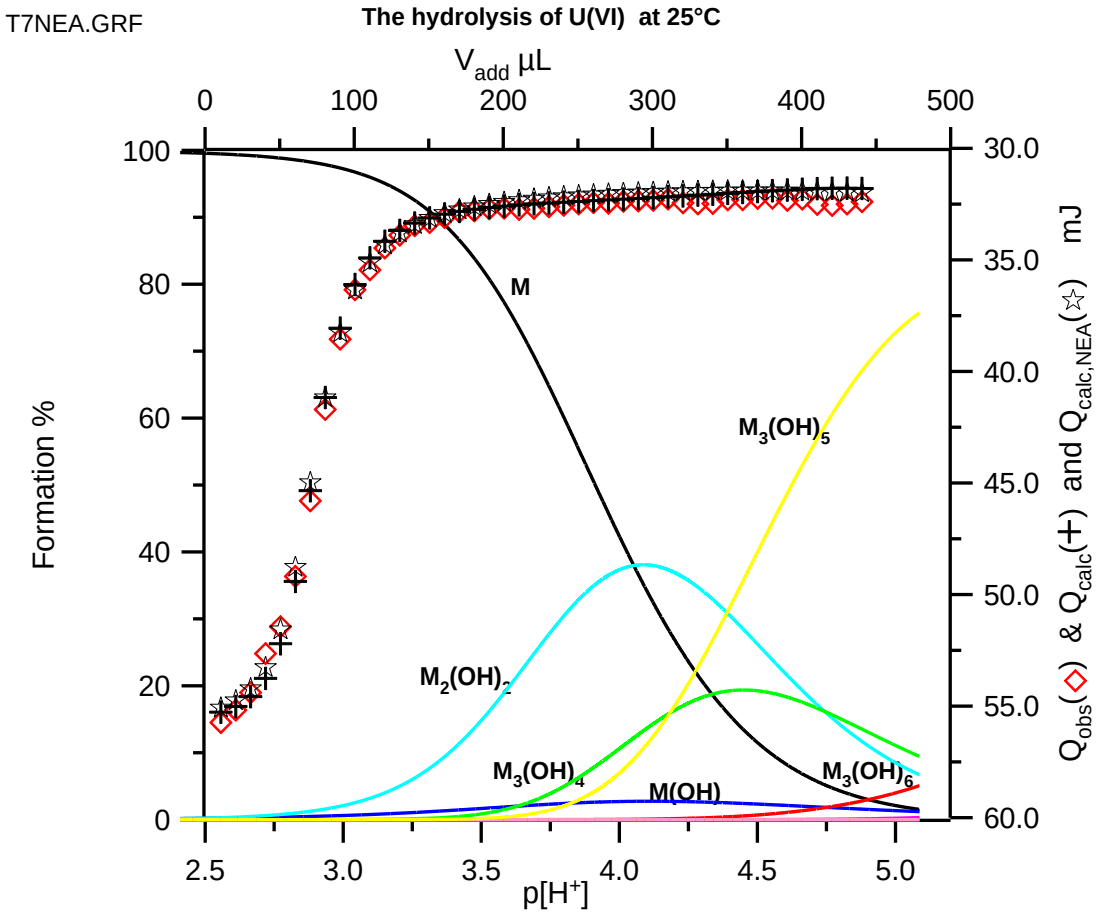

Figure S10

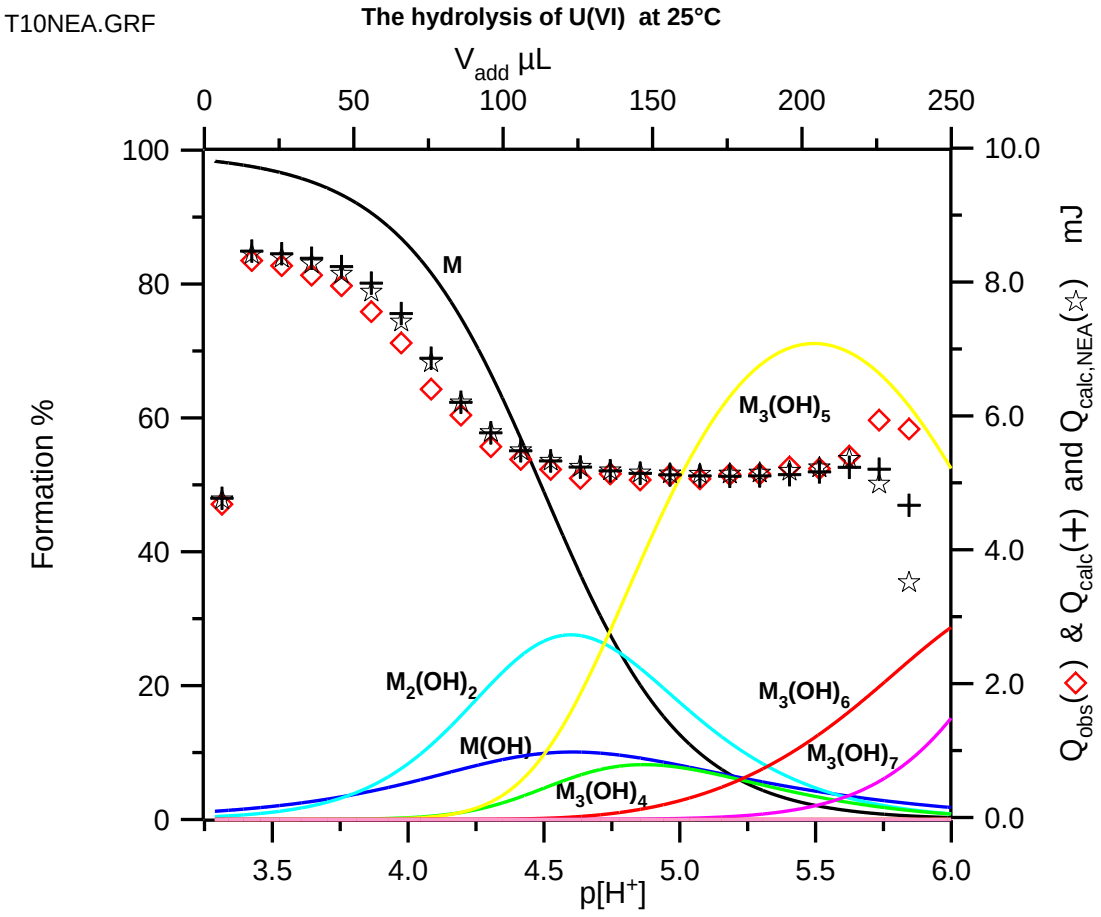

Figure S11

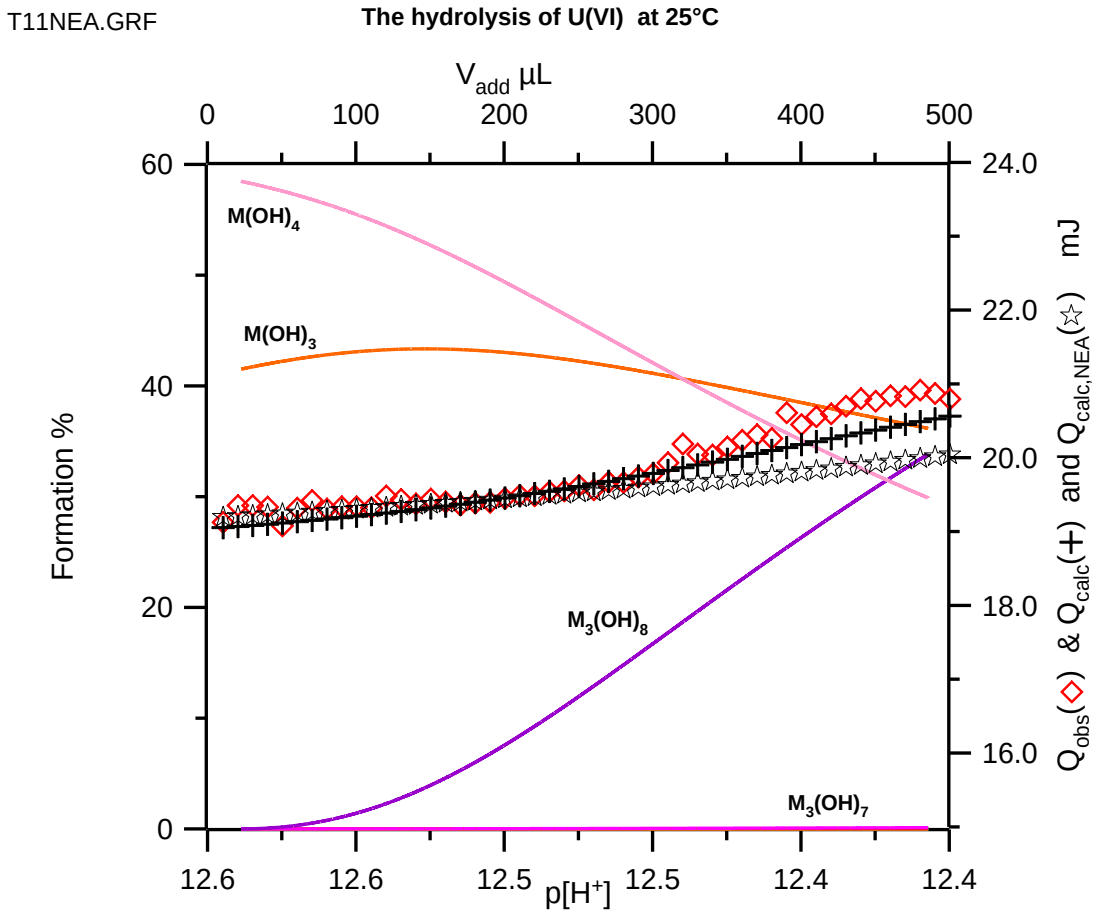

Figure S12

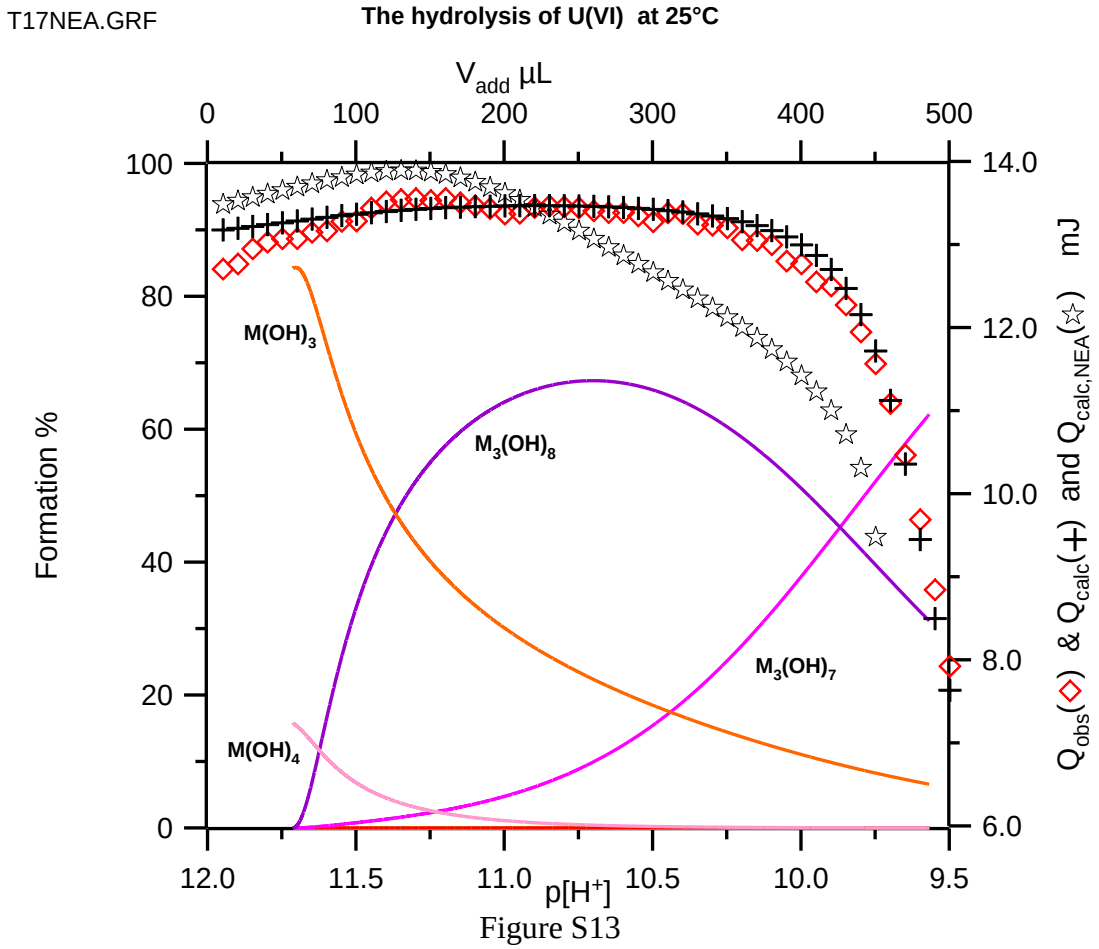

Figure S13

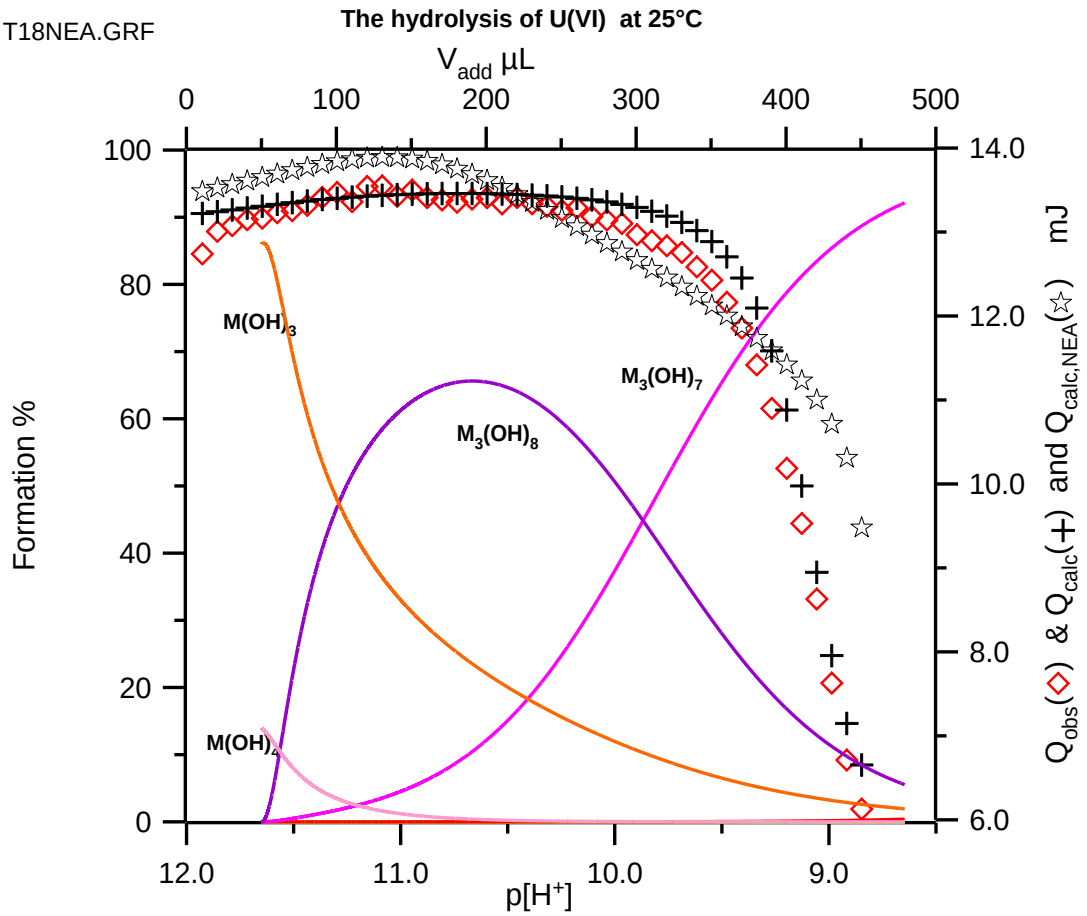

Figure S14

Figures S10 – S14. The observed (◇) and calculated (+) stepwise heat changes for the titrations T7, T10, T11, T17, and T18 in Table S2. The plots show also (left axis) the species distribution as a function of p[H^+] in the solutions. The heat changes calculated with the NEA constants (☆) for the titrations carried out in basic conditions differ significantly from the ones (+) calculated with the speciation and stability constants obtained in this work.

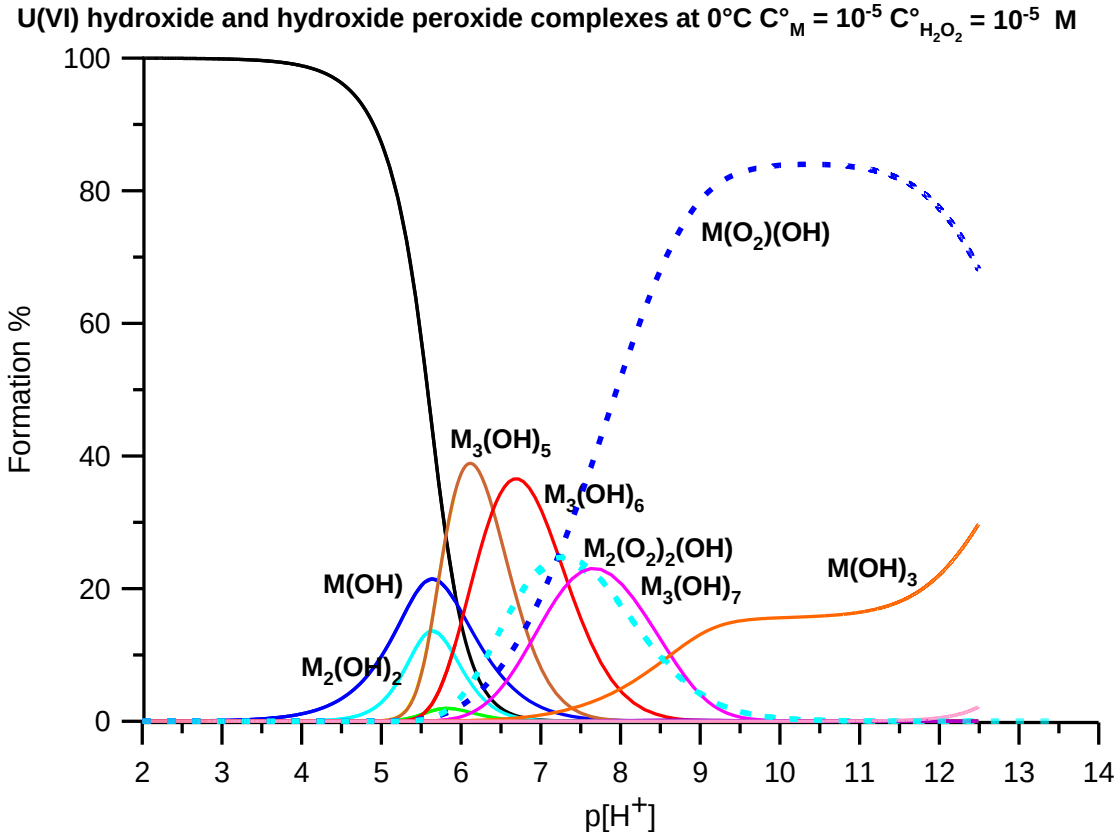

Figure S15

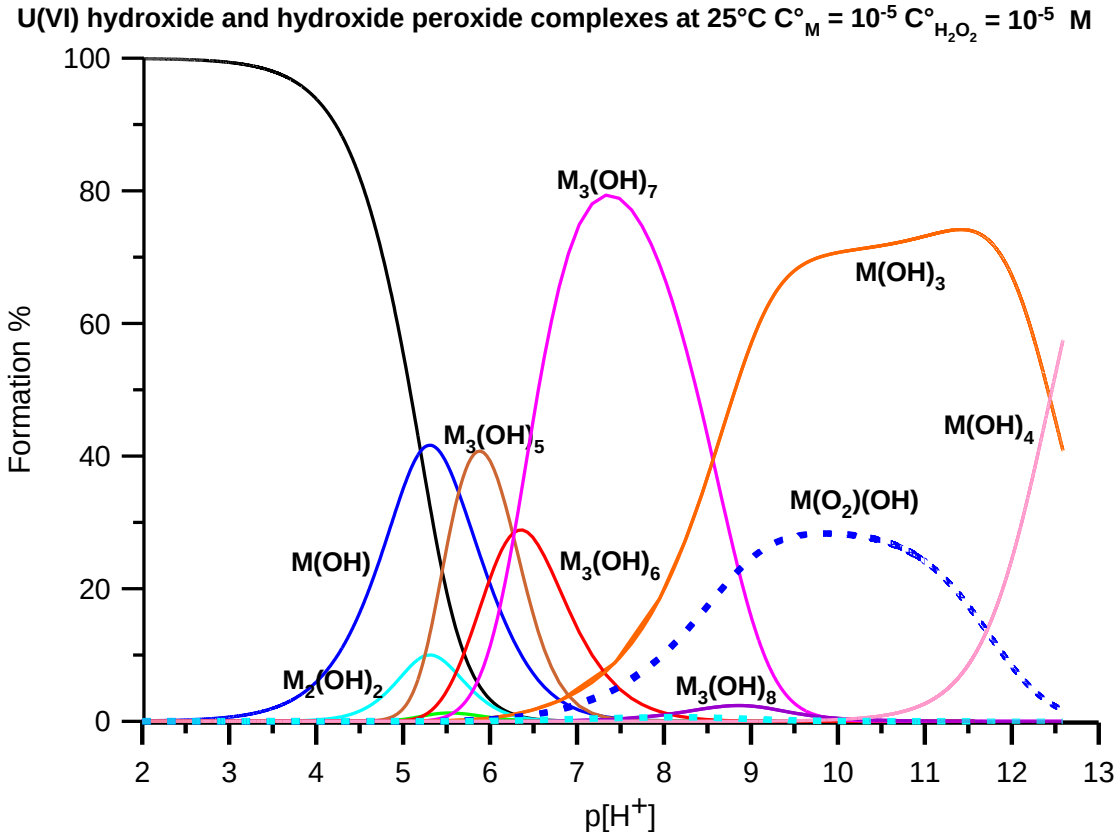

Figure S16

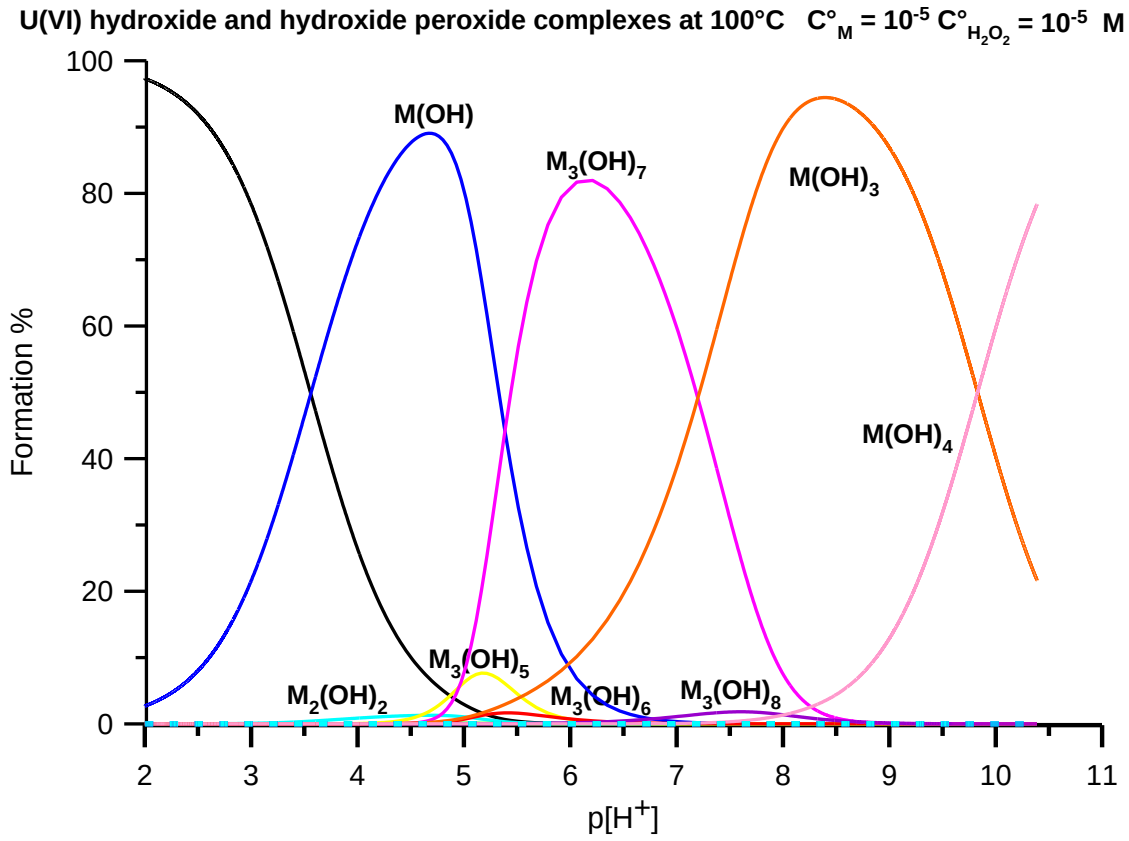

Figure S17

Figures S15 – S17. The distribution of the hydroxide peroxide complexes of U(VI) in a solution containing UO_2^{2+} and H_2O_2 10^{-5}M as a function of the solution p[H^+] at 0 °C, 25 °C and 100 °C**.**

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