

Table S1 Stability constants of Np(V) complexation with carbonate at different temperatures with varying ionic strength of 0.1–3.0 M.

Reaction	T/°C	Ionic medium	log β	Tech*	log β _m ⁰	ΔH kJ·mol ⁻¹	ΔS J·K ⁻¹ ·mol ⁻¹	Ref.			
$\text{NpO}_2^+ + \text{CO}_3^{2-} = \text{NpO}_2(\text{CO}_3)^-$	10	0.1 M LiClO ₄	4.28 ± 0.12	Spec.	4.67 ± 0.26	-8.6 ± 1.5	58.6 ± 5.0	15			
	25	0.1 M LiClO ₄	4.17 ± 0.12	Spec.	4.57 ± 0.26						
	40	0.1 M LiClO ₄	4.06 ± 0.15	Spec.	4.48 ± 0.27						
	55	0.1 M LiClO ₄	4.01 ± 0.15	Spec.	4.44 ± 0.28						
	70	0.1 M LiClO ₄	3.95 ± 0.18	Spec.	4.40 ± 0.30						
	23	0.1 M NaCl	4.68 ± 0.03	Spec.	4.878 ± 0.118						
	23	0.1 M NaCl	4.8 ± 0.1	Sol.							
	25	0.1 M NaClO ₄	4.34 ± 0.11	Spec.							
	25	0.1 M NaClO ₄	4.58 ± 0.04	Sol.							
	25	0.2 M NaClO ₄	4.13 ± 0.03	Dist.							
	25	0.37 M NaCl	4.368 ± 0.105	CE							
	25	0.5 M NaClO ₄	4.2 ± 0.1	Spec							
	25	1.0 M NaClO ₄	4.3 ± 0.2	Spec							
	25	1.0 M NaClO ₄	4.49 ± 0.06	Sol.							
	25	1.0 M NaClO ₄	4.14 ± 0.01	Dist.							
	25	1.0 M NaClO ₄	4.50 ± 0.04	Sol.							
	25	3.0 M NaClO ₄	4.76 ± 0.04	Sol.							
	25	3.0 M NaClO ₄	5.09	Sol.							
	25	3.0 M NaCl	4.3 ± 0.1	Sol.							
$\text{NpO}_2^+ + 2\text{CO}_3^{2-} = \text{NpO}_2(\text{CO}_3)_2^{3-}$	10	0.1 M LiClO ₄	6.09 ± 0.15	Spec.	6.04 ± 0.28	0.3 ± 1.7	117 ± 7.0	t.w.			
	25	0.1 M LiClO ₄	6.12 ± 0.18	Spec.	6.06 ± 0.30						
	40	0.1 M LiClO ₄	6.10 ± 0.18	Spec.	6.05 ± 0.31						
	55	0.1 M LiClO ₄	6.11 ± 0.18	Spec.	6.05 ± 0.31						
	70	0.1 M LiClO ₄	6.11 ± 0.15	Spec.	6.06 ± 0.31						
	25	0.1 M NaClO ₄	6.60 ± 0.04	Sol.	6.559 ± 0.108						
	25	0.2 M LiClO ₄	7.06 ± 0.04	Dist.							
	25	0.37 M NaCl	6.368 ± 0.11	CE							
	25	0.5 M NaClO ₄	6.4 ± 0.2	Spec.							
	25	1.0 M NaClO ₄	6.7 ± 0.3	Spec.							
	25	1.0 M NaClO ₄	6.78 ± 0.06	Dist.							
	25	1.0 M NaClO ₄	7.11 ± 0.07	Sol.							
	25	1.0 M NaClO ₄	6.96 ± 0.06	Sol.							
	25	3.0 M NaCl	7.1 ± 0.2	Sol.							
	25	3.0 M NaClO ₄	7.69 ± 0.07	Sol.							
	25	3.0 M NaClO ₄	8.15	Sol.							
$\text{NpO}_2^+ + 3\text{CO}_3^{2-} = \text{NpO}_2(\text{CO}_3)_5^{5-}$	10	0.1 M LiClO ₄	7.27 ± 0.21	Spec.	5.92 ± 0.31	-21.0 ± 2.0	40.6 ± 9.7	t.w.			
	25	0.1 M LiClO ₄	7.18 ± 0.24	Spec.	5.80 ± 0.35						
	40	0.1 M LiClO ₄	7.01 ± 0.27	Spec.	5.58 ± 0.36						
	55	0.1 M LiClO ₄	6.86 ± 0.27	Spec.	5.40 ± 0.35						
	70	0.1 M LiClO ₄	6.78 ± 0.33	Spec.	5.27 ± 0.41						
	25	0.37 M NaCl	7.764 ± 0.2	CE.	5.636 ± 0.145						
	25	0.5 M NaClO ₄	7.8 ± 0.3	Spec.	6.559 ± 0.108						
	25	1.0 M NaClO ₄	8.5 ± 0.4	Spec.							
	25	1.0 M NaClO ₄	8.53 ± 0.08	Sol							
	25	1.0 M NaClO ₄	8.67 ± 0.03	Sol							
	25	3.0 M NaClO ₄	10.46	Sol							
	25	3.0 M NaClO ₄	10.3 ± 0.09	Sol							
	25	3.0 M NaCl	9.2 ± 0.2	Sol							

*Spec. – spectrophotometry; Sol. – solubility; Dist. – solvent-solvent extraction distribution; CE. – Capillary electrochromatography; t.w. – this work.

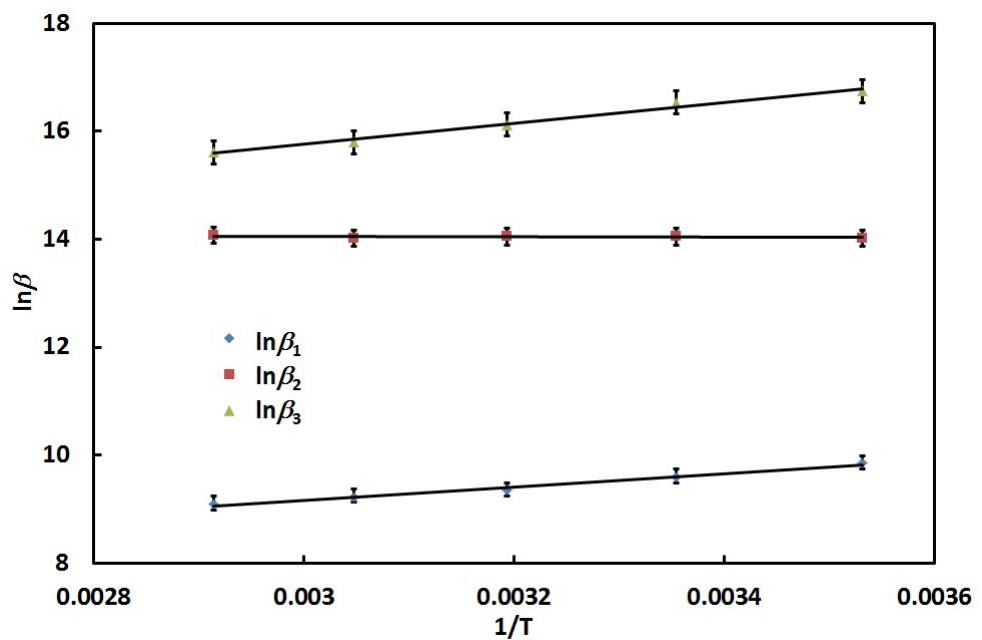


Figure S1 Plots of $\ln \beta$ vs. $1/T$ for Np(V)-carbonate complexation in 0.1 M LiClO₄.