Electronic Supporting Information to: Alkali - Metal Ion Coordination in Uranyl(VI) Poly-Peroxo Complexes in Solution, Inorganic Analogues to Crown-Ethers. Part 2. Complex Formation in the Tetramethyl Ammonium (TMA^+) -, Li^+ -, and K^+ – Uranyl(VI) – Peroxide – Carbonate Systems.

Pier Luigi Zanonato[a], Zoltan Szabo,[c] Plinio Di Bernardo,[a] Valerie Vallet[b], and Ingmar Grenthe[c]

A. *Potentiometric titrations, the K^+- uranyl(VI) - peroxide – carbonate system.*

Table S1A. Composition of test solutions used in the K^+ - uranyl(VI) – peroxide – carbonate system. Concentrations in mmol/dm^{-3}; the numbering is the same in the corresponding Figure S1.

	Titration Vessel					Titrant			
	V_0 mL	C°_{U} mM	$C^{\circ}_{Carbonate}$ mM	C°_{H2O2} mM	C°_{H} mM	C^{T}_{U} mM	$C^{T}_{Carbonate}$ mM	C^{T}_{H2O2} mM	C^{T}_{H} mM
1	43.4	4.24	17.0	4.45	-0.03	0	252	0	0
2	30.8	2.40	9.62	2.71	-1.32	0	252	0	0
3	68.2	1.09	4.36	1.43	-0.01	0	252	0	0
4	55.1	7.62	64.1	8.32	0.12	0	0	0	201
5	94.8	0.58	2.34	0.74	0.08	0	252	0	0
6	43.5	15.6	116.0	18.9	-0.19	0	0	0	201
7	87.8	3.81	28.7	4.60	0.10	0	0	0	201
8	109	1.51	13.71	0.0	0.12	0	0	264	0
9	110	1.20	16.56	0.0	0.15	0	0	264	0
10	126	0.79	13.85	0.0	0.17	0	0	264	0
11	127	0.65	3.87	0.0	0.27	0	0	264	0
12	79.2	4.24	31.8	0.0	0.14	0	0	274	0
13	57.8	8.74	43.6	0.0	0.18	0	0	274	0
14	85.9	4.26	20.6	0.0	0.27	0	0	274	0
15	108	3.07	14.04	0.0	-0.11	0	0	274	0
16	111	1.73	6.40	0.0	-0.01	0	0	274	0
17	38.5	10.2	36.9	0.0	-0.09	0	0	274	0
18	46.9	9.80	59.2	0.0	-0.08	0	0	274	0

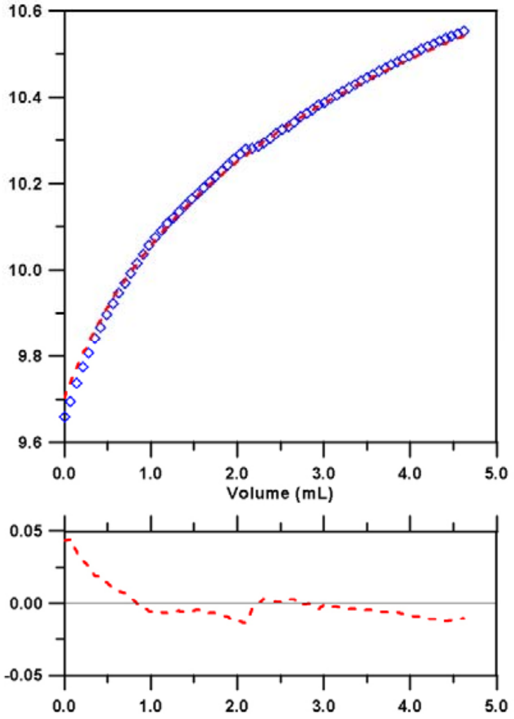
Table S1B. Results of the minimization procedures.

	Model 1	Model 2	Model 3	Model 4
Overall σ	1.04	1.04	1.04	1.18
-2*q*, *p*, *q*, *r*				
-2, 2, 1, 4	27.96 ± 0.05	27.96 ± 0.05	27.96 ± 0.05	27.96 ± 0.05
-2, 1, 1, 2	4.40 ± 0.03	4.40 ± 0.03	4.40 ± 0.03	4.40 ± 0.03
-2, 2, 1, 2	20.44 ± 0.10	20.44 ± 0.10	20.44 ± 0.10	20.44 ± 0.10
-10, 5, 5, 5	21.26 ± 0.15	---	---	-
-8, 4, 4, 4	---	16.18 ± 0.05	---	-
-12, 6, 6, 6	---	---	26.55 ± 0.01	-
-4, 3, 2, 4	-	-	-	27.96 ± 0.17

A straightforward least-squares analysis of the experimental data using the HYPERQUAD program might be misleading as a result of correlations that result in large estimated uncertainty in the equilibrium constants. The for this reason we have used a stepwise method as follows: In the first stage we used the equilibrium model established in Ref. 4 to obtain a first estimate of the equilibrium constants; in a second stage we used data where the concentration of the polymer ($[(UO_2)(O_2)(CO_3)]_n^{-2n}$, $n = 4, 5, 6$) was small and therefore of minor importance for the refinement of the other constants. In this refinement the value of log K_n was kept constant while refining the remaining constants, these values turned out to be very close to those obtained in the first stage. Finally, the experimental data with the highest concentration of the polymer where used to refine the value of its log K_n, keeping the other constants at the values obtained in the second stage; these constants with their estimated uncertainty are reported in Table S1B. All these models could describe the experimental data with about the same accuracy and other methods had to be used to distinguish between them.

Some of the complexes identified in the previous study in a $NaNO_3$ 0.5 M ionic medium (ref 7b) where negligible in the test solutions used.

#1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10.2
10.0
9.8
9.6
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1.0
2.0
3.0
4.0
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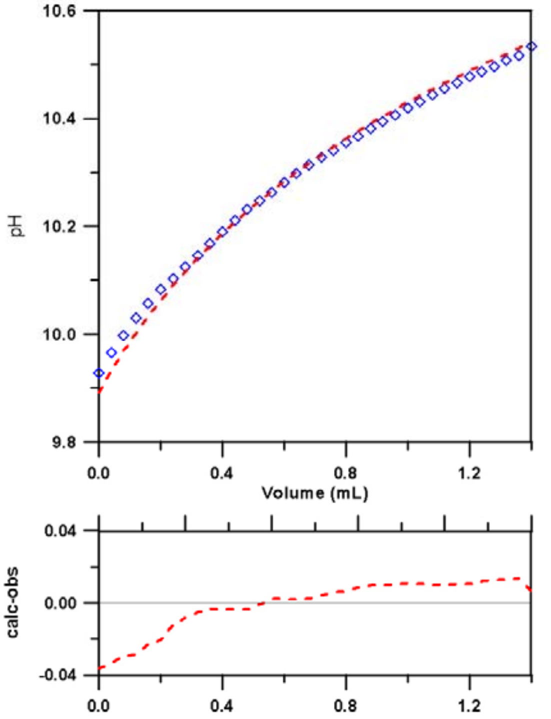
-0.05
0.0
1.0
2.0
3.0
4.0
5.0

#2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10.4
pH
10.2
10.0
9.8
0.0
0.4
0.8
1.2
Volume (mL)
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calc-obs
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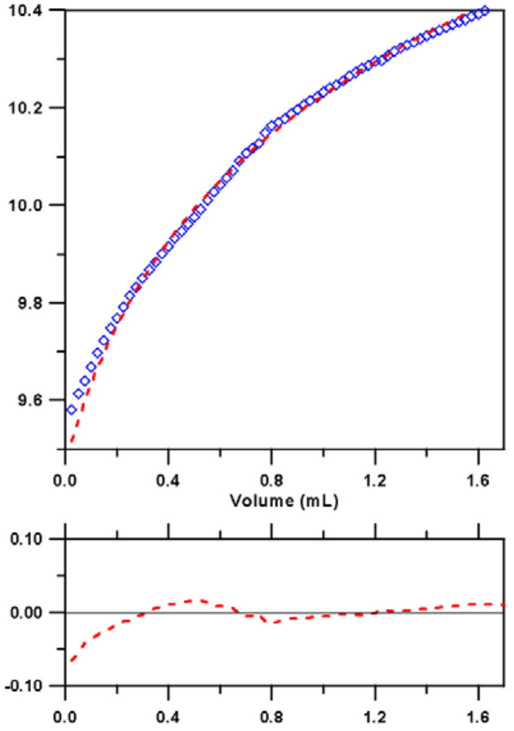
-0.04
0.0
0.4
0.8
1.2

#3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10.2
10.0
9.8
9.6
0.0
0.4
0.8
1.2
1.6
Volume (mL)
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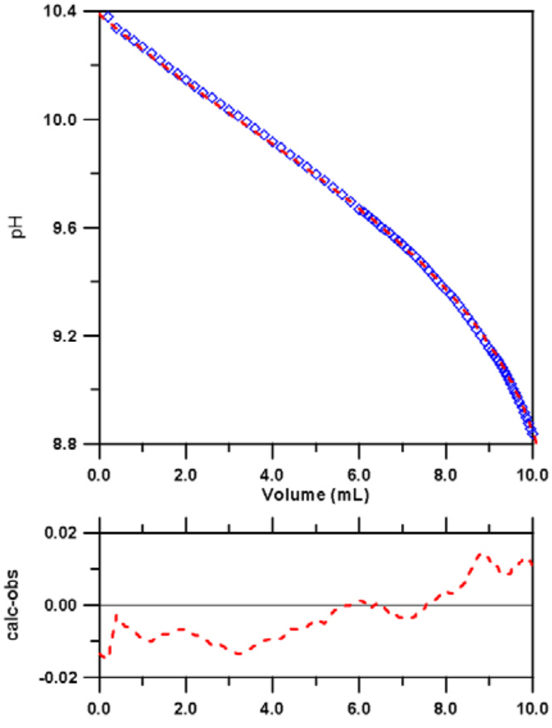
0.00
-0.10
0.0
0.4
0.8
1.2
1.6

#4


10.4
10.0
pH
9.6
9.2
8.8
0.0
2.0
4.0
6.0
8.0
10.0
Volume (mL)
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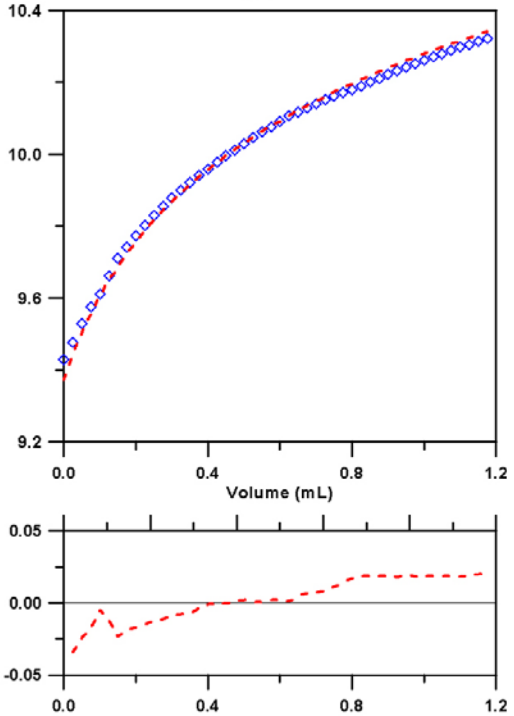
calc-obs
0.00
-0.02
0.0
2.0
4.0
6.0
8.0
10.0

#5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9.6
9.2
0.0
0.4
0.8
1.2
Volume (mL)
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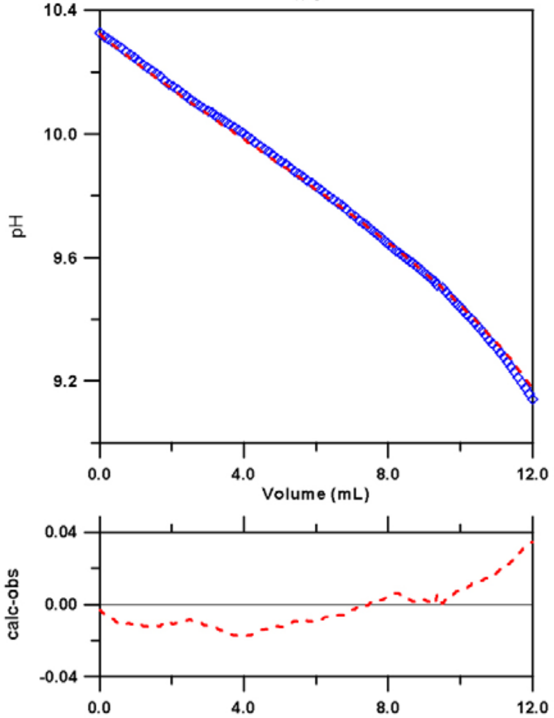
0.00
-0.05
0.0
0.4
0.8
1.2

#6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pH
9.6
9.2
0.0
4.0
8.0
12.0
Volume (mL)
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calc-obs
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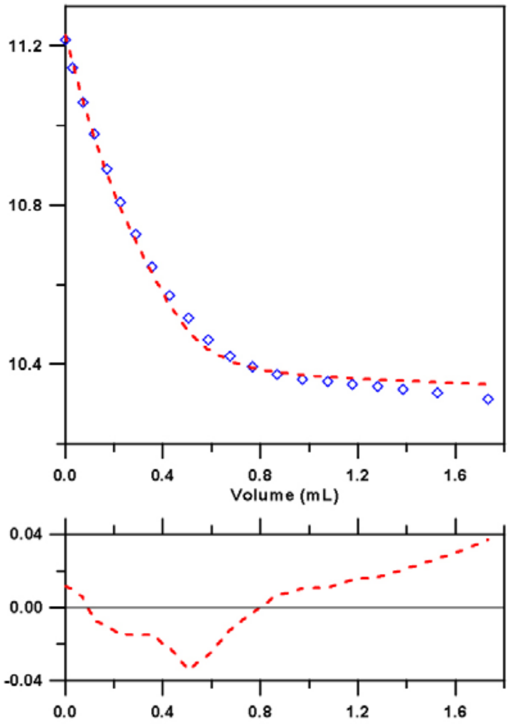
-0.04
0.0
4.0
8.0
12.0

#7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10.8
10.4
0.0
0.4
0.8
1.2
1.6
Volume (mL)
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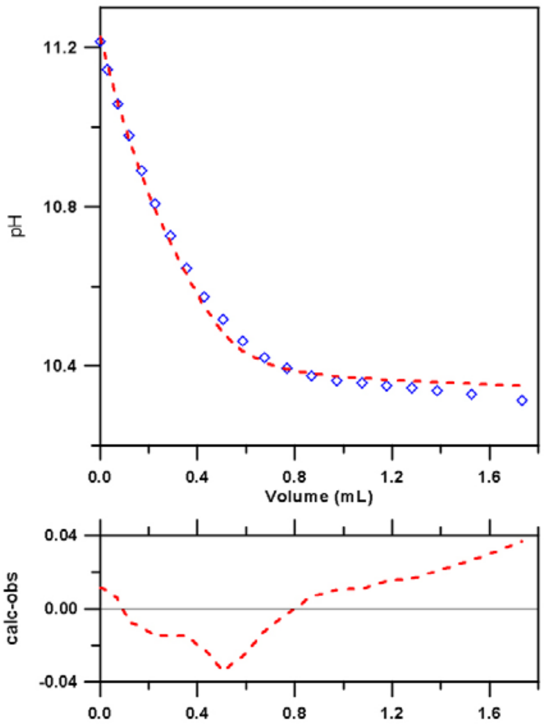
0.00
-0.04
0.0
0.4
0.8
1.2
1.6

#8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10.8
pH
10.4
0.0
0.4
0.8
1.2
1.6
Volume (mL)
0.04
calc-obs
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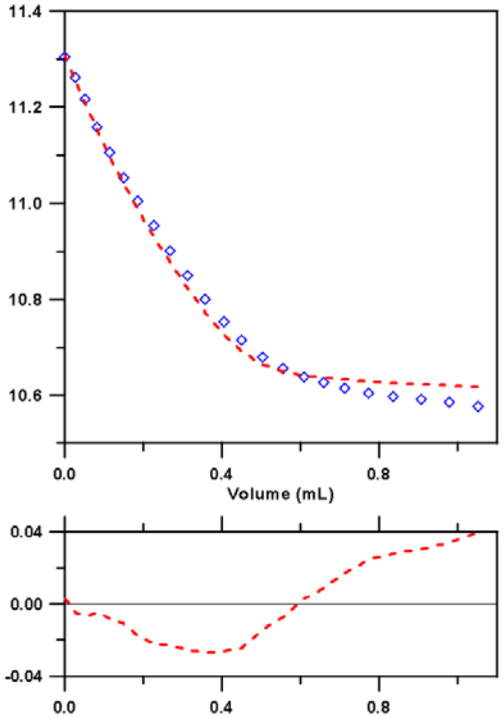
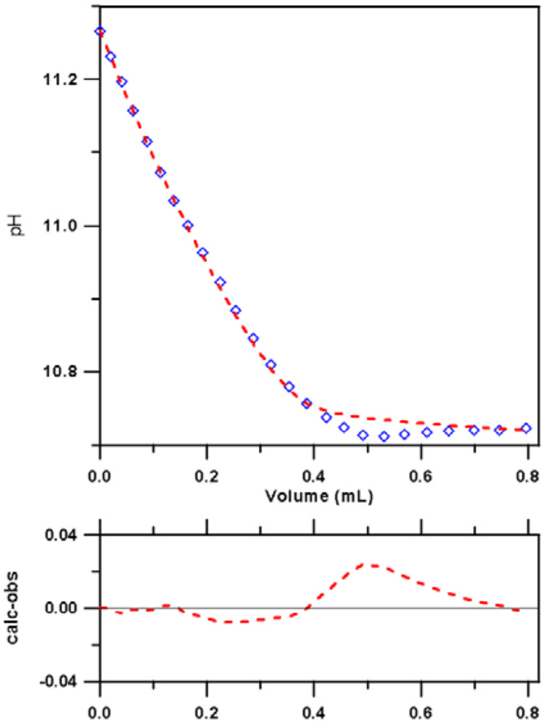
-0.04
0.0
0.4
0.8
1.2
1.6

#9


11.4
11.2
11.0
10.8
10.6
0.0
0.4
0.8
Volume (mL)
0.04
0.00
-0.04
0.0
0.4
0.8

#10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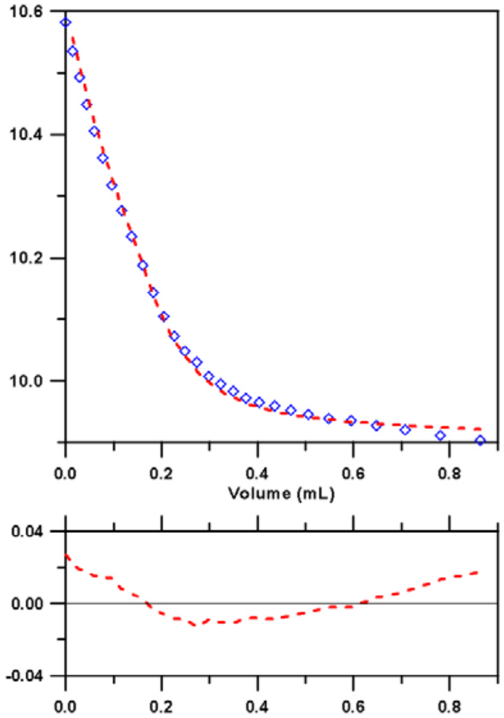
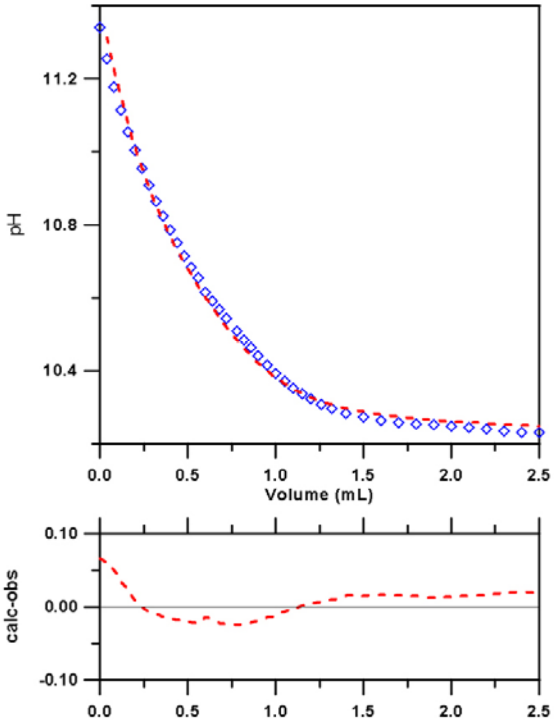
11.0
10.8
pH
0.0
0.2
0.4
0.6
0.8
Volume (mL)
0.04
0.00
-0.04
calc-obs
0.0
0.2
0.4
0.6
0.8

#11


10.6
10.4
10.2
10.0
0.0
0.2
0.4
0.6
0.8
Volume (mL)
0.04
0.00
-0.04
0.0
0.2
0.4
0.6
0.8

#12


11.2
10.8
10.4
pH
0.0
0.5
1.0
1.5
2.0
2.5
Volume (mL)
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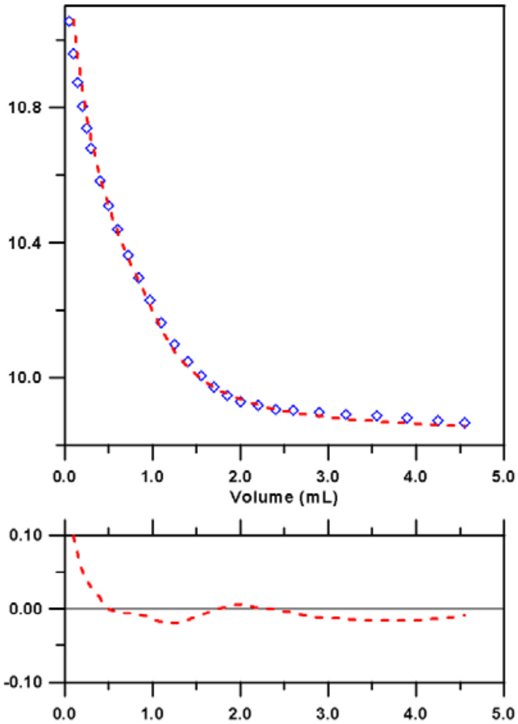
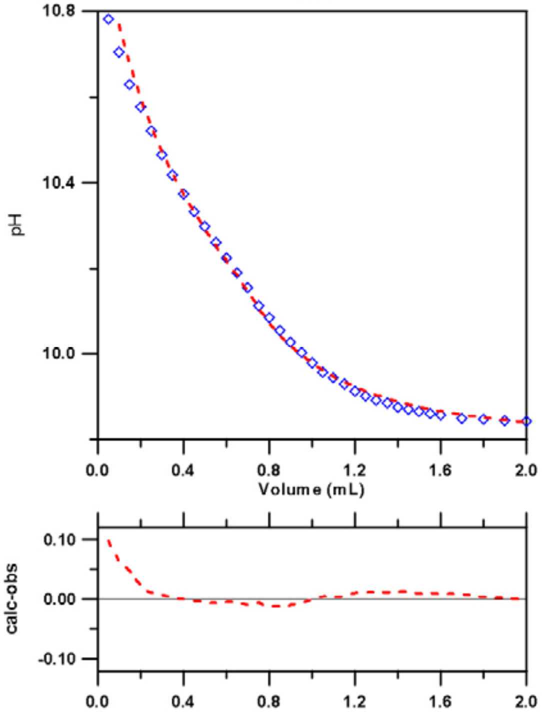
0.00
-0.10
calc-obs
0.0
0.5
1.0
1.5
2.0
2.5

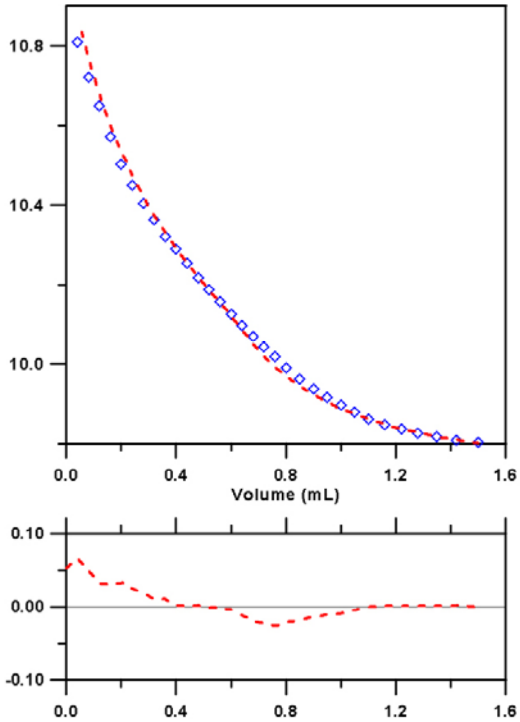
#13


10.8
10.4
10.0
0.0
1.0
2.0
3.0
4.0
5.0
Volume (mL)
0.10
0.00
-0.10
0.0
1.0
2.0
3.0
4.0
5.0

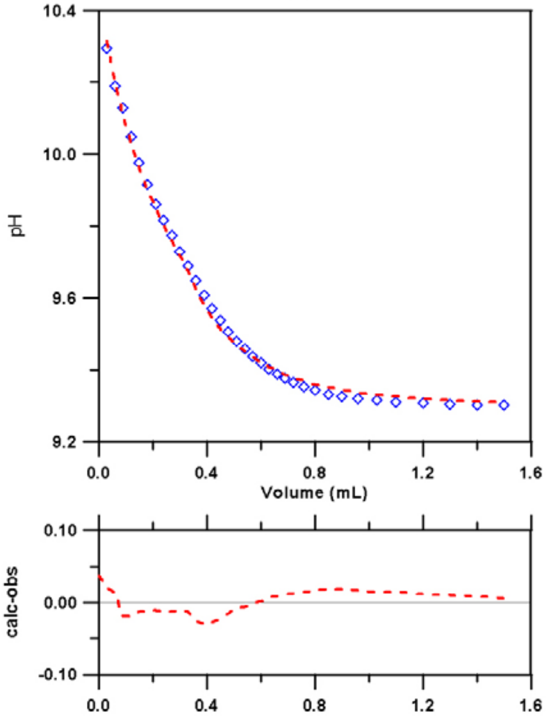
#14


10.8
10.4
pH
10.0
0.0
0.4
0.8
1.2
1.6
2.0
Volume (mL)
0.10
0.00
-0.10
calc-obs
0.0
0.4
0.8
1.2
1.6
2.0

#15


10.8
10.4
10.0
0.0
0.4
0.8
1.2
1.6
Volume (mL)
0.10
0.00
-0.10
0.0
0.4
0.8
1.2
1.6

#16


10.4
10.0
pH
9.6
9.2
0.0
0.4
0.8
1.2
1.6
Volume (mL)
0.10
0.00
-0.10
calc-obs
0.0
0.4
0.8
1.2
1.6

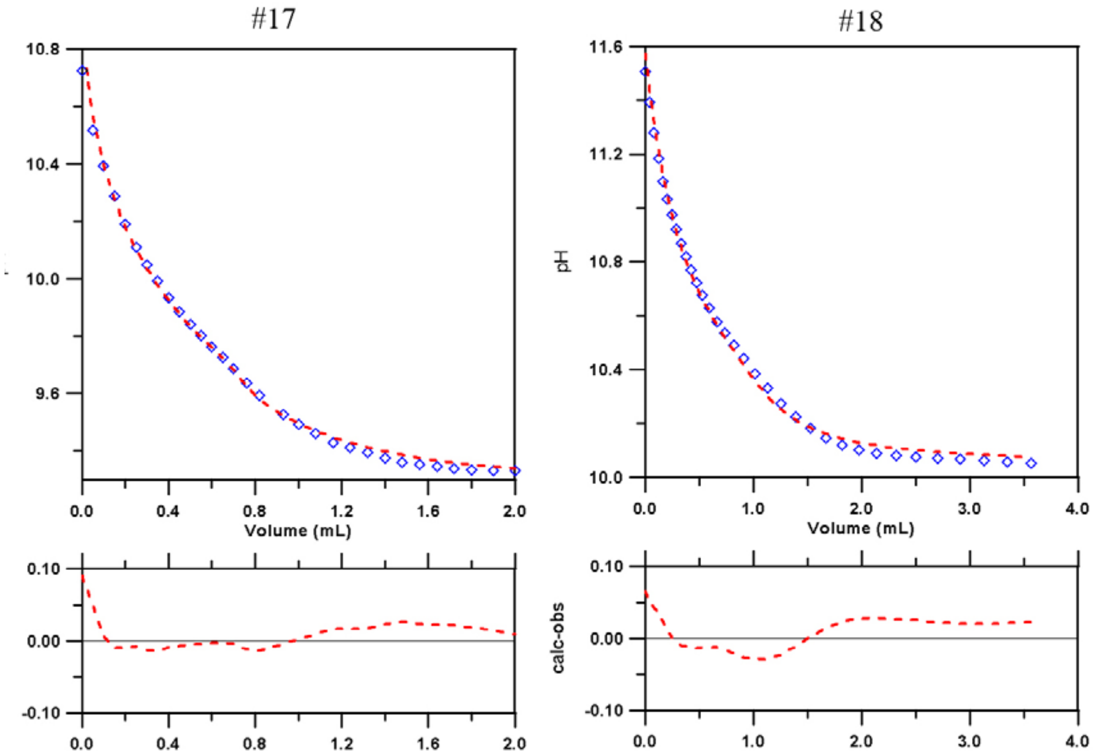


Figure S1. Comparison of experimental (diamonds) and calculated (**- -**) data for the K^+ - uranyl(VI) – peroxide – carbonate system. The pH values were calculated with the stability constants of Table 3.

B. *Potentiometric titrations, the Li$^+$– uranyl(VI) – peroxide – carbonate system.*

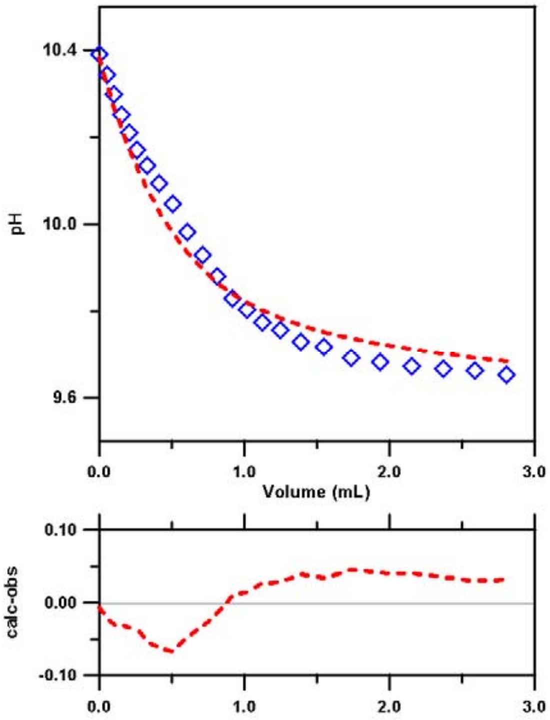
Table S2A. Composition of test solutions used in the Li$^+$ - uranyl(VI) – peroxide – carbonate system. Concentrations in mmol/dm^{-3}, the numbering is the same in the corresponding Figure S2.

	Titration Vessel					Titrant			
	V_0 mL	C°_{U} mM	$C^{\circ}_{Carbonate}$ mM	C°_{H2O2} mM	C°_{H} mM	C^{T}_{U} mM	$C^{T}_{Carbonate}$ mM	C^{T}_{H2O2} mM	C^{T}_{H} mM
1	34.1	3.33	20.43	0	1.84	0	0	101.1	0
2	101.9	1.57	20.13	1.46	-1.36	0	0	0	-488
3	99.0	1.60	12.46	1.57	-1.08	0	0	0	-488
4	92.8	1.66	6.65	1.62	-1.49	0	0	0	-488
5	65.3	2.39	15.06	2.32	-2.08	0	0	0	-488
6	62.3	2.50	19.66	2.43	-2.16	0	0	0	-488
7	58.2	2.66	11.66	2.66	-1.66	0	0	0	-488
8	40.0	3.38	40.95	3.53	-2.15	0	0	0	-488
9	36.0	3.66	15,32	3.74	-2.37	0	0	0	-488
10	101.6	2.03	8.10	1.00	0.00	0	136.2	0	0
11	60.6	3.31	13.58	1.71	0.32	0	136.2	0	0
12	35.6	5.65	23.41	2.75	0.58	0	136.2	0	0
13	91.5	1.55	5.96	1.58	-0.16	0	136.2	0	0
14	76.0	2.24	9.14	2.28	0.703	0	136.2	0	0
15	57.5	3.53	14.45	3.55	1.35	0	136.2	0	0
16	36.7	5.98	22.19	6.22	2.37	0	136.2	0	0
17	84.7	1.17	8.05	0	0.43	0	0	101.1	0
18	80.8	1.40	17.05	0	3.53	0	0	101.1	0
19	59.1	2.00	11.67	0	1.23	0	0	101.1	0
20	101.0	1.18	3.51	0	0.01	0	0	101.1	0

Table S2B. Results of the minimization procedures.

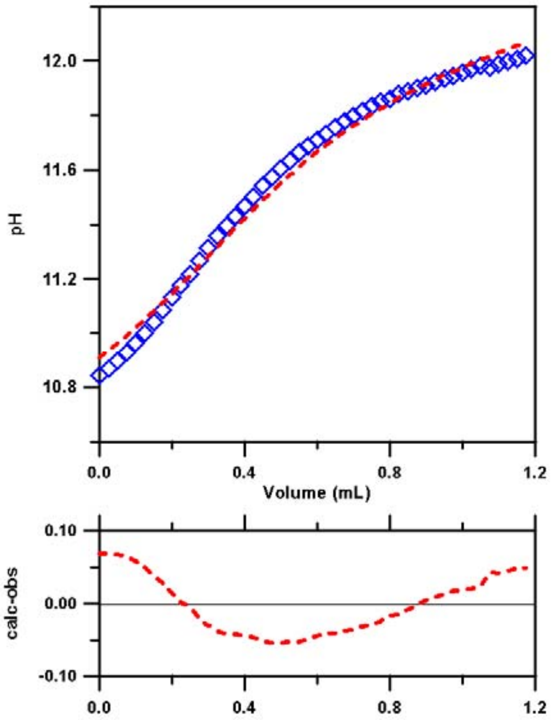
	Model 1	Model 2	Model 3	Model 4
Overall σ	1.97	1.98	1.97	??
-2*q*, *p*, *q*, *r*				
-2, 2, 1, 4	27.25 ± 0.11	27.25 ± 0.11	27.25 ± 0.11	27.25 ± 0.11
-2, 1, 1, 2	4.30 ± 0.02	4.30 ± 0.02	4.30 ± 0.02	4.30 ± 0.02
-2, 2, 1, 2	20.26 ± 0.03	20.26 ± 0.03	20.26 ± 0.03	20.26 ± 0.03
-8, 4, 4, 4	---	16.22 ± 0.20	---	-
-10, 5, 5, 5	20.95 ± 0.08	---	---	-
-12, 6, 6, 6	---	---	25.92 ± 0.09	-
-4, 3, 2, 4	-	-	-	28.91 ± 0.06

All models with cyclic oligomers could describe the experimental data with about the same accuracy, but the one where they were replaced by $[(UO_2)_3(O_2)_2(CO_3)_4]^{6-}$ (-4, 3, 2, 4) the agreement between experimental and calculated data is significantly better as can be seen by comparing titrations 1, 2, 17 and 18.



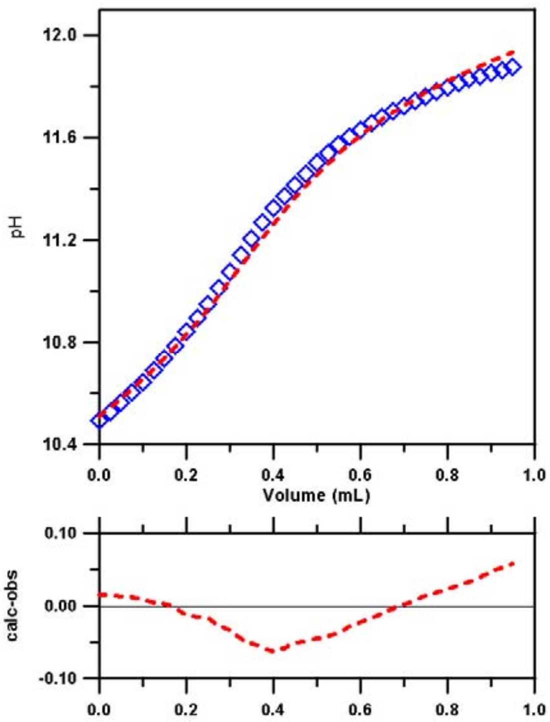
#1

pH
10.4
10.0
9.6
Volume (mL)
0.0
1.0
2.0
3.0
calc-obs
0.10
0.00
-0.10
0.0
1.0
2.0
3.0



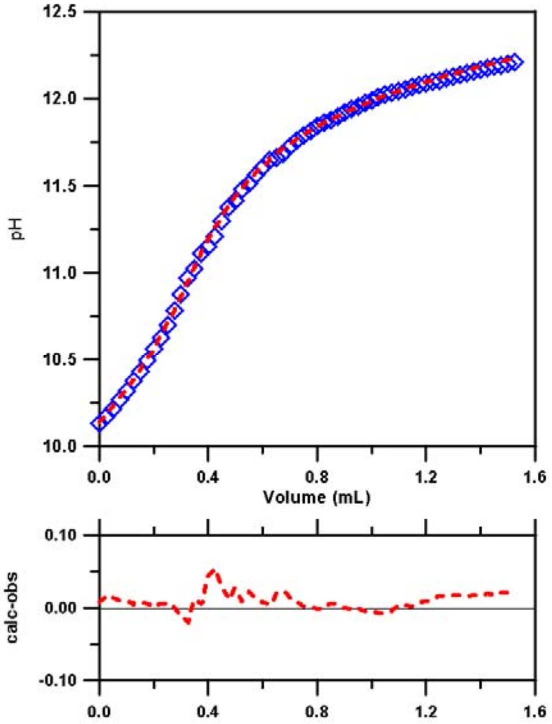
#2

pH
12.0
11.6
11.2
10.8
Volume (mL)
0.0
0.4
0.8
1.2
calc-obs
0.10
0.00
-0.10
0.0
0.4
0.8
1.2



#3

pH
12.0
11.6
11.2
10.8
10.4
Volume (mL)
0.0
0.2
0.4
0.6
0.8
1.0
calc-obs
0.10
0.00
-0.10
0.0
0.2
0.4
0.6
0.8
1.0



#4

pH
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12.0
11.5
11.0
10.5
10.0
Volume (mL)
0.0
0.4
0.8
1.2
1.6
calc-obs
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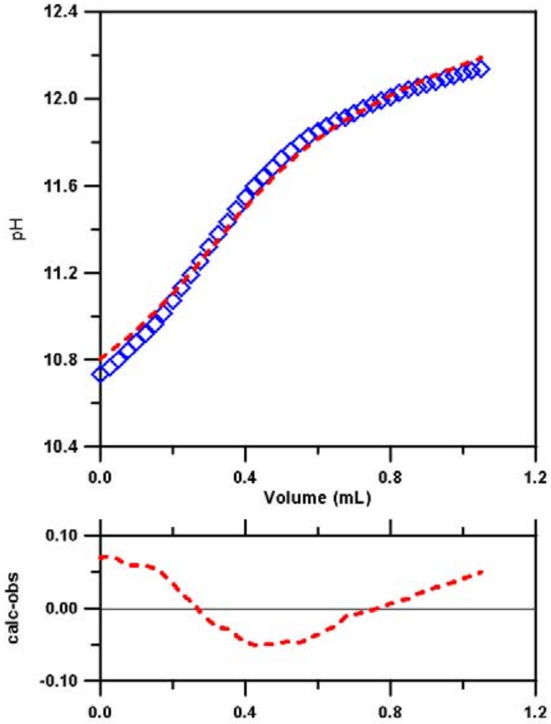
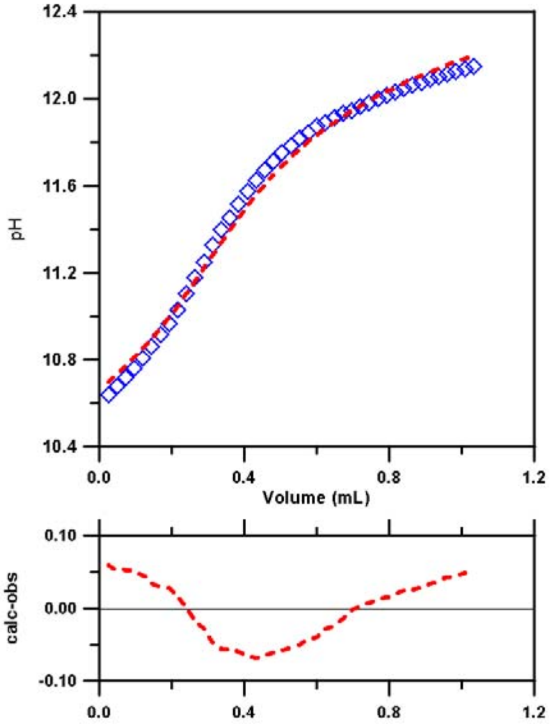
0.00
-0.10
0.0
0.4
0.8
1.2
1.6

#5



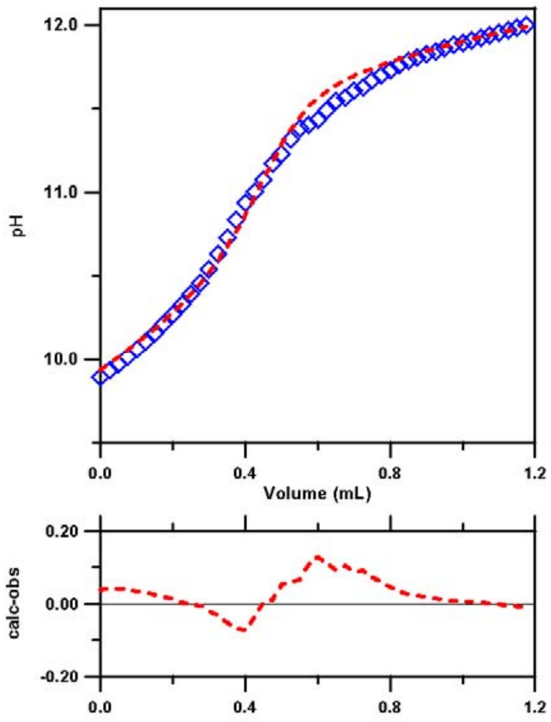
12.4
12.0
11.6
11.2
10.8
10.4
pH
0.0
0.4
0.8
1.2
Volume (mL)
0.10
0.00
-0.10
calc-obs
0.0
0.4
0.8
1.2

#6



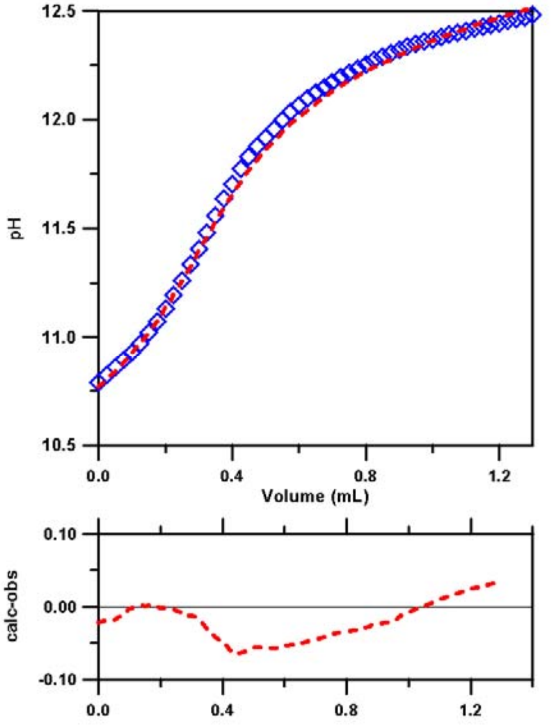
12.4
12.0
11.6
11.2
10.8
10.4
pH
0.0
0.4
0.8
1.2
Volume (mL)
0.10
0.00
-0.10
calc-obs
0.0
0.4
0.8
1.2

#7



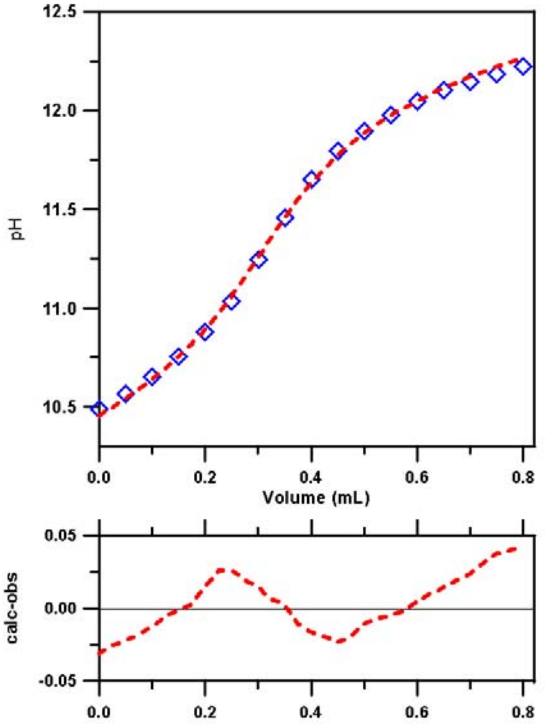
12.0
11.0
10.0
pH
0.0
0.4
0.8
1.2
Volume (mL)
0.20
0.00
-0.20
calc-obs
0.0
0.4
0.8
1.2

#8

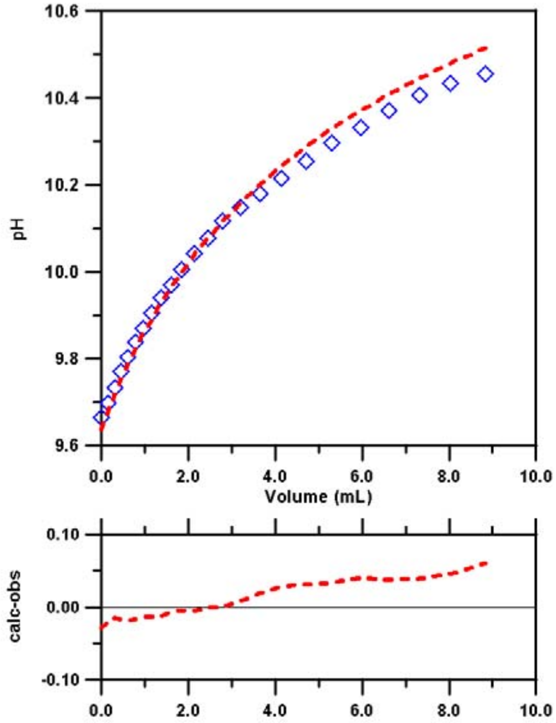


12.5
12.0
11.5
11.0
10.5
pH
0.0
0.4
0.8
1.2
Volume (mL)
0.10
0.00
-0.10
calc-obs
0.0
0.4
0.8
1.2

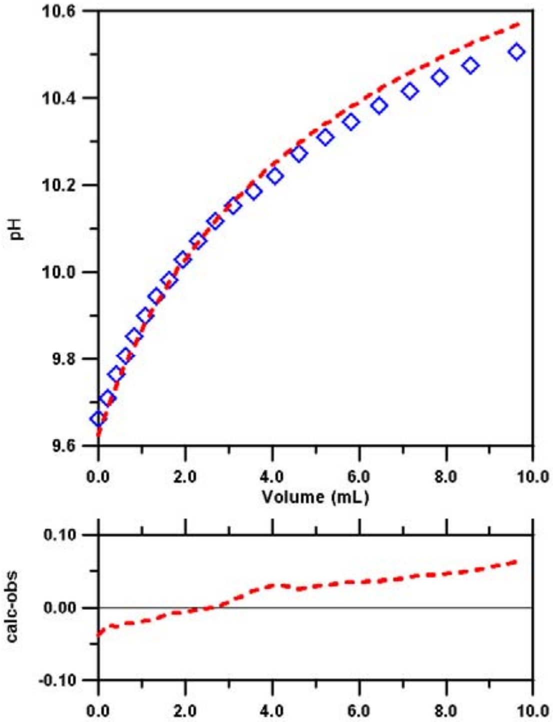
#9


pH
12.5
12.0
11.5
11.0
10.5
0.0
0.2
0.4
0.6
0.8
Volume (mL)
calc-obs
0.05
0.00
-0.05
0.0
0.2
0.4
0.6
0.8

#10


pH
10.6
10.4
10.2
10.0
9.8
9.6
0.0
2.0
4.0
6.0
8.0
10.0
Volume (mL)
calc-obs
0.10
0.00
-0.10
0.0
2.0
4.0
6.0
8.0
10.0

#11


pH
10.6
10.4
10.2
10.0
9.8
9.6
0.0
2.0
4.0
6.0
8.0
10.0
Volume (mL)
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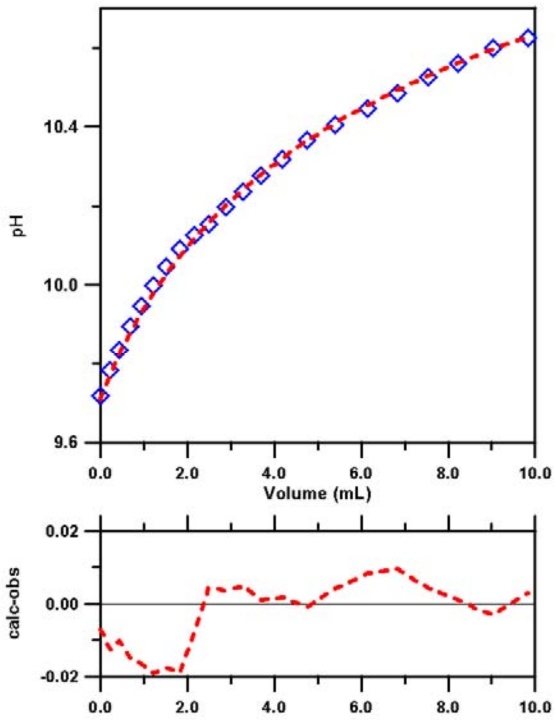
0.00
-0.10
0.0
2.0
4.0
6.0
8.0
10.0

#12


pH
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10.0
9.6
0.0
2.0
4.0
6.0
8.0
10.0
Volume (mL)
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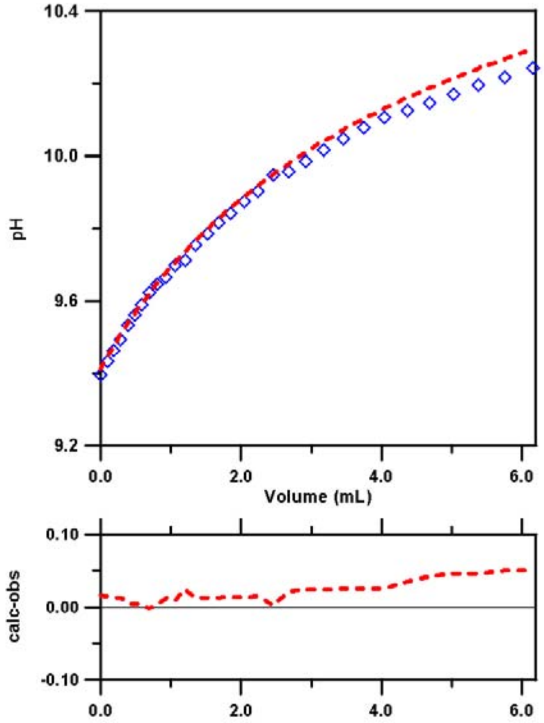
0.00
-0.02
0.0
2.0
4.0
6.0
8.0
10.0

#13


10.4
10.0
9.6
9.2
pH
0.0
2.0
4.0
6.0
Volume (mL)
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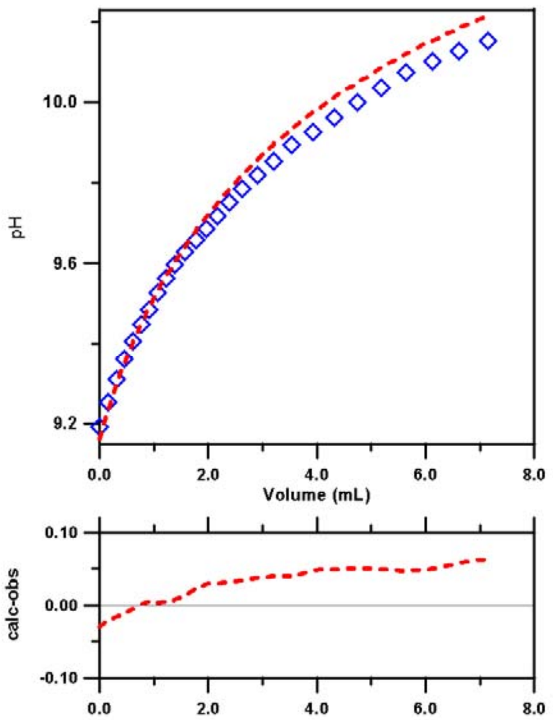
-0.10
calc-obs
0.0
2.0
4.0
6.0

#14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9.6
9.2
pH
0.0
2.0
4.0
6.0
8.0
Volume (mL)
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0.00
-0.10
calc-obs
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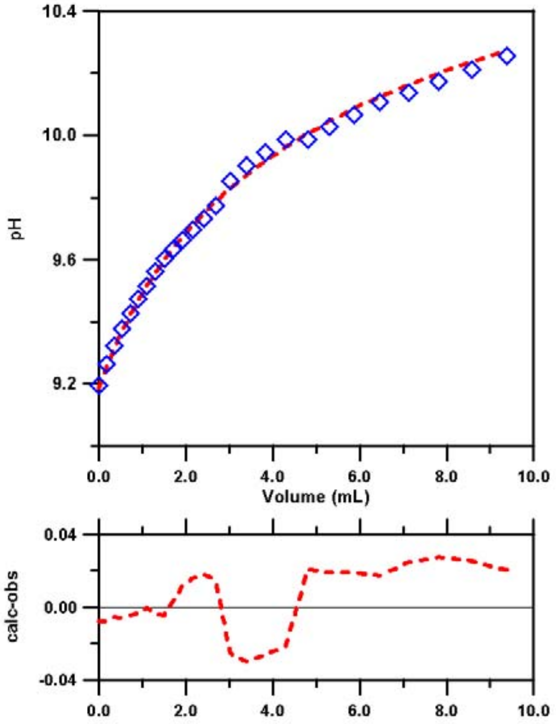
2.0
4.0
6.0
8.0

#15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9.6
9.2
pH
0.0
2.0
4.0
6.0
8.0
10.0
Volume (mL)
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0.00
-0.04
calc-obs
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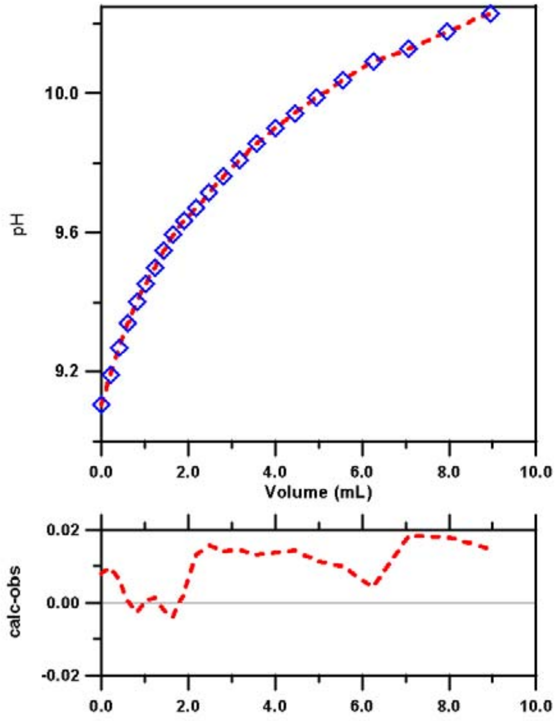
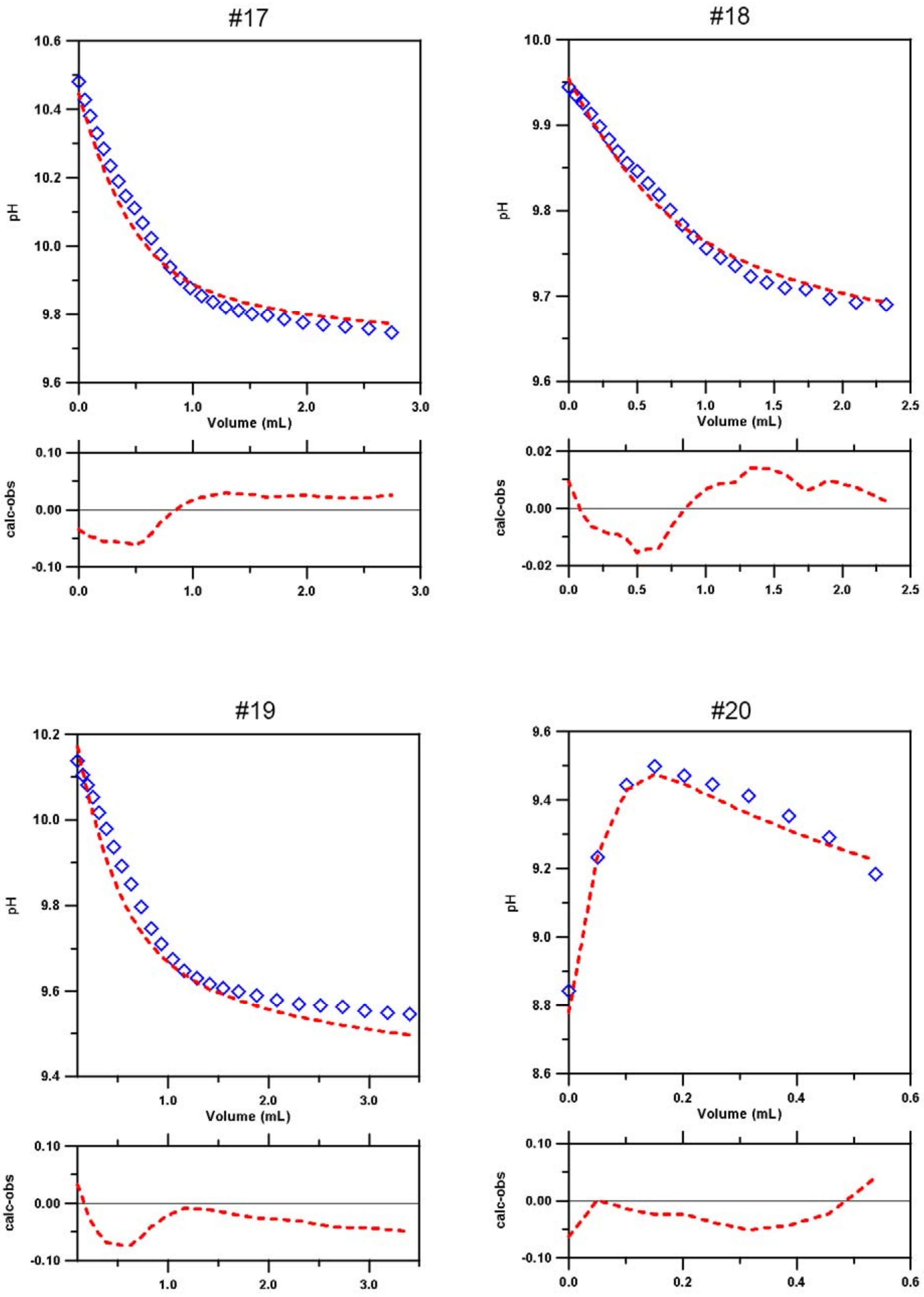
2.0
4.0
6.0
8.0
10.0

#16


10.0
9.6
9.2
pH
0.0
2.0
4.0
6.0
8.0
10.0
Volume (mL)
0.02
0.00
-0.02
calc-obs
0.0
2.0
4.0
6.0
8.0
10.0



Example of agreement between experiment and model using the cyclic oligomers.

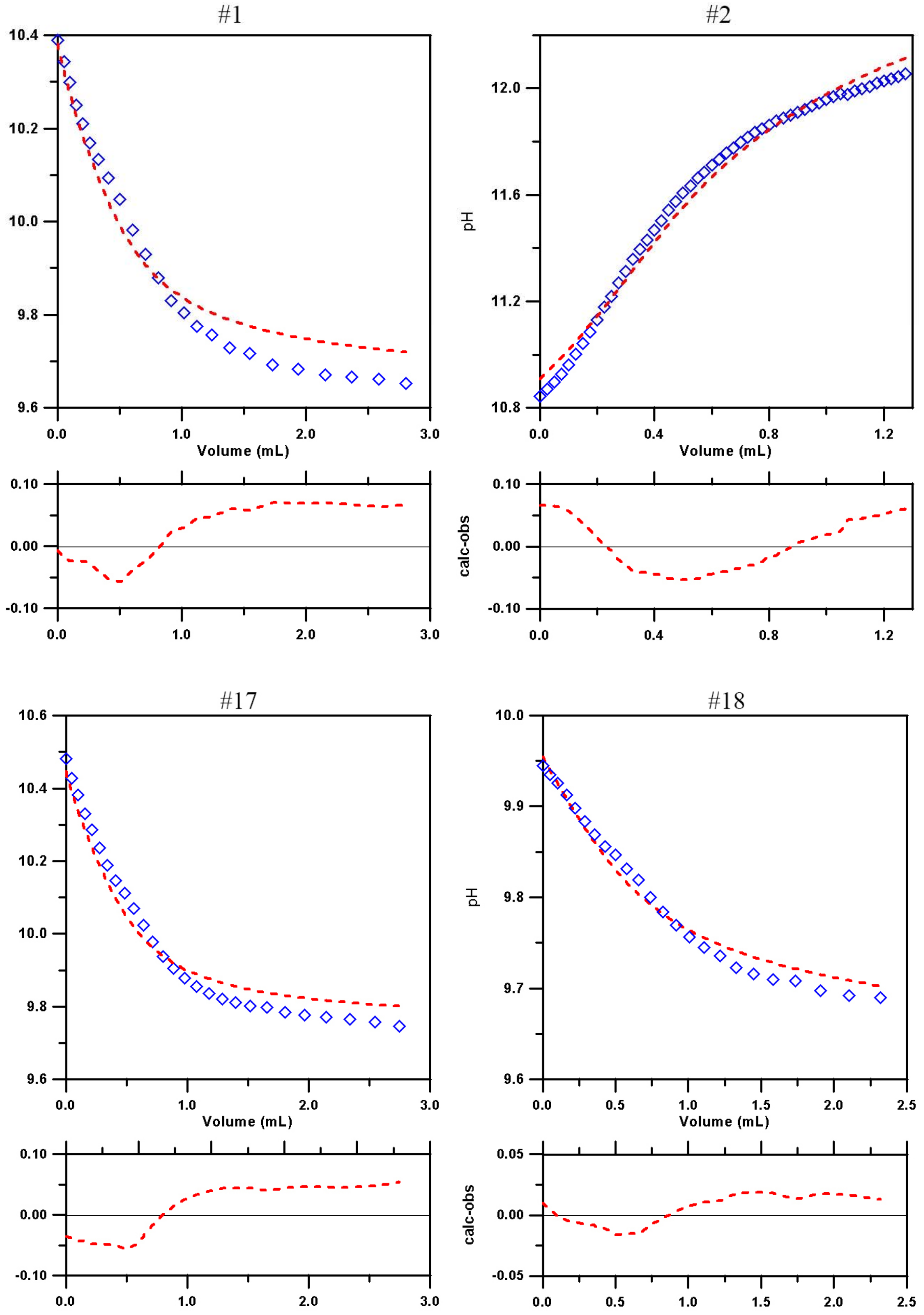


Figure S2. Comparison of experimental (diamonds) and calculated (- -) data for the Li$^+$ - uranyl(VI) – peroxide – carbonate system. The pH values were calculated with the stability constants of Table 3. Figures referring to titrations 1, 2, 17 and 18 that follow the ones for titrations 1 – 20 have been calculated using the model with cyclic oligomers.

C. *Potentiometric titrations, the TMA$^+$– uranyl(VI) – peroxide – carbonate system.*

Table S3A. Composition of test solutions used in the TMA$^+$ - uranyl(VI) – peroxide – carbonate system. Concentrations in mmol/dm^{-3}; the numbering is the same in the corresponding Figures S3.

	Titration Vessel								
	V_0 mL	C°_U mM	$C^\circ_{Carbonate}$ mM	C°_{H2O2} mM	C°_H mM	C^T_H mM	CT_U mM	C^T_{H2O2} mM	$C^T_{Carbonate}$ mM
1	44.5	-23.59	10.18	10.37	43.57	146.4	0	0	0
2	41.2	-27.9	5.48	5.84	47.2	146.4	0	0	0
3	77.0	-27.9	5.48	5.84	47.2	146.4	0	0	0
4	100.0	-11.4	1.33	1.31	19.4	146.4	0	0	0
5	77.6	-1.53	6.43	6.43	27.9	-156.0	0	0	0
6	41.2	0.87	22.0	24.0	71.4	-156.0	0	0	0
7	53.8	3.63	25.2	27.9	119	-156.0	0	0	0
8	41.4	3.46	7.68	8.47	32.8	-156.0	0	0	0
9	51.8	-6.62	4.34	5.15	18.9	0	0	0	193
10	77.9	-3.35	2.91	3.43	12.5	0	0	0	193
11	58.0	0.27	5.03	0	20.7	0	0	324	0
12	58.7	0.10	1.46	0	8.69	0	0	324	0
13	38.4	0.07	1.18	0	4.72	0	0	324	0
14	38.2	0.06	1.18	0	7.60	0	0	324	0
15	49.2	1.10	20.3	0	67.6	0	0	324	0
16	43.4	1.01	17.0	0	117.5	0	0	324	0
17	40.2	1.58	11.6	0	108	0	0	324	0
18	83.5	0.17	0.58	0	4.64	0	0	324	0
19	87.4	0.11	1.00	0	8.03	0	0	324	0

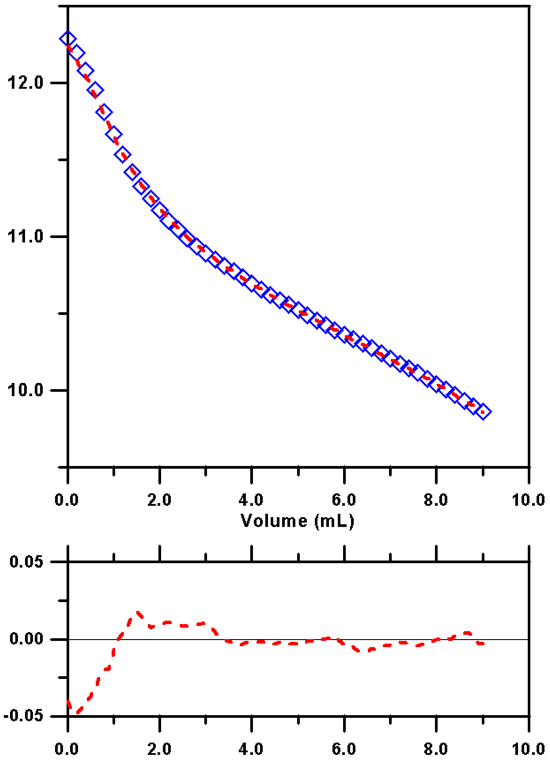
Table S3B. Results of the minimization procedures.

Model 1			Model 2		
Complex	log *K* ± σ	Overall σ	Complex	log *K* ± σ	Overall σ
-2, 2, 1, 4	27.59 ± 0.13	1.65	-2, 2, 1, 4	27.62 ± 0.14	1.65
-2, 1, 1, 2	3.72 ± 0.06		-2, 1, 1, 2	3.72 ± 0.06	
-10, 5, 5, 5	17.55 ± 0.31		-12, 6, 6, 6	21.76 ± 0.37	
Model 3			Model 4		
-2, 2, 1, 4	29.09 ± 0.09	1.14	-2, 2, 1, 4	29.09 ± 0.09	1.13
-2, 1, 1, 2	4.45 ± 0.04		-2, 1, 1, 2	4.45 ± 0.04	
-2, 2, 1, 3	25.36 ± 0.09		-2, 2, 1, 3	25.36 ± 0.09	
-10, 5, 5, 5	21.18 ± 0.13		-12, 6, 6, 6	25.96 ± 0.14	
Model 5					
-2, 2, 1, 4	29.09 ± 0.09	1.13			
-2, 1, 1, 2	4.45 ± 0.04				
-2, 2, 1, 3	25.36 ± 0.07				
-8, 4, 4, 4	16.42 ± 0.11				

Comparison between Model 1 and Model 3 demonstrates the importance of including species -2, 2, 1, 3 into the speciation scheme. Results of the error minimizations with Models 3, 4, and 5 show that the titration data are described equally well by the complexes -10, 5, 5, 5, -12, 6, 6, 6, and -8, 4, 4, 4. Attempts to use models which include any combination of the polymers in the minimization scheme failed. However the NMR measurements demonstrate that *only* a model that includes both -10, 5, 5, 5 and -12, 6, 6, 6, is consistent with the experimental data. It is not possible to make a least-squares optimization using a model which includes the stability constants of complexes with 5- and 6-membered rings of the data in the TMANO$_3$ system, but we can safely conclude that both are present as shown by the following reaction,, where the equilibrium constant for formation of [(UO$_2$)(O$_2$)(CO$_3$)]$^{2-}$ is taken from ref 7b.

$$[(UO_2)(O_2)(CO_3)]^{2-} + [(UO_2)(O_2)(CO_3)]_5^{-10} \rightarrow [(UO_2)(O_2)(CO_3)]_6^{-12} \qquad \log K_{6\text{-}5} \approx 3.3$$

#1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11.0
10.0
0.0
2.0
4.0
6.0
8.0
10.0
Volume (mL)
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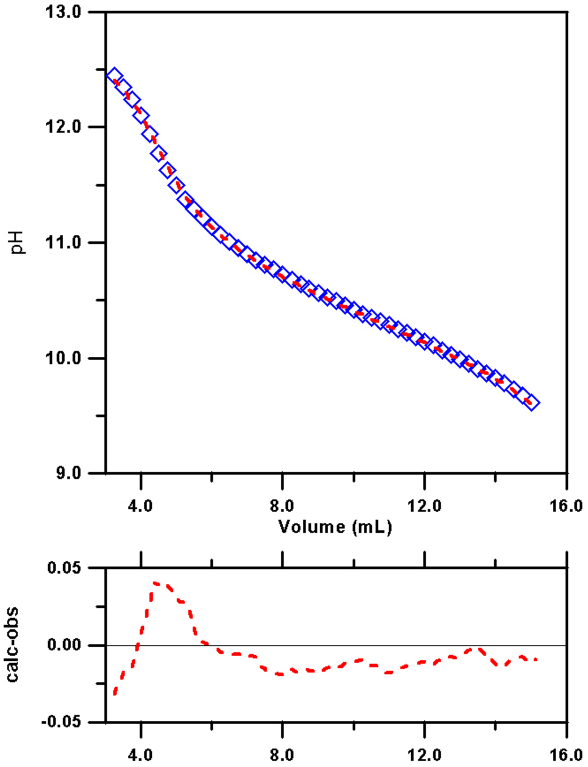
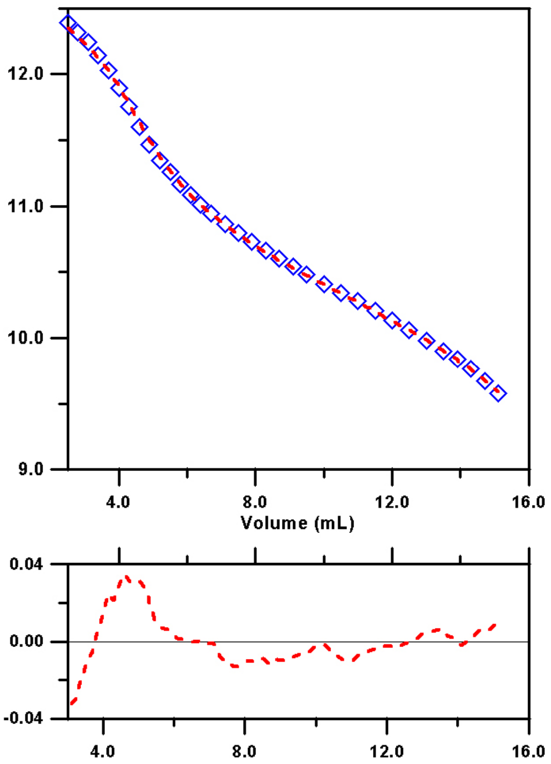
0.00
-0.05
0.0
2.0
4.0
6.0
8.0
10.0

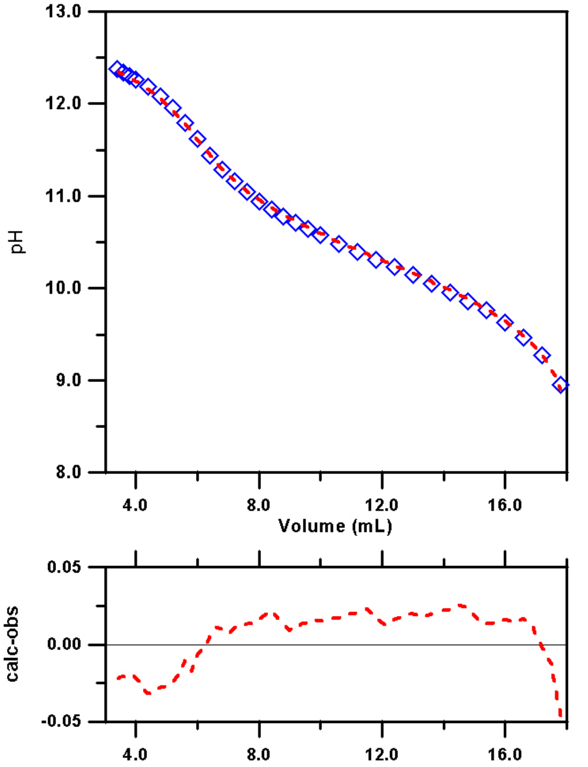
#2


13.0
12.0
pH
11.0
10.0
9.0
4.0
8.0
12.0
16.0
Volume (mL)
0.05
calc-obs
0.00
-0.05
4.0
8.0
12.0
16.0

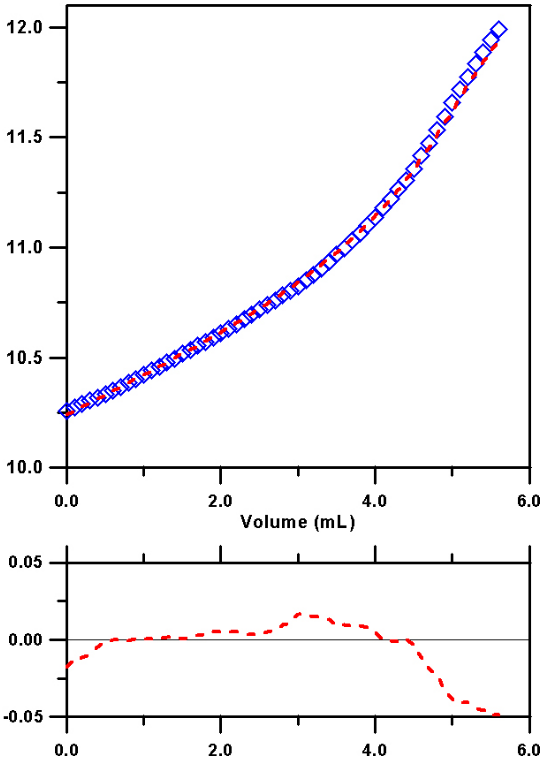
#3


12.0
11.0
10.0
9.0
4.0
8.0
12.0
16.0
Volume (mL)
0.04
0.00
-0.04
4.0
8.0
12.0
16.0

#4


13.0
12.0
pH
11.0
10.0
9.0
8.0
4.0
8.0
12.0
16.0
Volume (mL)
0.05
calc-obs
0.00
-0.05
4.0
8.0
12.0
16.0

#5


12.0
11.5
11.0
10.5
10.0
0.0
2.0
4.0
6.0
Volume (mL)
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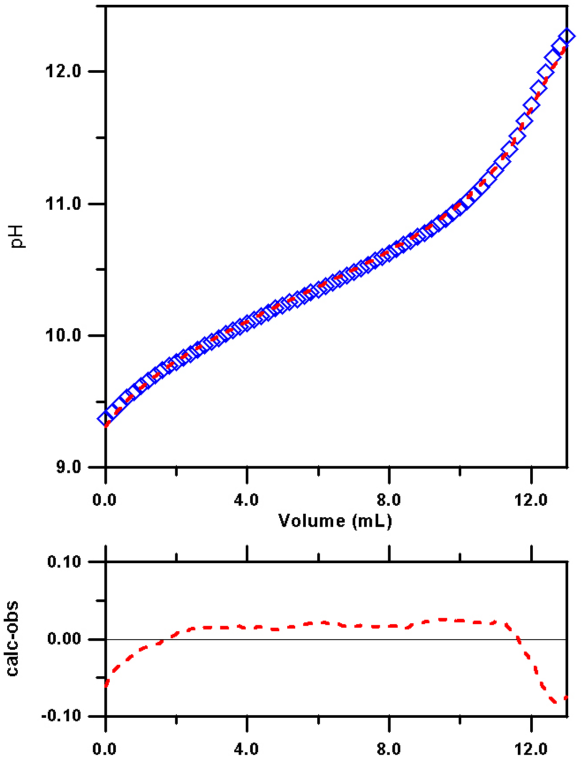
0.00
-0.05
0.0
2.0
4.0
6.0

#6


pH
12.0
11.0
10.0
9.0
0.0
4.0
8.0
12.0
Volume (mL)
calc-obs
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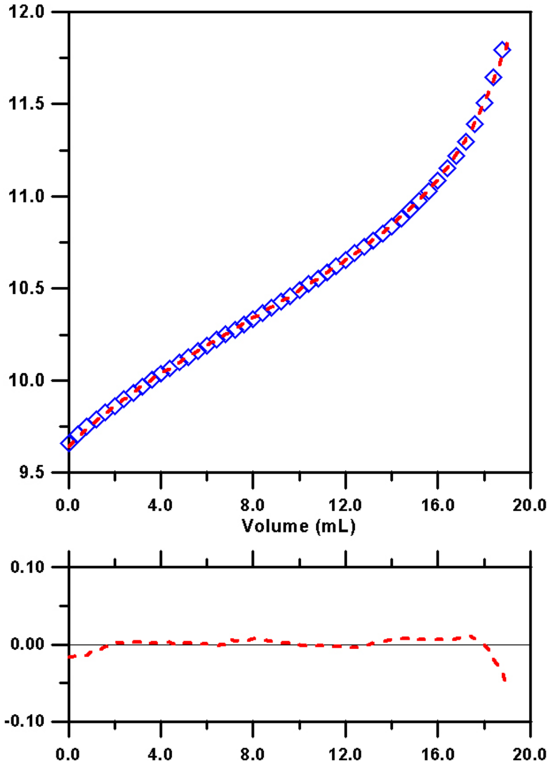
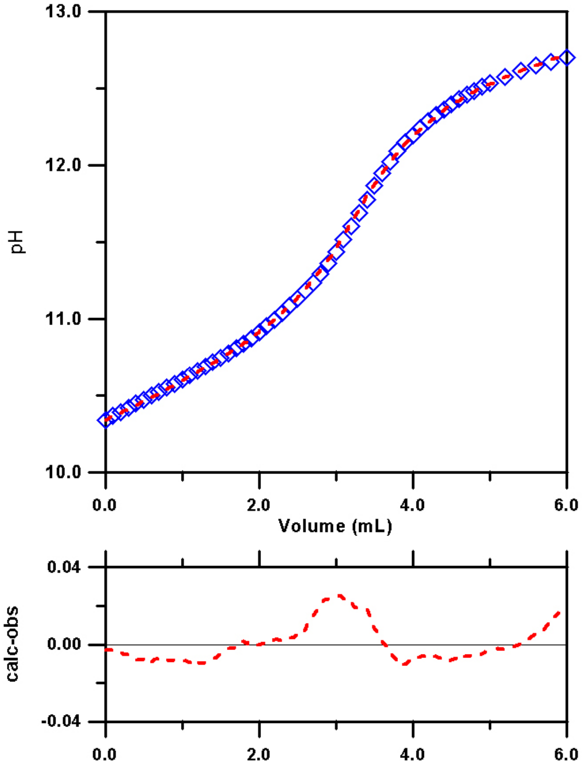
0.00
-0.10
0.0
4.0
8.0
12.0

#7


12.0
11.5
11.0
10.5
10.0
9.5
0.0
4.0
8.0
12.0
16.0
20.0
Volume (mL)
0.10
0.00
-0.10
0.0
4.0
8.0
12.0
16.0
20.0

#8


pH
13.0
12.0
11.0
10.0
0.0
2.0
4.0
6.0
Volume (mL)
calc-obs
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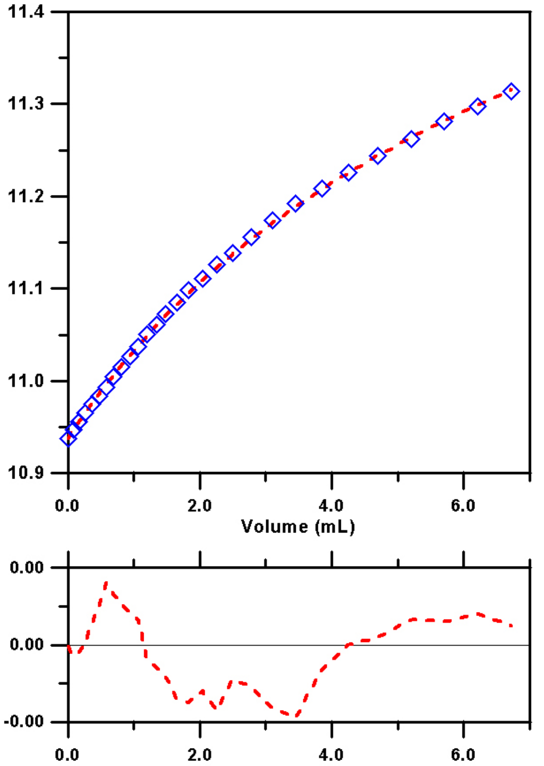
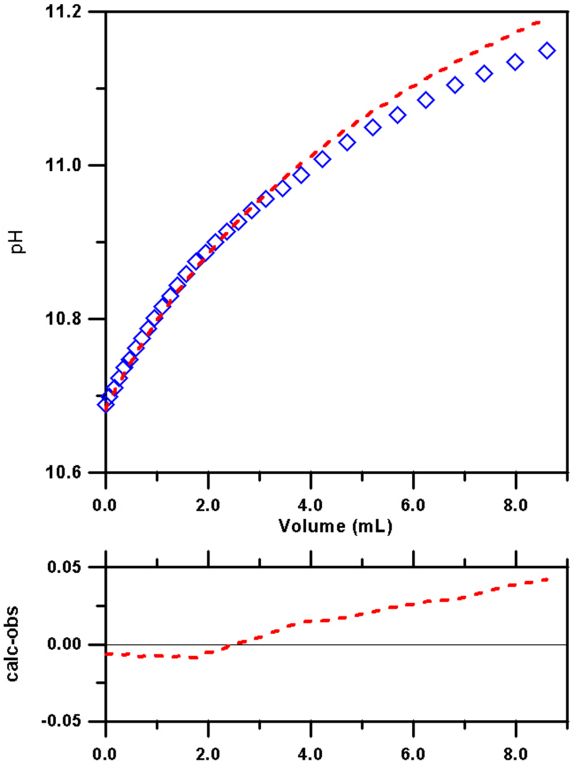
0.00
-0.04
0.0
2.0
4.0
6.0

#9


11.4
11.3
11.2
11.1
11.0
10.9
0.0
2.0
4.0
6.0
Volume (mL)
0.00
0.00
-0.00
0.0
2.0
4.0
6.0

#10


11.2
11.0
10.8
10.6
pH
0.0
2.0
4.0
6.0
8.0
Volume (mL)
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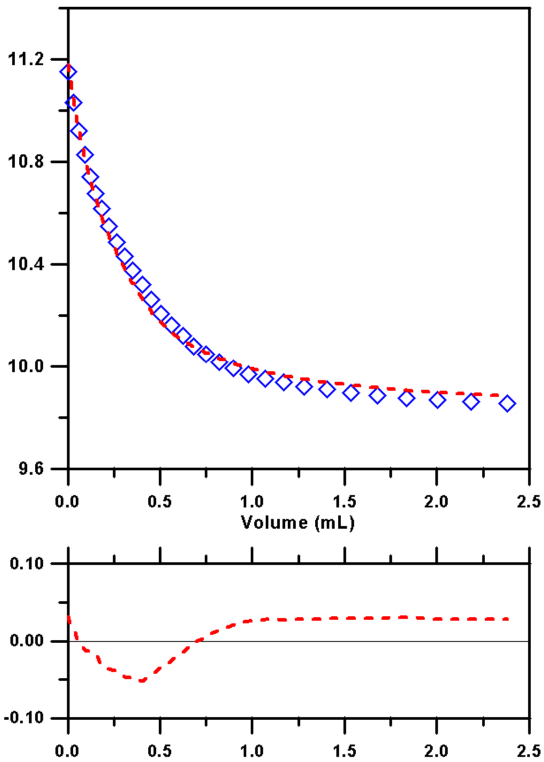
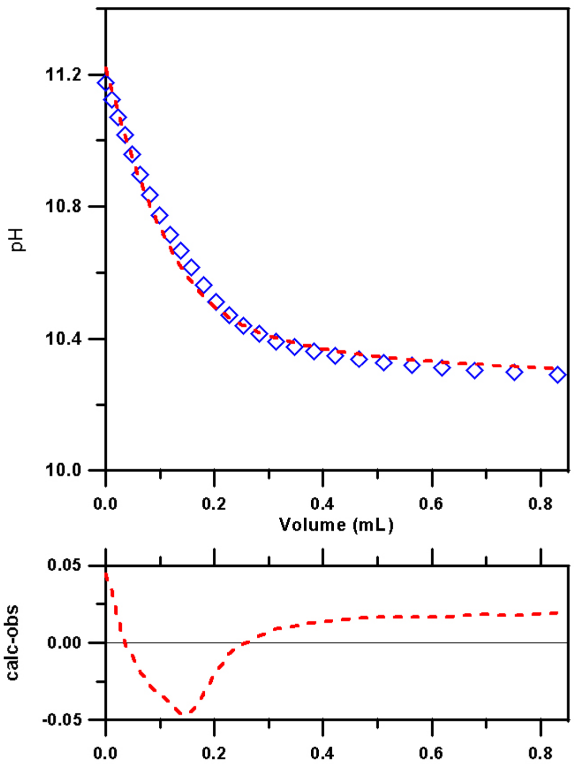
0.00
-0.05
calc-obs
0.0
2.0
4.0
6.0
8.0

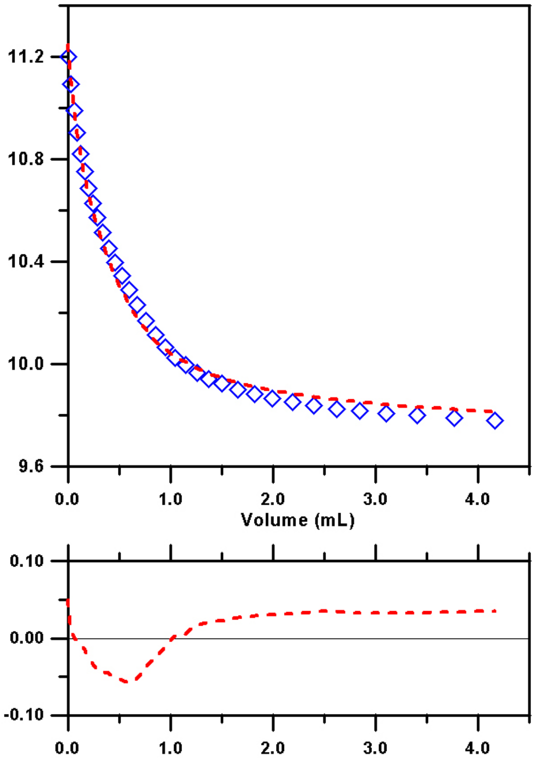
#11


11.2
10.8
10.4
10.0
9.6
0.0
0.5
1.0
1.5
2.0
2.5
Volume (mL)
0.10
0.00
-0.10
0.0
0.5
1.0
1.5
2.0
2.5

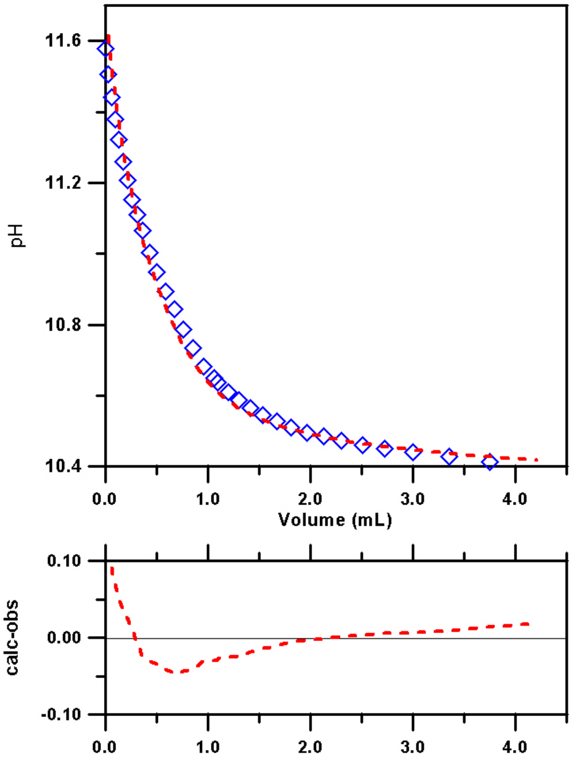
#12


11.2
10.8
10.4
10.0
pH
0.0
0.2
0.4
0.6
0.8
Volume (mL)
0.05
0.00
-0.05
calc-obs
0.0
0.2
0.4
0.6
0.8

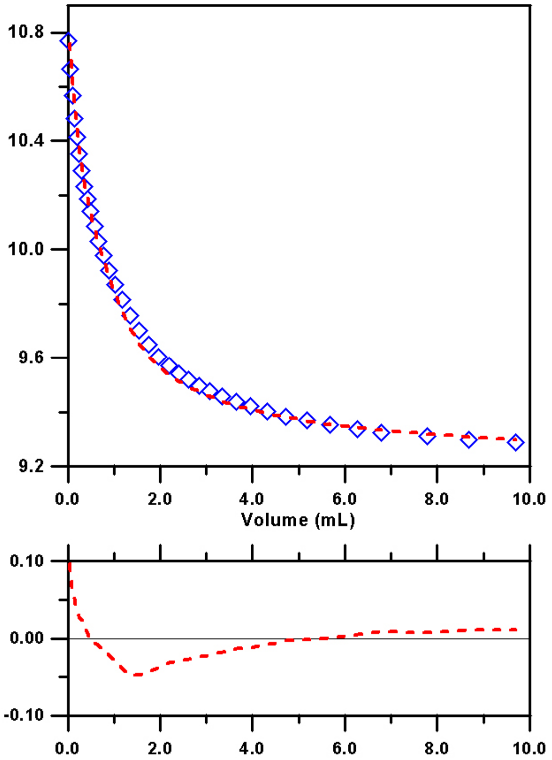
#13


11.2
10.8
10.4
10.0
9.6
0.0
1.0
2.0
3.0
4.0
Volume (mL)
0.10
0.00
-0.10
0.0
1.0
2.0
3.0
4.0

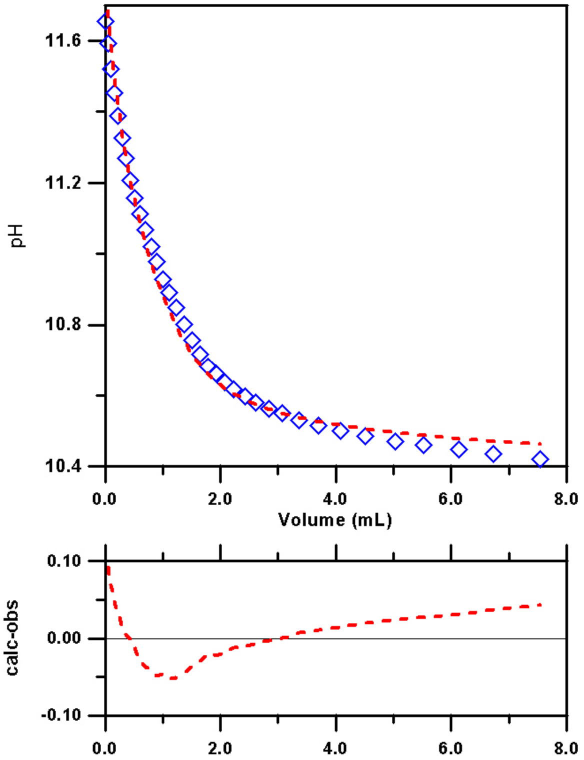
#14


11.6
11.2
10.8
10.4
pH
0.0
1.0
2.0
3.0
4.0
Volume (mL)
0.10
0.00
-0.10
calc-obs
0.0
1.0
2.0
3.0
4.0

#15


10.8
10.4
10.0
9.6
9.2
0.0
2.0
4.0
6.0
8.0
10.0
Volume (mL)
0.10
0.00
-0.10
0.0
2.0
4.0
6.0
8.0
10.0

#16


11.6
11.2
10.8
10.4
pH
0.0
2.0
4.0
6.0
8.0
Volume (mL)
0.10
0.00
-0.10
calc-obs
0.0
2.0
4.0
6.0
8.0

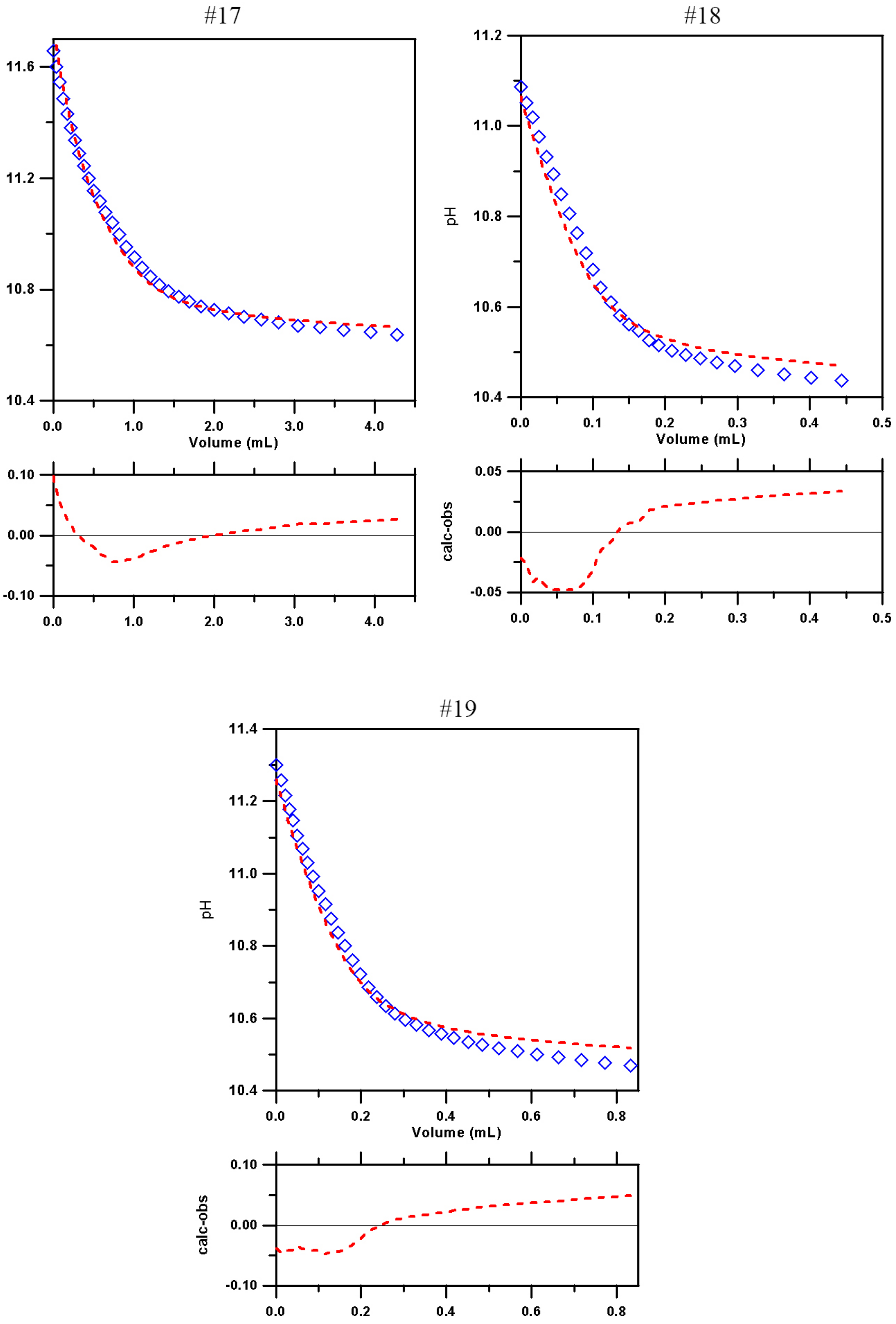


Figure S3. Comparison of experimental (diamonds) and calculated (- -) data for the TMA$^+$ - uranyl(VI) – peroxide – carbonate system. The pH values were calculated with the stability constants of Table 3, assuming the only presence of -10,5,5,5 in solution.

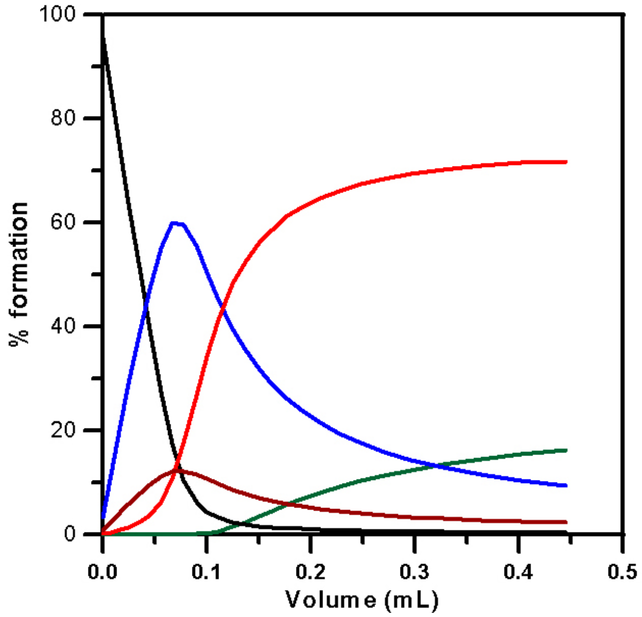


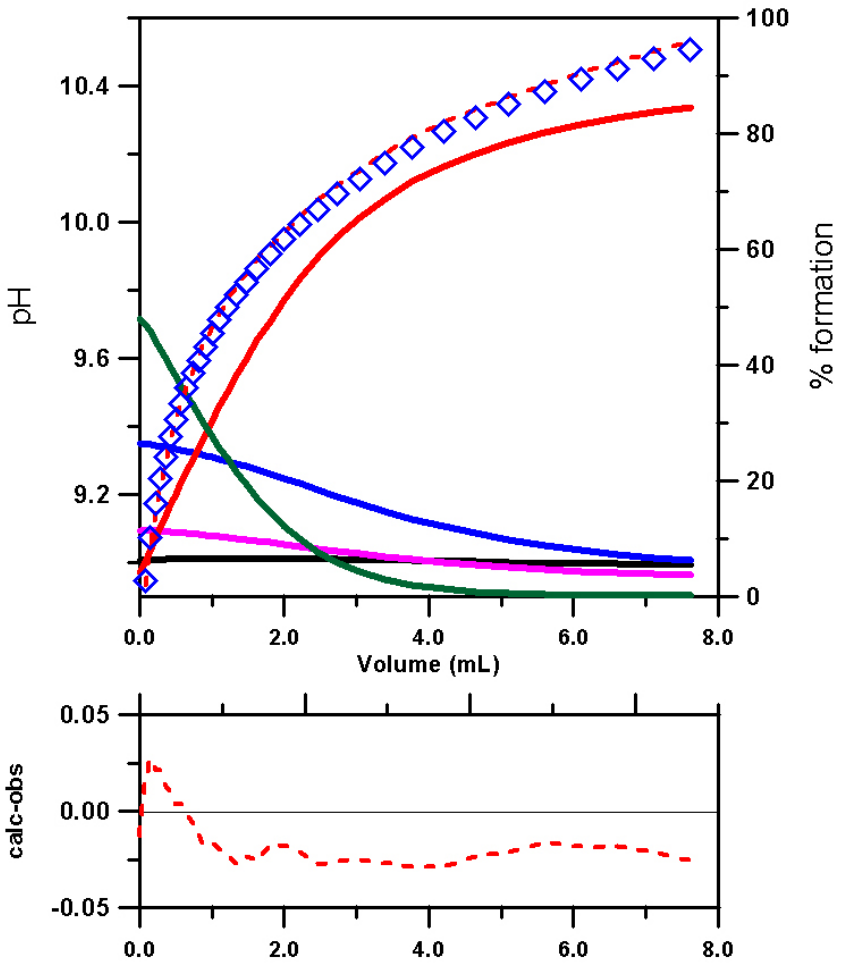
Figure S3b. Speciation in 0.50 M $TMANO_3$ - U(VI) – carbonate – peroxide system; color code (0, 1, 1, 3) black, (-2. 1, 2, 1, 4) blue; (-2. 2, 1, 3) green, (-10, 5, 5, 5) + (-12, 6, 6, 6), brown.

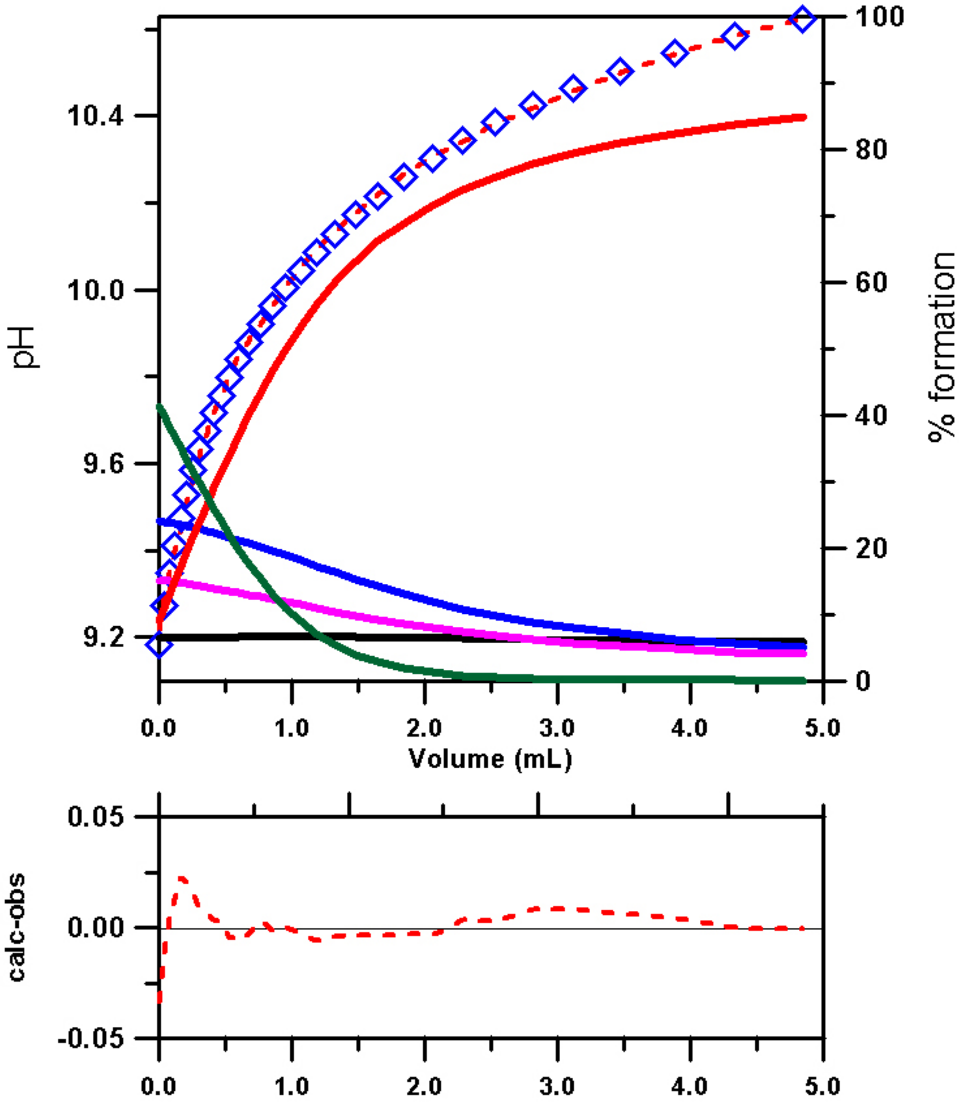
Table S4 A. Composition of test solutions used in the TMA^+ - uranyl(VI) – peroxide – carbonate system in 0.40 M $TMANO_3$ / 0.10 M $NaNO_3$ ionic medium. Concentrations in mmol/dm^{-3}.

	CUP				TITRANT		
	V_0	UO_2^{2+}	CO_3^{2-}	H_2O_2	H^+	CO_3^{2-}	H_2O_2
1	45.0	6.85	24.2	7.71	25	259	0
2	29.8	2.65	8.67	2.48	25	259	0
3	33.6	4.63	16.37	4.96	25	259	0

Table S4b. Result of least-squares optimization

Chi-squared = 13.73 sigma = 0.86911
0 1 0 3 constant 22.7900 **BLACK**
-2 2 1 4 constant 27.6900 **BLUE**
-2 1 1 1 constant 1.4700 **MAGENTA**
-2 1 1 2 constant 4.3700 **RED**
-2 2 1 2 constant 18.3100, the concentration of this complex is negligible and was removed from the optimization
-10 5 5 5 refined 19.6915 0.0951 **GREEN**


10.4
10.0
9.6
9.2
pH
100
80
60
40
20
0
% formation
0.0
2.0
4.0
6.0
8.0
Volume (mL)
0.05
0.00
-0.05
calc-obs
0.0
2.0
4.0
6.0
8.0


pH
10.4
10.0
9.6
9.2
% formation
100
80
60
40
20
0
0.0
1.0
2.0
3.0
4.0
5.0
Volume (mL)
calc-obs
0.05
0.00
-0.05
0.0
1.0
2.0
3.0
4.0
5.0

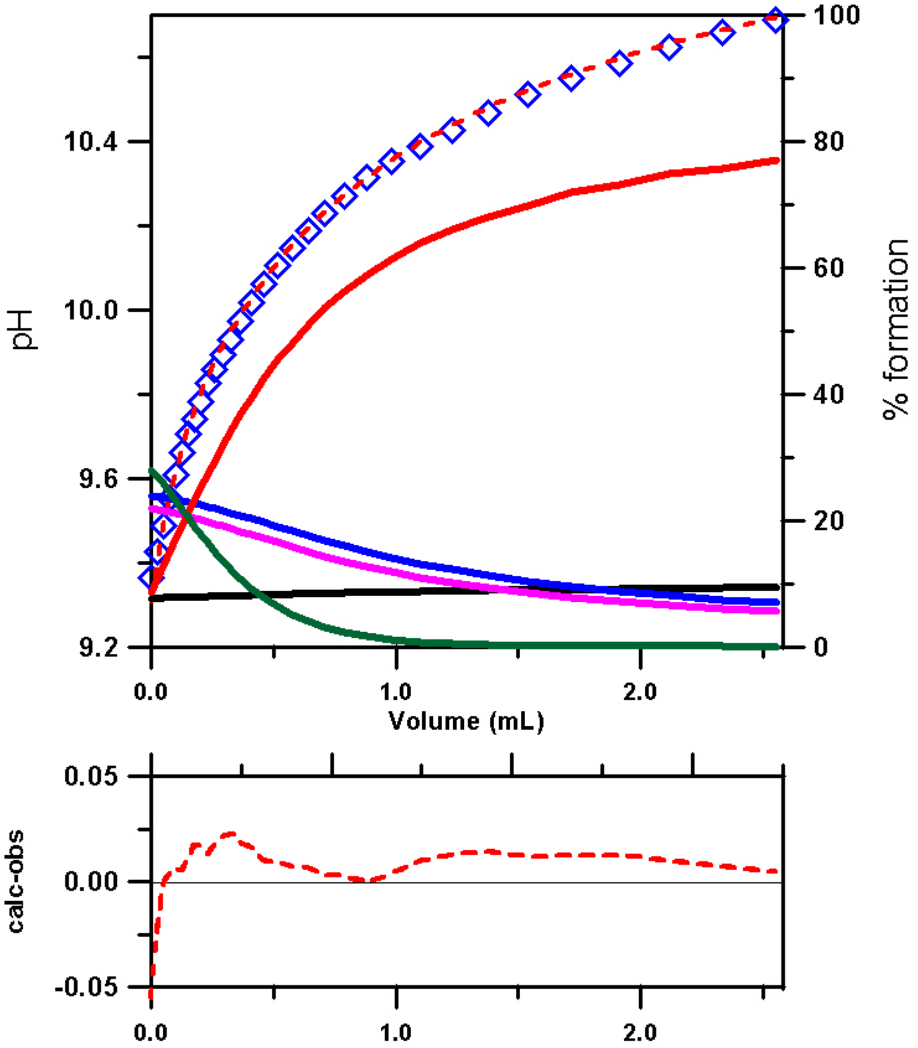
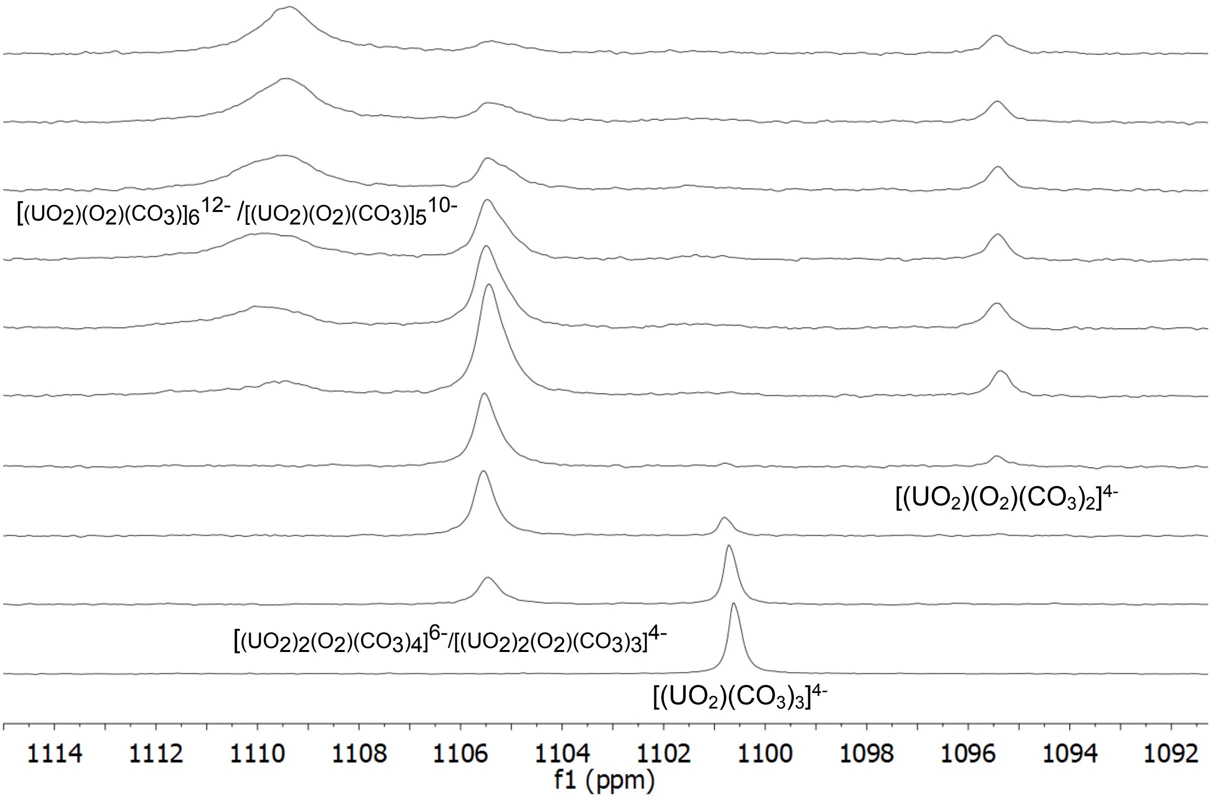
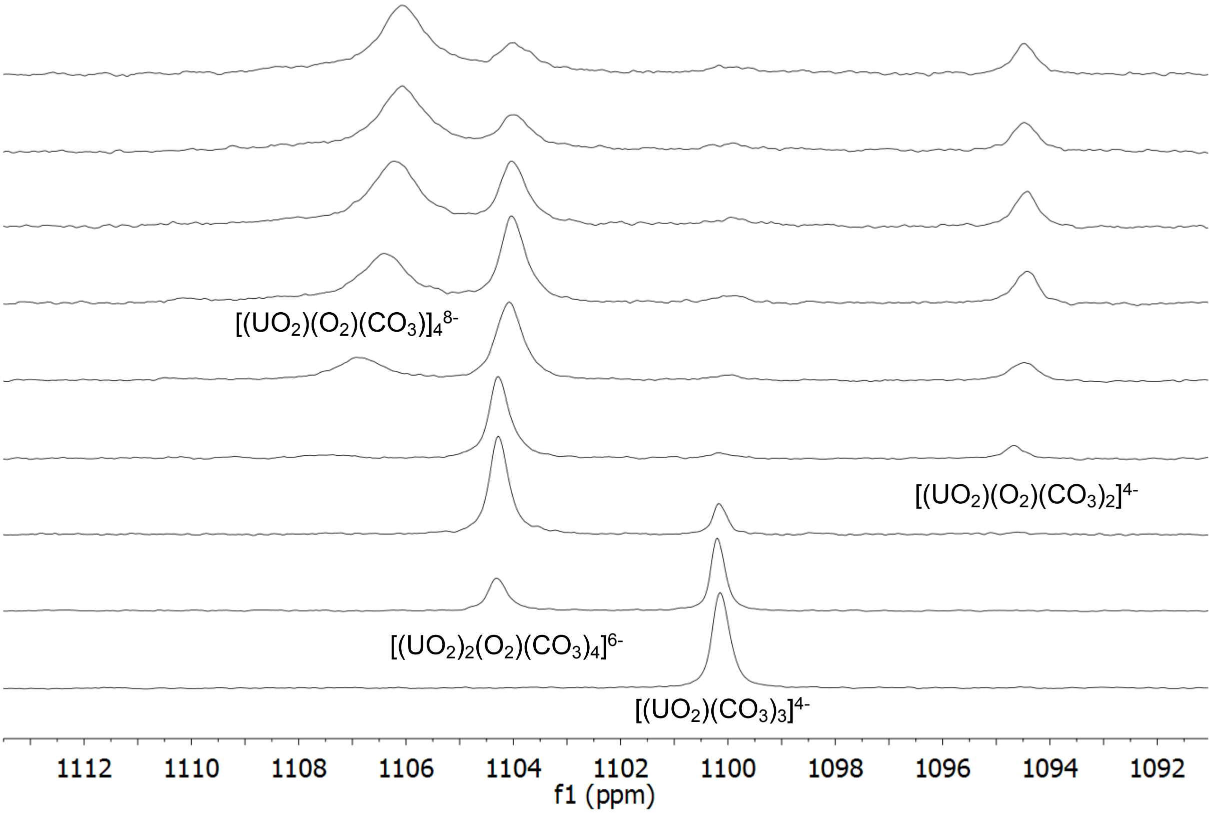


Figure S4. Comparison of experimental (diamonds) and calculated (- -) data for the TMA$^+$ - uranyl(VI) – peroxide – carbonate system. The pH values were calculated with the stability constants of Table S4b. Color code: (0,1, 0, 3) black; (-2, 2, 1, 4) blue; (-2, 1, 1, 1) magenta; (-2, 1, 1, 2) red; (-10, 5, 5, 5) green.

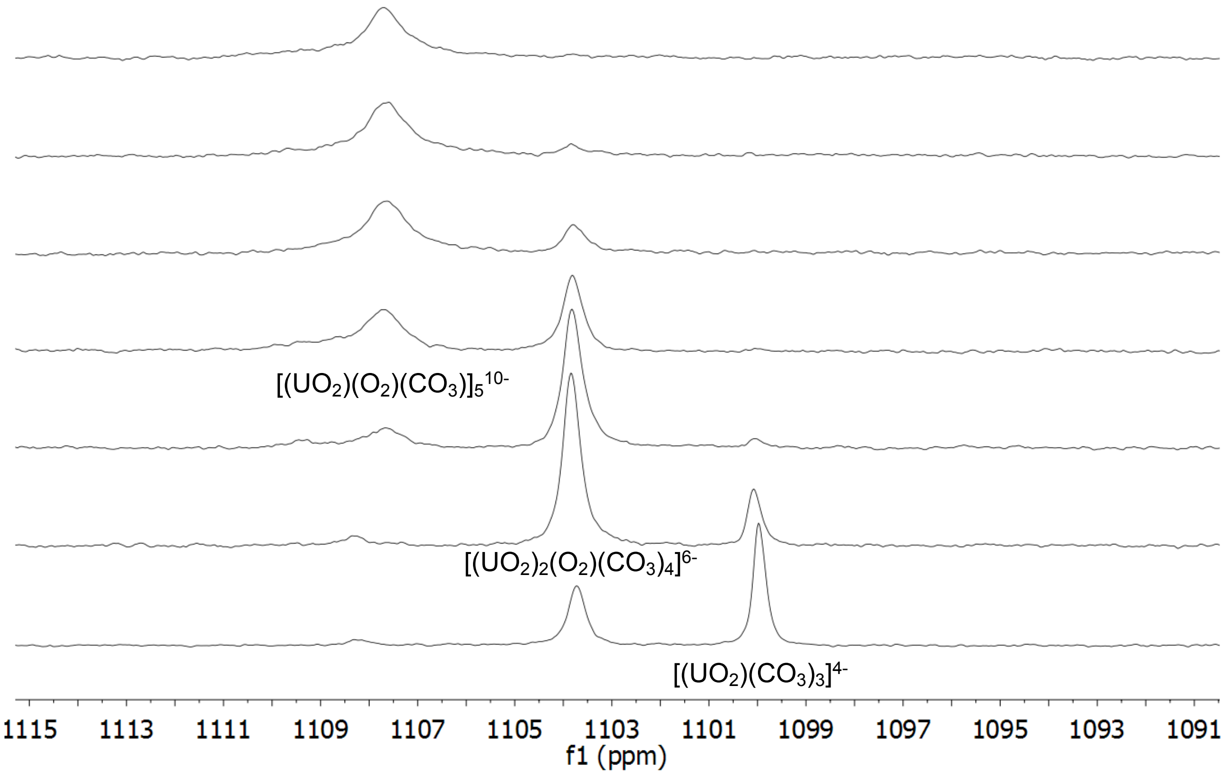
D. ^{17}O-NMR titrations



a.) H_2O_2 concentration dependence of the ^{17}O-NMR spectra measured in the TMA-carbonate system. The initial test solution had a total concentration of U(VI) equal to 20 mM and a total concentration of TMA_2CO_3 equal to 70 mM. The total H_2O_2 concentrations from bottom to top: 0, 4.7, 9.2, 13.7, 17.9, 22.0, 27.7, 38.3, 48.0 and 61.2 mM. The deconvoluted peaks for the broad signals at around 1110 and 1105 ppm are shown in Figure 3 in the main text.



b.) H_2O_2 concentration dependence of the ^{17}O-NMR spectra measured in the Li-carbonate system. The initial test solution had a total concentration of U(VI) equal to 20 mM and a total concentration of Li_2CO_3 equal to 70 mM. The total H_2O_2 concentrations from bottom to top: 0, 4.7, 9.2, 13.7, 17.9, 22.0, 27.7, 38.3 and 48.0 mM.



c.) H_2O_2 concentration dependence of the ^{17}O-NMR spectra measured in the K-carbonate system. The initial test solution had a total concentration of U(VI) equal to 20 mM and a total concentration of K_2CO_3 equal to 70 mM. The total H_2O_2 to concentrations from bottom to top: 4.7, 9.2, 13.7, 17.9, 22.0, 27.7 and 38.3 mM.

Figure S5. ^{17}O NMR titrations of test solutions with the initial concentrations of uranyl and carbonate those are 20 and 70 mM. The carbonate solutions were prepared from $(TMA)_2CO_3$ Figure (a), Li_2CO_3 Figure (b) and K_2CO_3 Figure (c). 4.00 ml of test solutions were titrated with successive amounts of a 274.4 mM solution of H_2O_2. The total concentrations of H_2O_2 are given below the figures.

Table S5. ^{17}O-NMR chemical shifts of the exchange averaged signal of TMA[$(UO_2)(O_2)(CO_3)]_6^{11-}$ (1) and Na[$(UO_2)(O_2)(CO_3)]_6^{11-}$ (2). The total concentrations of the complexes were calculated from the intensities of the deconvoluted peaks (red signals) shown in Figure 3. The values (*in italic*) calculated for samples 3, 4 and 5 reflect the unambiguity of the deconvolution procedure.

Sample	Chemical shift (ppm)	Total conc. of (1) and (2) mM	Total conc. of Na^+ mM	*X*
1	1109.22	14.7	0	1.0
2	1109.04	10.6	9.5	0.94
3	1108.62	*9.2*	19.0	0.78
4	1108.35	*10.0*	28.4	0.67
5	1107.97	*10.2*	37.6	0.53
6	1107.33	7.4	48.4	0.28
7	1107.08	3.8	111.8	0.18
8	1106.91	3.2	146.7	0.12

E Spectrophotometric titrations

Table S6. Spectrophotometric titration in the uranyl(VI) – Peroxide – $(TMA)_2CO_3$ system at 25 ^oC. All concentrations are given in $mmol/dm^{-3}$.

N	$C^0(UO_2^{2+})$ mM	$C^0(CO_3^{2-})$ mM	$C^0(H^+)$ mM	Titrant (H_2O_2) mM
1	0.048	50.1	0.018	2.17
2	0.102	47.3	0.038	2.17
3	0.197	44.0	0.073	2.17
4	0.863	49.9	0.323	13.10
5	2.09	9.80	0.78	87.7

The agreement between the experimental and calculated absorptivity of titration 5 at five selected wave-lengths is given in Figure S5 below, together with the relative amounts of the different complexes. The concentration of the complexes -2, 2, 1, 3 and the polymers is so small to have a noticeable influence in this titration.

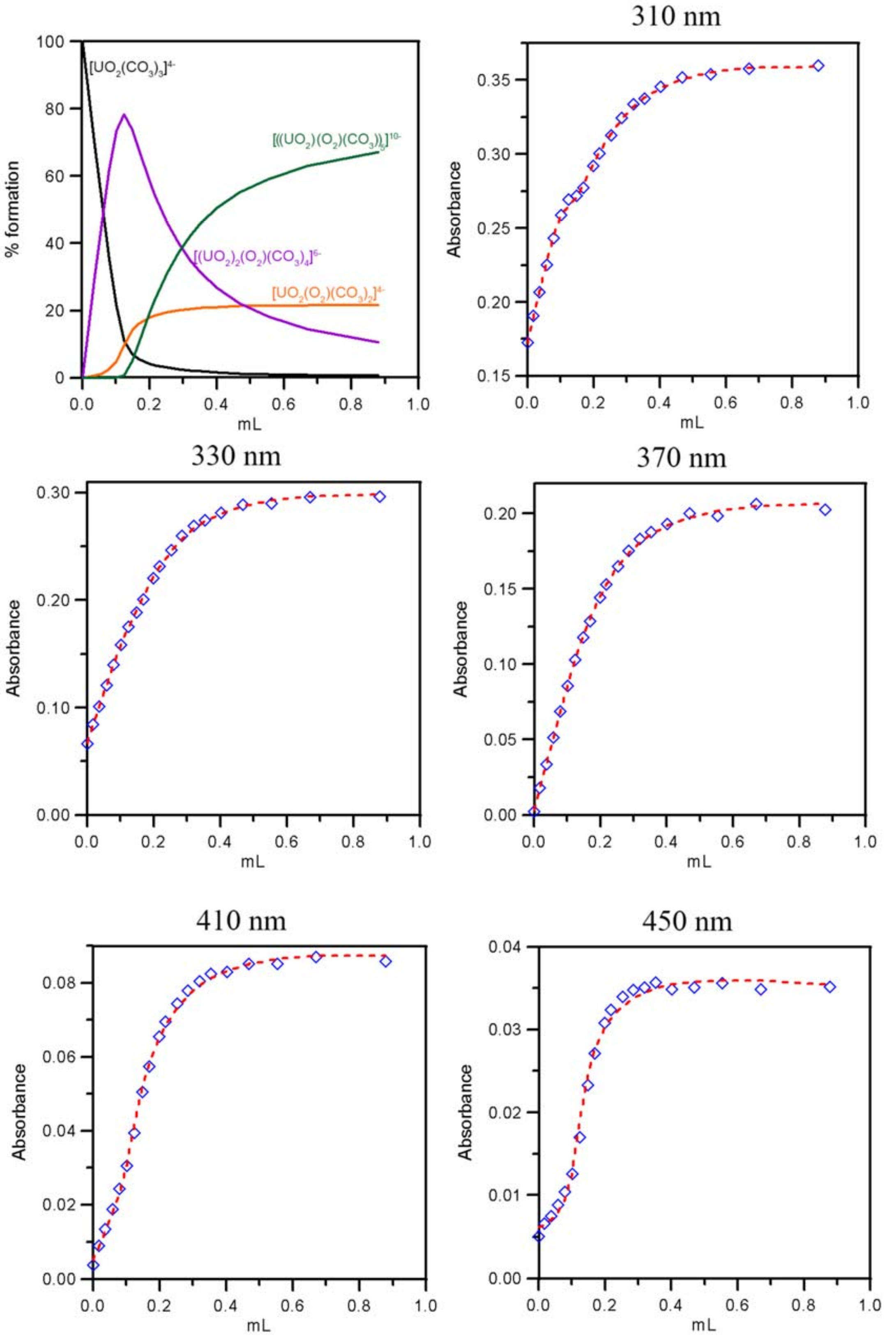


Figure S6. Spectrophotometric titration in the uranyl(VI) – Peroxide – $(TMA)_2CO_3$ system at 25 °C. Color code: $[(UO_2)(CO_3)_3]^{4-}$, black; $[(UO_2)_2(O_2)(CO_3)]_4^{6-}$**,** purple; $[(UO_2)(O_2)(CO_3)_2]^{4-}$, orange; $[(UO_2)(O_2)(CO_3)]_5^{10-}$, green.

Table S7. Spectrophotometric titration in the uranyl(VI) – Peroxide – Li_2CO_3 system at 25 ^oC. All concentrations are given in mmol dm^{-3}.

N	$C^0(UO_2^{2+})$ mM	$C^0(CO_3^{2-})$ mM	$C^0(H^+)$ mM	Titrant (H_2O_2) mM
1	0.044	50.2	0.016	1.66
2	0.102	49.8	0.038	1.66
3	0.190	49.2	0.071	5.58
4	0.456	47.6	0.164	14.1
5	2.10	12.3	0.79	68.6

The agreement between the experimental and calculated absorptivity of titration 5 at five selected wave-lengths is given in Figure S6 below together with the relative amounts of the different complexes. The concentration of the complex -2, 2, 1, 2 is negligible in this titration.

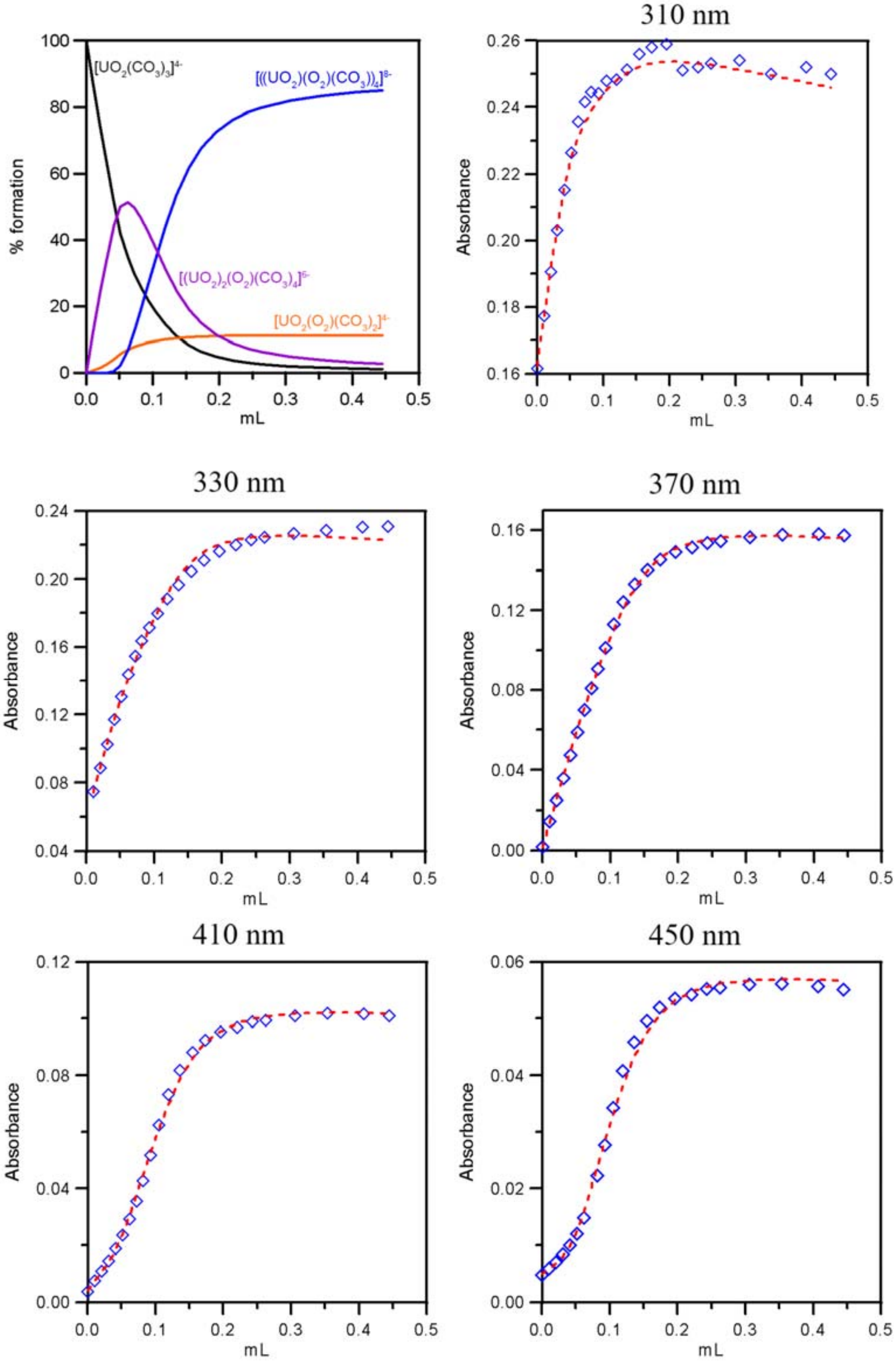


Figure S7. Spectrophotometric titration in the uranyl(VI) – Peroxide – Li_2CO_3 system at 25 °C. Color code: $[(UO_2)(CO_3)_3]^{4-}$, black; $[(UO_2)_2(O_2)(CO_3)_4]^{6-}$, purple; $[(UO_2)(O_2)(CO_3)_2]^{4-}$, orange; $[(UO_2)(O_2)(CO_3)]_4{}^{8-}$, blue.

Table S8. Spectrophotometric titrations in the uranyl(VI) – Peroxide – K_2CO_3 system at 25 ^oC. All concentrations are given as mmol dm^{-3}.

N	$C^0(UO_2^{2+})$ mM	$C^0(CO_3^{2-})$ mM	$C^0(H^+)$ mM	Titrant (H_2O_2) mM
1	0.050	50.2	0.019	4.63
2	0.101	49.0	0.038	4.63
3	0.354	49.4	0.130	4.63
4	0.842	48.3	0.310	13.10
5	2.04	10.1	0.76	33.3

The agreement between the experimental and calculated absorptivity of titration 5 at five selected wave-lengths is given in Figure S7 below together with the relative amounts of the different complexes. The concentration of the complex -2, 2, 1, 2 is negligible in this titration.

Table S9. Conditional equilibrium constants, log*K*, at 25 °C for the formation of the major complexes at 25 °C in 0.50 M $\mathrm{MNO_3}$ ionic media, M = $\mathrm{TMA^+}$, $\mathrm{Li^+}$ and $\mathrm{K^+}$ using spectrophotometric titrations. The constants refer to reaction (3) $p\mathrm{UO_2}^{2+} + q\mathrm{H_2O_2} + r\mathrm{CO_3}^{2-} \rightarrow [(\mathrm{UO_2})_p(\mathrm{O_2})_q(\mathrm{CO_3})_r]^{2(p-q-r)} + 2q\mathrm{H^+}$; the notation is the same as in Table 1. The estimated uncertainty is reported at the 3σ level and the overall agreement between the measured and calculated absorptivity varies between 0.002 and 0.005 absorption units.

Model 1			
-2*q*, *p*, *q*, *r*	0.5 M TMANO$_3$	0.5 M LiNO$_3$	0.5 M KNO$_3$
-2, 2, 1, 4	27.58 ± 0.02	26.65 ± 0.03	27.43 ± 0.03
-2, 1, 1, 2	4.20 ± 0.01	3.50 ± 0.02	4.09 ± 0.03
-10, 5, 5, 5	20.85 ± 0.05	20.56 ± 0.36	21.23 ± 0.13
σ	0.0024	0.0053	0.0045
Model 2			
-2, 2, 1, 4	27.56 ± 0.02	26.65 ± 0.03	27.43 ± 0.03
-2, 1, 1, 2	4.20 ± 0.01	3.51 ± 0.02	4.09 ± 0.03
-8, 4, 4, 4	16.16 ± 0.05	16.76 ± 0.18	16.18 ± 0.11
σ	0.0023	0.0054	0.0045
Model 3			
- 2, 2, 1, 4	27.52 ± 0.02	26.65 ± 0.03	27.43 ± 0.03
-2, 1, 1, 2	4.18 ± 0.01	3.56 ± 0.02	4.09 ± 0.03
-12, 6, 6, 6	25.81 ± 0.05	25.26 ± 0.42	26.55 ± 0.15
σ	0.0023	0.0053	0.0044

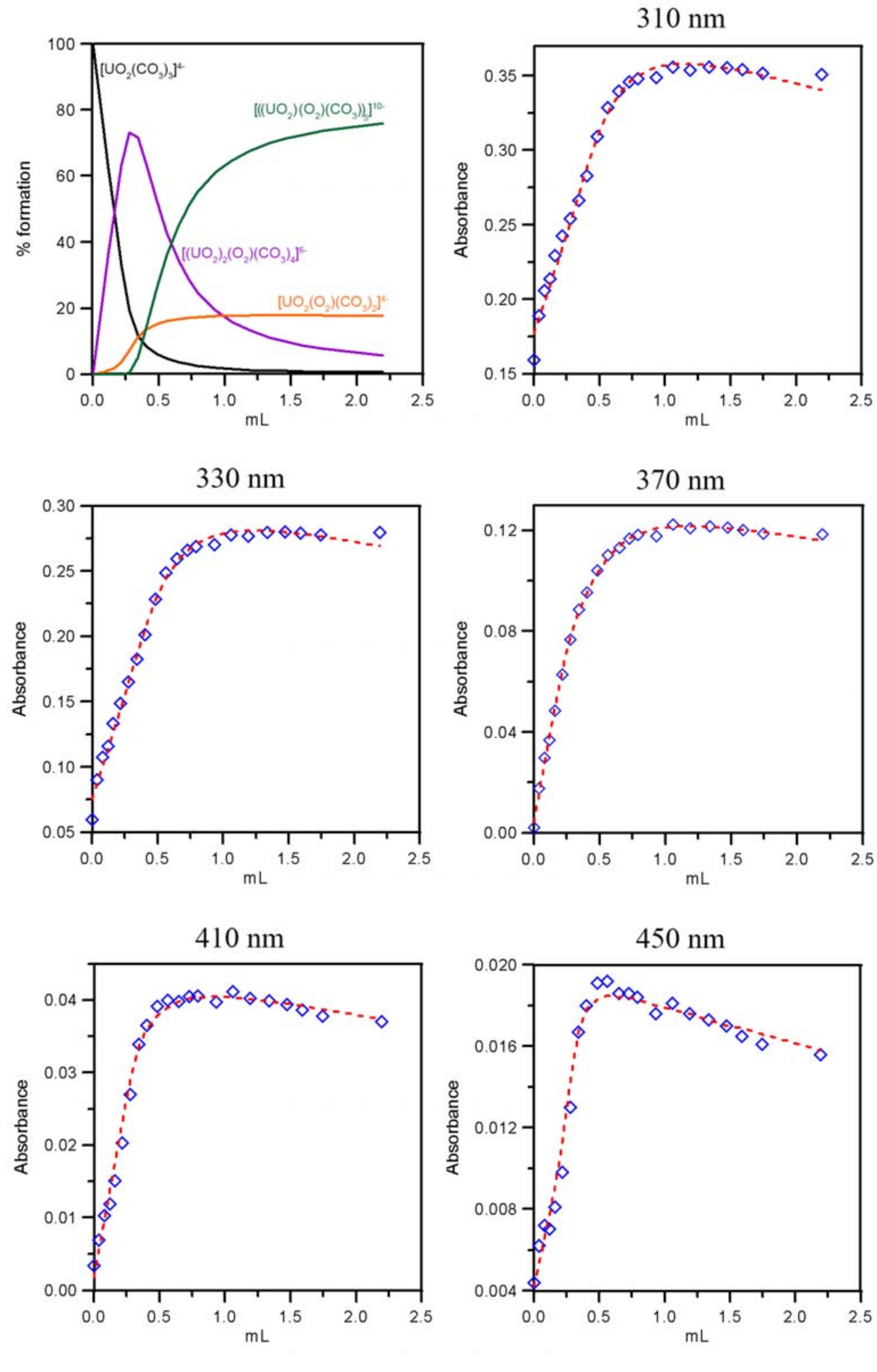


Figure S8. Spectrophotometric titration in the uranyl(VI) – Peroxide – K_2CO_3 system at 25 °C. Color code: $[(UO_2{}^{)}(CO_3)_3]^{4-}$, black; $[(UO_2)_2(O_2)(CO_3)_4]^{6-}$, purple; $[(UO_2)(O_2)(CO_3)_2]^{4-}$, orange; $[(UO_2)(O_2)(CO_3)]_5{}^{10-}$, green. The concentration of the complex -2, 2, 1, 2 is negligible in this titration.

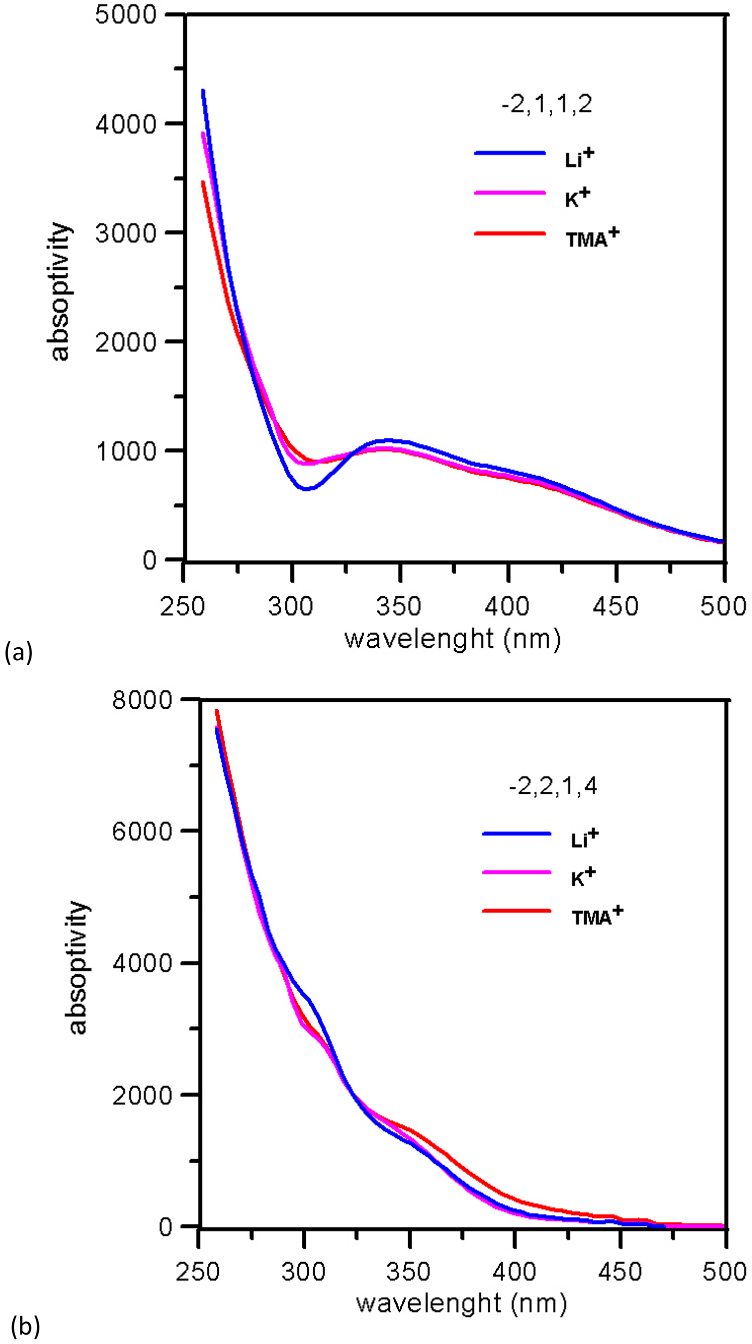


Figure S9. Absorption spectra of the complexes (a) $[(UO_2)(O_2)(CO_3)_2]^{4-}$ and (b) $[(UO_2)_2(O_2)(CO_3)_4]^{6-}$ in MNO_3 ionic media, M = Li, K, TMA.

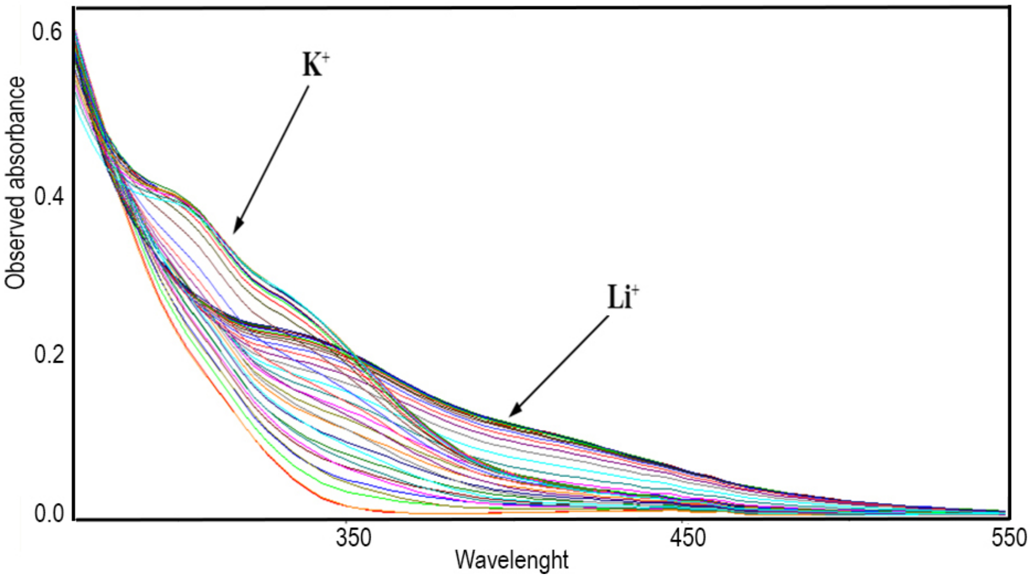


Figure S10. Comparison of spectrophotometric titration data for the potassium and lithium peroxide – carbonate systems. Note that the wave length scale goes from higher to lower wave lengths. Analytical details are given in Table S9, titr. 5 and Table S8, titr. 5, for the K^+ and Li^+ systems, respectively. The corresponding speciation at pH 9.6 – 10.3 are shown in Figures S7 and S8.