Electronic Supplementary Information for Dalton Transactions

Paper: Thermodynamics of the Complexation of Uranium(VI) with Oxalate in Aqueous Solution at 10 - 70 °C

Plinio Di Bernardo*[,a], Pier Luigi Zanonato[a], Guoxin Tian[b], Marilena Tolazzi[c], Linfeng Rao*[,b]

Electronic supplementary information

Table S1: Experimental conditions of potentiometry for oxalate protonation.
Table S2: Experimental conditions of spectrophotometry for U(VI)/oxalate complexation.
Table S3. Experimental conditions of calorimetry for oxalate protonation.
Table S4. Experimental conditions of calorimetry for U(VI)/oxalate complexation.
Figures S1a, S1b, S1c: The distribution plots concerning the systems U(VI)/oxalate studied by spectrophotometric titrations at different –log[H^+].

Table S1. Experimental conditions of potentiometry for oxalate protonation. I = 1.05 mol·kg^{-1} $NaClO_4$. $C_{H,T}$ and $C°_{ox}$ represent the stoichiometric concentrations of proton and total oxalate.

t, °C	Cup Solution		Titrant
	V^0 / cm^3	$C_{ox}°$ / mmol·dm^{-3}	$C_{H,T}$ / mol·dm^{-3}
10	25.09	9.22	1.015
	25.09	19.13	1.015
	25.09	31.11	1.015
25	25.00	15.10	1.015
	25.00	27.05	1.015
	36.50	38.58	1.015
40	25.00	11.04	1.015
	31.85	21.74	1.015
	25.00	36.39	1.015
55	25.09	13.80	1.015
	25.09	24.04	1.015
	25.00	41.00	1.015
70	25.09	11.22	1.015
	25.09	22.13	1.015
	25.09	36.70	1.015

Table S2. Experimental conditions of spectrophotometry for U(VI)/oxalate complexation. I = 1.05 mol·kg^{-1} $NaClO_4$. C_U, C_H and C_{ox} represent the stoichiometric concentrations of uranium, proton and total oxalate. * Indicates titrations carried out at LBNL.

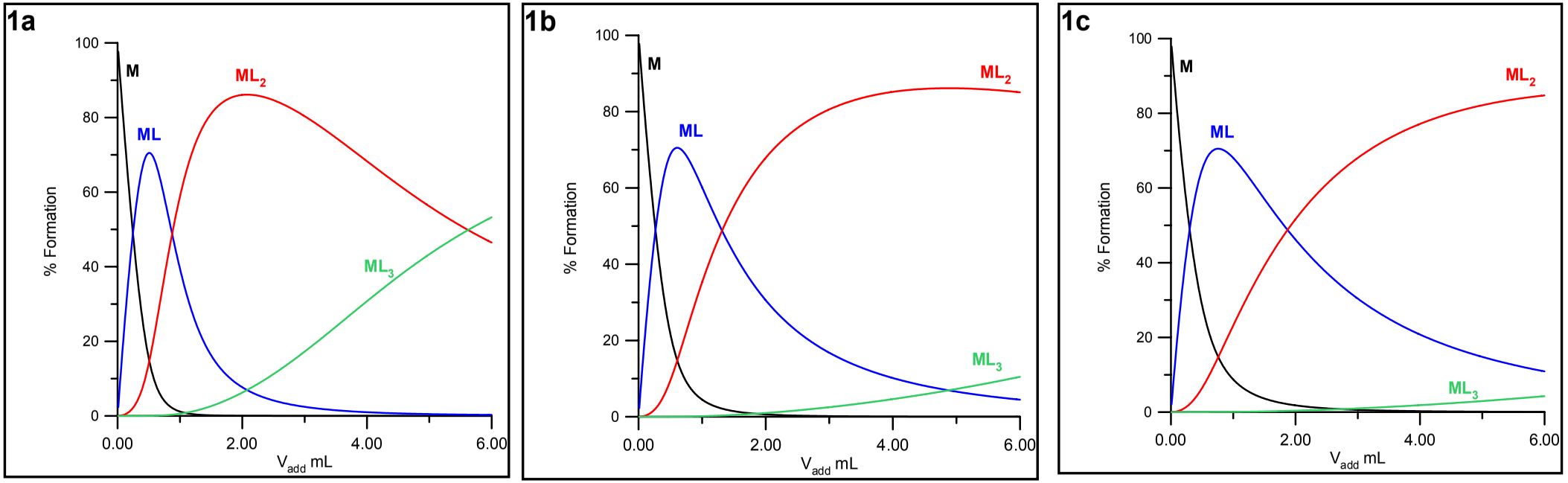
t, °C	Cup Solution				Titrant			
	V^0 cm^3	$C_U°$ mmol·dm^{-3}	$C_H°$ mmol·dm^{-3}	$C_{ox}°$ mmol·dm^{-3}	$C_{H,T}$ mmol·dm^{-3}	$C_{ox,T}$ mmol·dm^{-3}	$C_{U,T}$ mmol·dm^{-3}	
10	2.99	12.68	19.97	0.0	30.0	90.34	12.67	
	3.01	12.75	120.0	0.0	30.0	90.34	12.67	
	2.97	12.85	220.0	0.0	30.0	90.34	12.67	
	2.50	14.16	16.96	0.0	0.0	100.0	0.0	*
25	3.00	12.68	20.02	0.0	30.0	90.34	12.67	
	3.00	12.73	120.0	0.0	30.0	90.34	12.67	
	3.00	12.88	220.0	0.0	30.0	90.34	12.67	
	2.50	70.8	84.8	0.0	0.0	100.0	0.0	*
	2.50	14.16	29.44	0.0	0.0	100.0	0.0	*
40	3.02	12.68	20.02	0.0	30.0	90.34	12.67	
	3.05	12.73	120.0	0.0	30.0	90.34	12.67	
	3.02	12.88	220.0	0.0	30.0	90.34	12.67	
	2.50	14.16	16.96	0.0	0.0	100.0	0.0	*
55	3.00	12.68	20.02	0.0	30.0	90.34	12.67	
	3.06	12.73	120.0	0.0	30.0	90.34	12.67	
	3.03	12.88	220.0	0.0	30.0	90.34	12.67	
	2.50	14.16	29.36	0.0	0.0	100.0	0.0	*
	2.50	14.16	29.36	0.0	0.0	100.0	0.0	*
70	3.03	12.68	20.02	0.0	30.0	90.34	12.67	
	3.06	12.73	120.0	0.0	30.0	90.34	12.67	
	3.08	12.88	220.0	0.0	30.0	90.34	12.67	
	2.50	14.16	16.96	0.0	0.0	100.0	0.0	*

Table S3. Experimental conditions of calorimetry for oxalate protonation. I = 1.05 mol·kg^{-1} $NaClO_4$. C_H and C_{ox} represent the stoichiometric concentrations of proton and total oxalate. * Indicates titrations carried out at LBNL.

t, °C	Cup Solution			Titrant		
	V^0 cm^3	$C_H°$ mmol·dm^{-3}	$C_{ox}°$ mmol·dm^{-3}	$C_{H,T}$ mmol·dm^{-3}	$C_{ox,T}$ mmol·dm^{-3}	
10	2.50	0.0	45.35	99.63	0.0	
	2.50	297.7	0.0	0.0	40.35	
	2.50	199.2	0.0	0.0	40.35	
25	2.50	0.0	43.35	99.63	0.0	
	2.50	199.0	0.0	0.0	40.35	
	2.50	319.0	0.0	0.0	40.35	
	2.50	996.0	0.0	0.0	43.88	
	0.900	0.0	50.00	250.0	0.0	*
	0.900	0.0	25.00	250.0	0.0	*
	0.900	0.0	11.10	103.2	0.0	*
	0.900	0.0	8.33	103.2	0.0	*
40	2.50	0.0	39.32	99.63	0.0	
	2.50	199.0	0.0	0.0	39.32	
	2.50	319.0	0.0	0.0	39.32	
55	0.900	0.0	8.33	103.2	0.0	*
	0.900	0.0	8.33	103.2	0.0	*
70	0.900	0.0	5.56	103.2	0.0	*
	0.900	0.0	6.94	103.2	0.0	*
	0.900	0.0	8.33	103.2	0.0	*

Table S4. Experimental conditions of calorimetry for U(VI)/oxalate complexation. I = 1.05 mol·kg^{-1} $NaClO_4$. C_U, C_H and C_{ox} represent the stoichiometric concentrations of uranium, proton and total oxalate. * Indicates titrations carried out at LBNL.

		Cup Solution			Titrant	
t, ^oC	*Symbols in Figure 4*	V^0 cm^3	$C_H°$ mmol·dm^{-3}	$C_U°$ mmol·dm^{-3}	$C_{H,T}$ mmol·dm^{-3}	$C_{ox,T}$ mmol·dm^{-3}
10	△	2.50	18.64	24.16	0.0	40.35
	□	2.50	1.02	1.33	0.0	40.35
	○	2.50	2.05	2.65	0.0	40.35
	◇	2.50	3.28	4.25	0.0	40.35
		2.51	10.17	1.00	49.72	24.86
		2.51	29.87	1.01	49.72	24.86
		2.50	49.97	1.00	49.72	24.86
25	△	2.49	17.95	23.27	0.0	40.35
		2.50	0.94	1.22	0.0	40.35
		2.51	10.02	0.99	0.0	12.35
	◇	2.42	27.05	1.03	0.0	12.35
	□	2.48	1.84	2.38	49.72	40.35
	○	2.46	3.68	4.77	49.72	40.35
		2.64	9.47	0.38	49.72	12.35
	*	0.900	4.71	3.93	0.0	50.00
	*	0.900	3.53	2.95	0.0	50.00
40	△	2.50	18.68	24.21	0.0	39.32
	□	2.37	1.09	1.41	0.0	39.32
	○	2.38	1.90	2.46	0.0	39.32
		2.44	3.31	4.29	0.0	39.32
	*	0.900	4.71	3.93	0.0	50.00
	*	0.900	7.07	5.90	0.0	50.00
55	*□	0.900	4.71	3.93	0.0	50.00
	*○	0.900	7.07	5.90	0.0	50.00
70	*○	0.900	4.71	3.93	0.0	50.00
	* □	0.900	5.89	4.92	0.0	50.00
	*◇	0.900	7.07	5.90	0.0	50.00



Figures S1a-S1c.

The distribution plots concerning the systems U(VI)/oxalate studied by spectrophotometric titrations at different –log[H^+]. I = 1.05 mol kg^{-1}. The initial volume V° (cm^3), metal ion concentration, C_U° (mmol dm^{-3}), and inorganic acid concentration, C_H° (mmol dm^{-3}), are: Figure S1a, 3.000, 12.68, 20.02; Figure S1b, 2.995, 12.75, 120.0; Figure S1c, 3.007, 12.85, 220.0. The metal ion concentration, the inorganic acid concentration and the oxalate concentration (mmol dm^{-3}) in the titrant solution are: $C_{U,T}$ = 12.67, $C_{H,T}$ = 30.0; $C_{ox,T}$ = 90.34. The stability constants of Tables 1 and 2 were employed to obtain the plots.