

Supporting Information

Table S1 Hydrolysis constants of U(VI) at different temperatures relevant to this work.

Reaction	T K	$\text{Log } \beta^o$	$\text{Log } \beta_M$	$\text{Log } \beta_M$
			(0.1 mol·dm ⁻³ (C ₂ H ₅) ₄ NClO ₄)	(1.0 mol·dm ⁻³ NaClO ₄)
$\text{UO}_2^{2+} + \text{H}_2\text{O} = \text{UO}_2\text{OH}^+ + \text{H}^+$	298	-5.40 ± 0.24	-5.58 ± 0.24	-5.45 ± 0.46
	313	-4.92 ± 0.12	-5.11 ± 0.11	-4.98 ± 0.42
	328	-4.88 ± 0.24	-5.07 ± 0.24	-4.95 ± 0.46
	343	-4.31 ± 0.12	-4.51 ± 0.11	-4.39 ± 0.42
	353			-4.19 ± 0.42
	358	-4.03 ± 0.15	-4.24 ± 0.15	-4.09 ± 0.43
$2\text{UO}_2^{2+} + 2\text{H}_2\text{O} = (\text{UO}_2)_2(\text{OH})_2^{2+} + 2\text{H}^+$	298	-5.62 ± 0.04	-5.83 ± 0.02	-5.98 ± 0.11
	313	-5.21 ± 0.03	-5.43 ± 0.01	-5.61 ± 0.10
	328	-4.84 ± 0.05	-5.06 ± 0.03	-5.25 ± 0.11
	343	-4.50 ± 0.05	-4.73 ± 0.03	-4.93 ± 0.12
	353			-4.73 ± 0.12
	358	-4.25 ± 0.05	-4.49 ± 0.03	-4.64 ± 0.12
$3\text{UO}_2^{2+} + 5\text{H}_2\text{O} = (\text{UO}_2)_3(\text{OH})_5^{3+} + 5\text{H}^+$	298	-15.74 ± 0.05	-16.37 ± 0.02	-16.73 ± 0.24
	313	-14.70 ± 0.04	-15.35 ± 0.01	-15.73 ± 0.23
	328	-13.78 ± 0.05	-14.45 ± 0.02	-14.84 ± 0.24
	343	-12.92 ± 0.05	-13.61 ± 0.02	-14.03 ± 0.24
	353			-13.60 ± 0.12
	358	-12.22 ± 0.05	-12.94 ± 0.02	-13.38 ± 0.24

- (1) The values of $\log \beta_0$ and $\log \beta_M$ at $I = 0.1 \text{ mol} \cdot \text{dm}^{-3}$ (C₂H₅)₄NClO₄ are from the literature [18].
 (2) The values of $\log \beta_M$ at $I = 1.0 \text{ mol} \cdot \text{dm}^{-3}$ NaClO₄ except those at $T = 353 \text{ K}$ were obtained by using the specific ion interaction approach (SIT) from the $\log \beta_0$ values. The values of $\log \beta_M$ at $T = 353 \text{ K}$ were calculated by interpolation of the values at other temperatures.

Table S2 Spectrophotometric titration conditions of U(VI) by benzoate (1.0 mol·dm⁻³ NaClO₄)

T K	Titr NO.	Initial solution in cuvette			Titrant solution		
		V^0 mL	C_U^0 mol·dm ⁻³	C_H^0 mol·dm ⁻³	C_{ligand} mol·dm ⁻³	C_H mol·dm ⁻³	V_{add} mL
298	1	2.10	1.05×10^{-2}	1.20×10^{-2}	0.286	1.09×10^{-2}	0.150
	2	2.10	9.98×10^{-3}	1.14×10^{-2}	0.286	1.09×10^{-2}	0.150
	3	2.10	1.32×10^{-2}	1.49×10^{-2}	0.286	1.09×10^{-2}	0.125
313	4	2.10	1.11×10^{-2}	1.26×10^{-2}	0.286	1.09×10^{-2}	0.175
	5	2.10	1.05×10^{-2}	1.20×10^{-2}	0.286	1.09×10^{-2}	0.175
	6	2.10	1.30×10^{-2}	1.46×10^{-2}	0.286	1.09×10^{-2}	0.150
328	7	2.10	1.05×10^{-2}	1.20×10^{-2}	0.286	1.09×10^{-2}	0.225
	8	2.10	9.98×10^{-3}	1.14×10^{-2}	0.286	1.09×10^{-2}	0.225
	9	2.10	2.89×10^{-3}	3.29×10^{-3}	0.0886	3.60×10^{-3}	0.275
	10	2.10	2.79×10^{-3}	3.17×10^{-3}	0.0886	3.60×10^{-3}	0.275
343	11	2.10	1.05×10^{-2}	1.20×10^{-2}	0.286	1.09×10^{-2}	0.275
	12	2.10	1.01×10^{-2}	1.14×10^{-2}	0.286	1.09×10^{-2}	0.275
	13	2.20	2.71×10^{-3}	3.09×10^{-3}	0.0886	3.60×10^{-3}	0.350
	14	2.20	2.61×10^{-3}	2.97×10^{-3}	0.0886	3.60×10^{-3}	0.350
353	15	2.10	1.09×10^{-2}	1.24×10^{-2}	0.286	1.09×10^{-2}	0.275
	16	2.10	1.05×10^{-2}	1.20×10^{-2}	0.286	1.09×10^{-2}	0.275
	17	2.10	2.89×10^{-3}	3.29×10^{-3}	0.0886	3.60×10^{-3}	0.350
	18	2.10	2.79×10^{-3}	3.17×10^{-3}	0.0886	3.60×10^{-3}	0.350

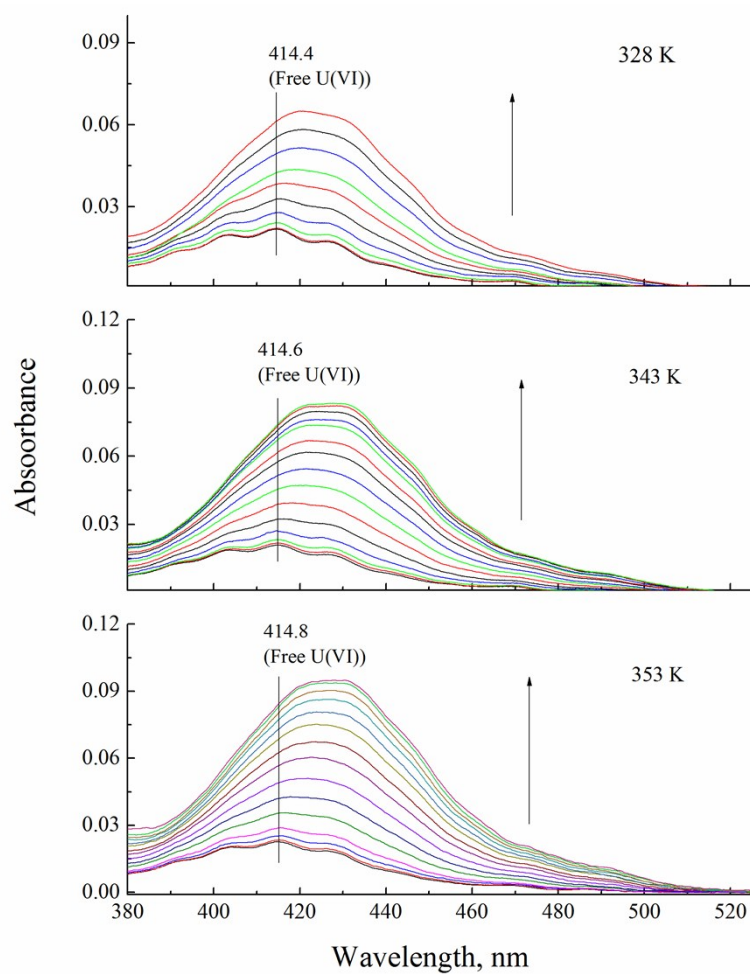


Figure S1 Spectrophotometric titrations of U(VI) by benzoate with lower concentrations of U(VI) at 328, 343 and 353 K. The titration conditions correspond to those of No. 10 (328 K), No.14 (343 K) and No.18 (353 K) in Table S1 of ESI.

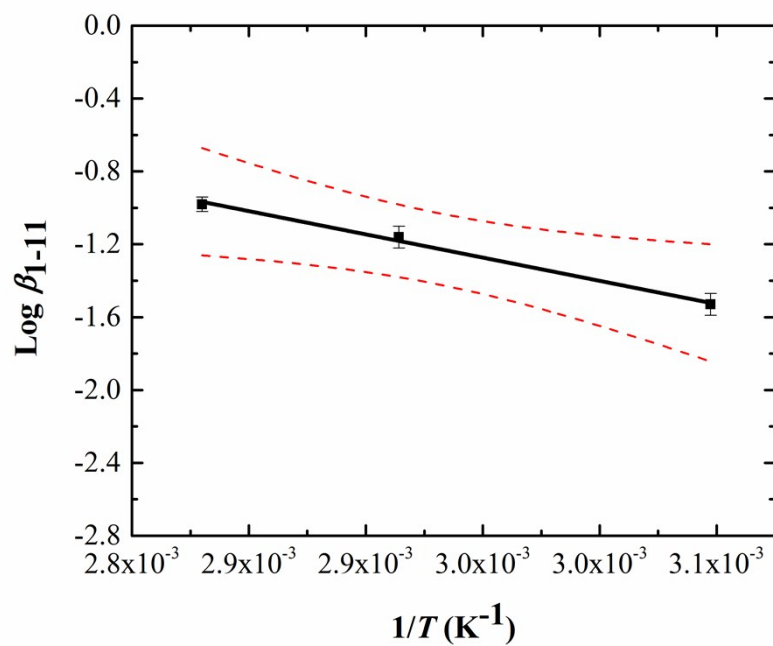


Figure S2 Van't Hoff plot for the complexation constant β_{1-11} of U(VI) with benzoate. Symbol (■) – experimental points from this work ($I = 1.05 \text{ mol} \cdot \text{kg}^{-1} \text{ NaClO}_4$), solid line – linear fit, dashed lines – upper and lower limits of the confidence band at the 95% level.