Kinetics of complexation of V(V), U(VI), and Fe(III) with glutaroimide-dioxime: studies by stopped-flow and conventional absorption spectroscopy

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Electronic Supporting Information

Additional spectra and kinetic traces

Vanadium

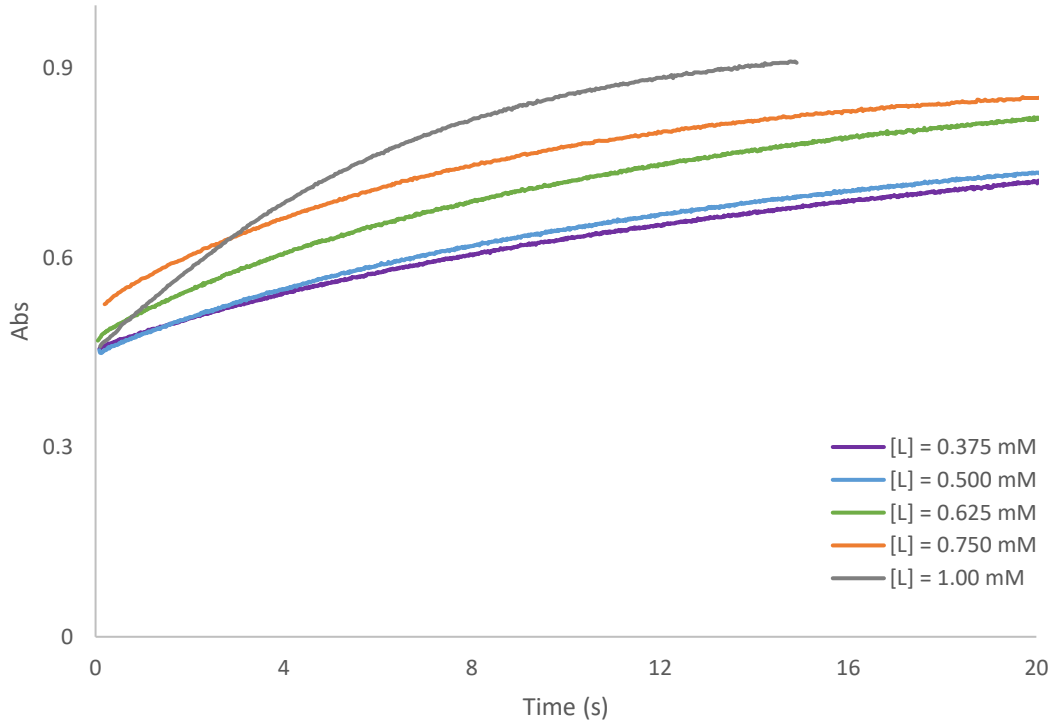

Figure S1: Sample curves for the formation of complex **1** from stopped-flow kinetic experiments showing the effect of ligand concentration. Conditions: [V] = 0.200 mM, pH = 8.

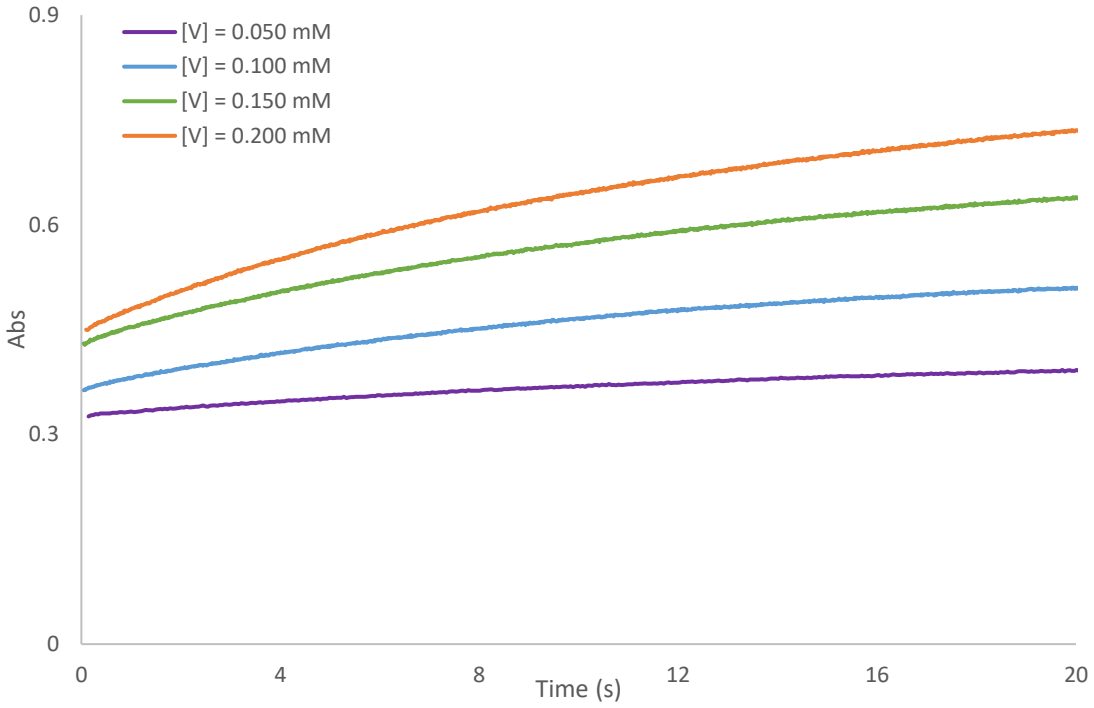

Figure S2: Sample curves for the formation of complex **1** from stopped-flow kinetic experiments showing the effect of vanadium concentration. Conditions: [L] = 0.500 mM, pH = 8.

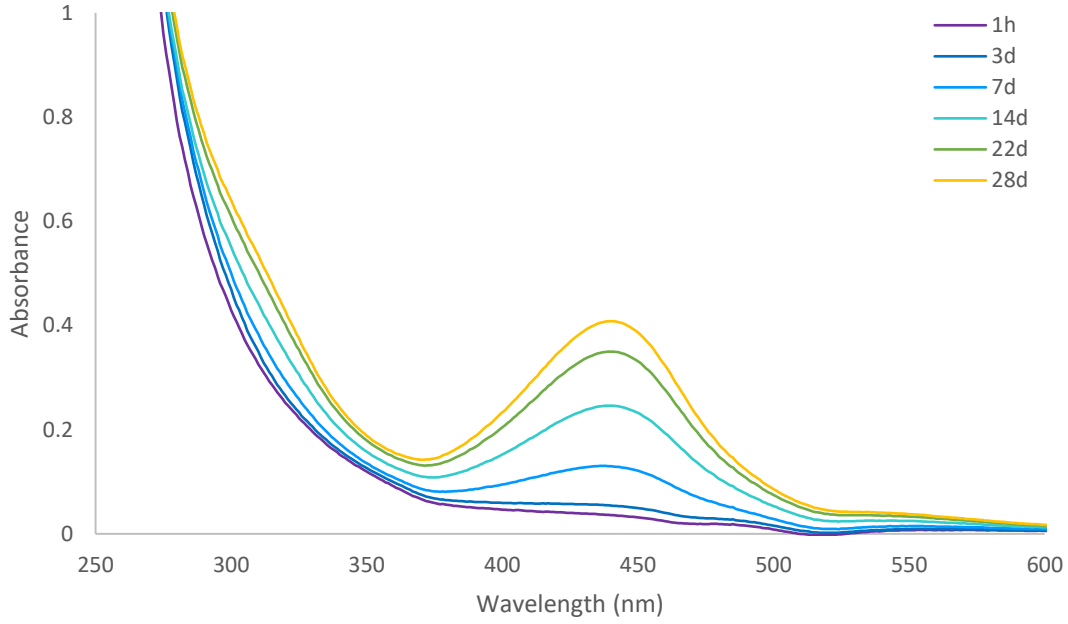

Figure S3: Spectra monitoring the formation of **2** over time by conventional UV-Vis spectroscopy. Conditions: [V] = 0.200 mM; [L] = 0.500 mM. The number of spectra shown has been reduced for clarity.

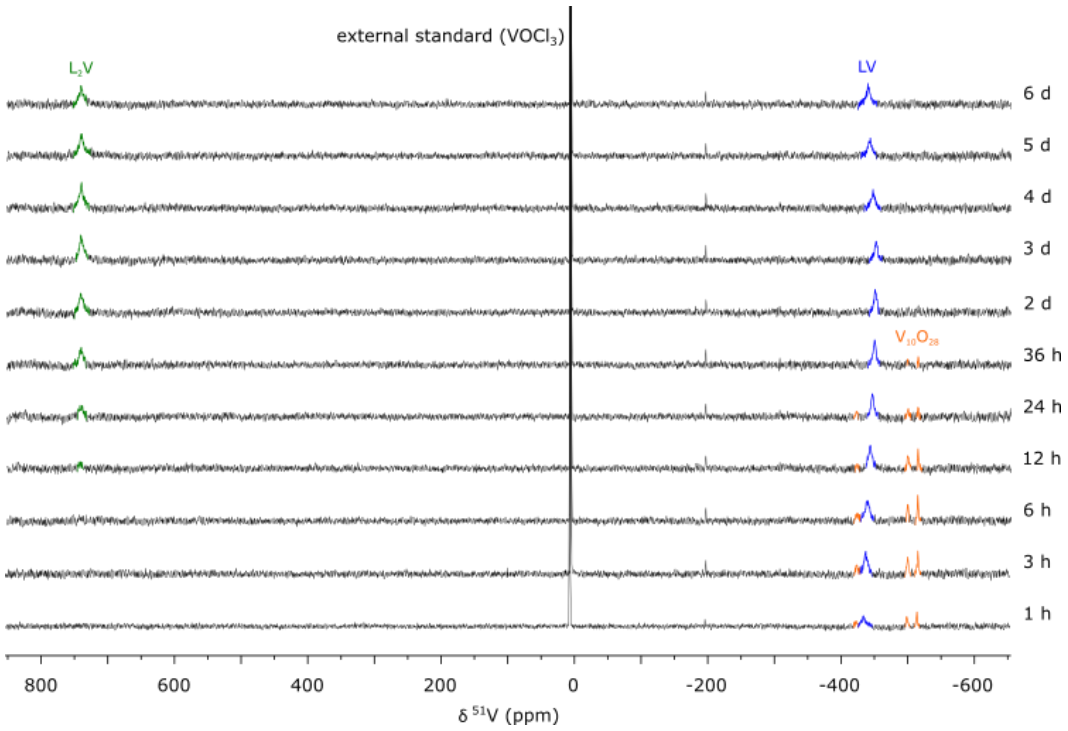

Figure S4: ^{51}V NMR spectra monitoring speciation of a V/L mixture over time (see Figure 5a in the main text). Conditions; [V] = 3 mM, [L] = 6 mM, pH = 7-8.

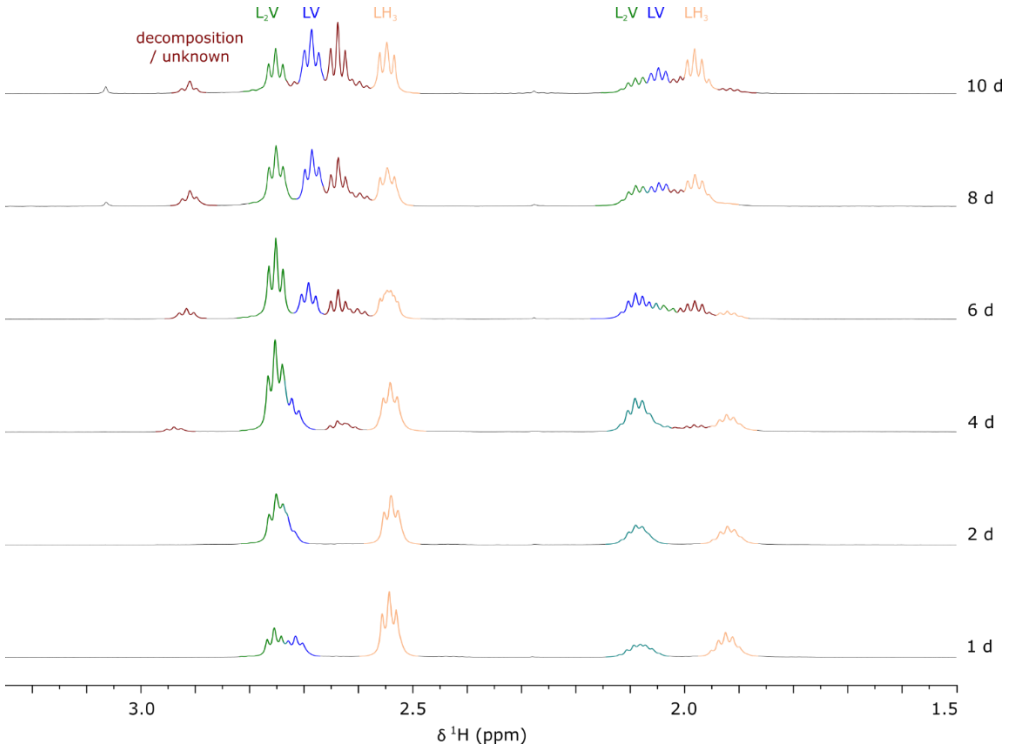

Figure S5: ^{1}H NMR spectra monitoring speciation of a V/L mixture over time (see figure 5b in the main text). Conditions; [V] = 3 mM, [L] = 6 mM, pH = 7-8.

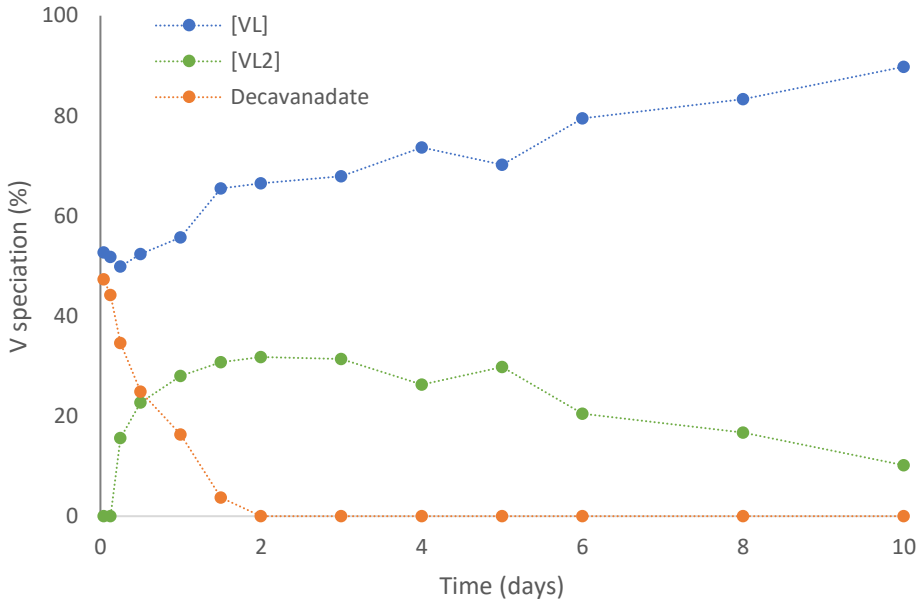

Figure S6: ^{51}V speciation of a V/L mixture changing over time. Conditions; [V] = 6 mM, [L] = 6 mM, pH = 7-8. Uncertainties of measurements are estimated to be < ±5%.

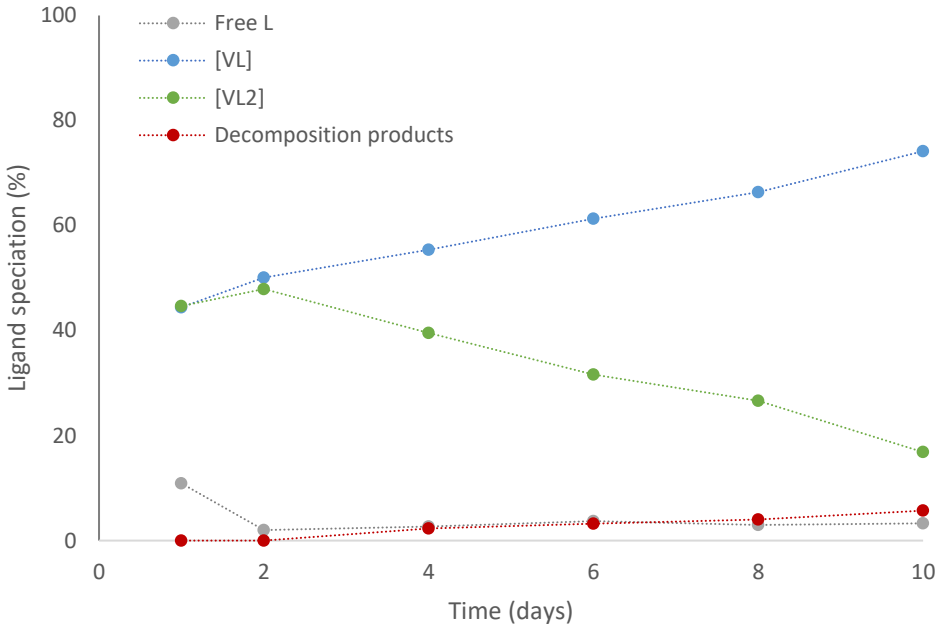

Figure S7: ^{1}H speciation of a V/L mixture changing over time (note: [VL] and [VL_2] ratio determined from ^{51}V NMR due to overlap in the ^{1}H spectra; see Figure S9). Conditions; [V] = 6 mM, [L] = 6 mM, pH = 7-8. Uncertainties of measurements are estimated to be < ±5%.

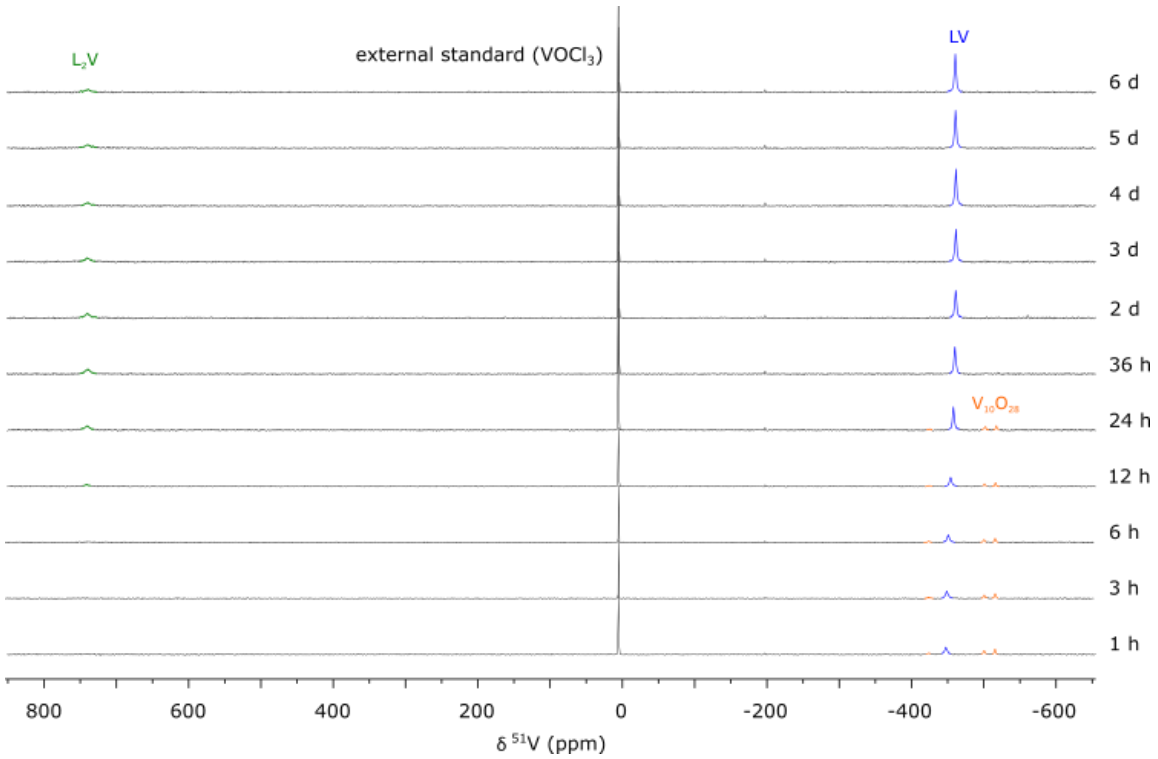

Figure S8: ^{51}V NMR spectra monitoring speciation of a V/L mixture over time (see figure S6). Conditions; [V] = 6 mM, [L] = 6 mM, pH = 7-8.

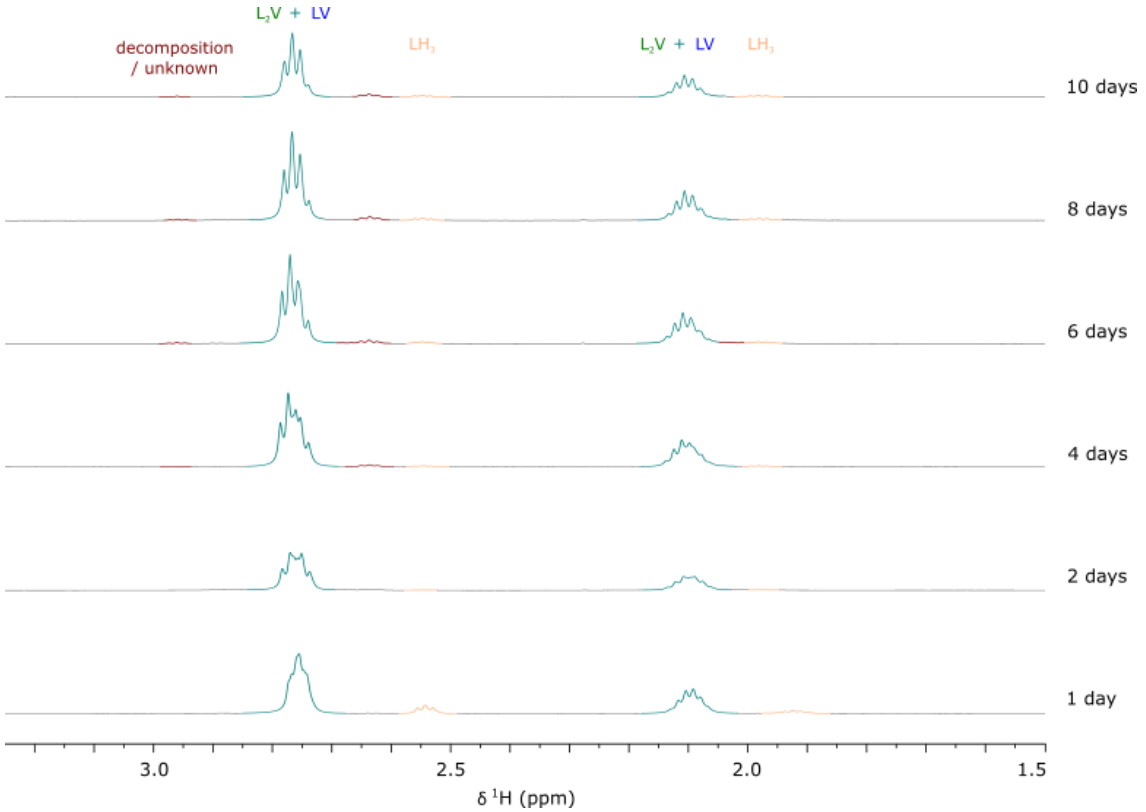

Figure S9: ^{1}H NMR spectra monitoring speciation of a V/L mixture over time (see figure S7). Conditions; [V] = 6 mM, [L] = 6 mM, pH = 7-8.

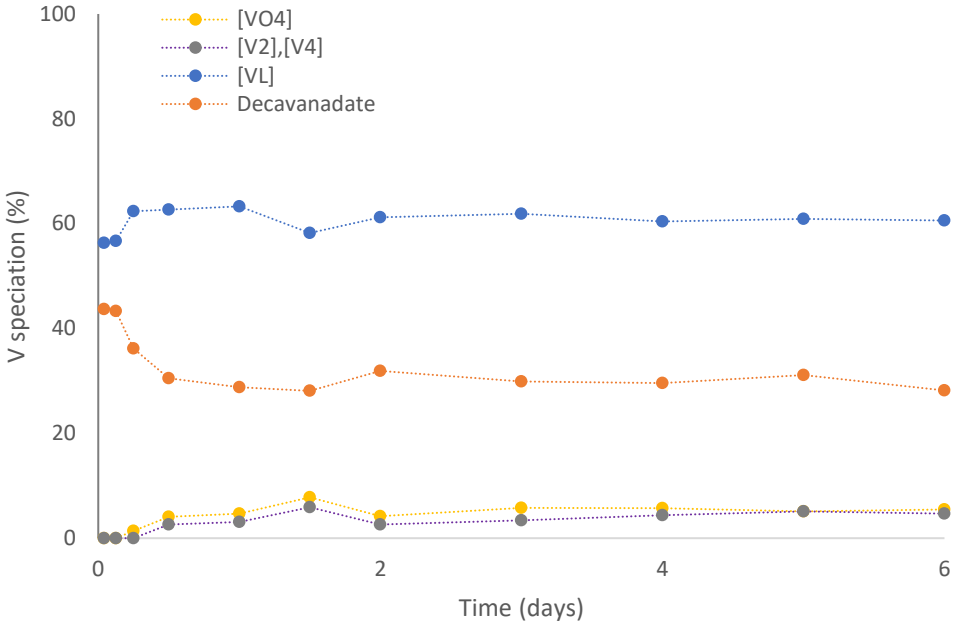

Figure S10: ^{51}V speciation of a V/L mixture changing over time. Conditions; [V] = 12 mM, [L] = 6 mM, pH = 7-8. ^{1}H speciation (starting at 1 day) shows only VL.

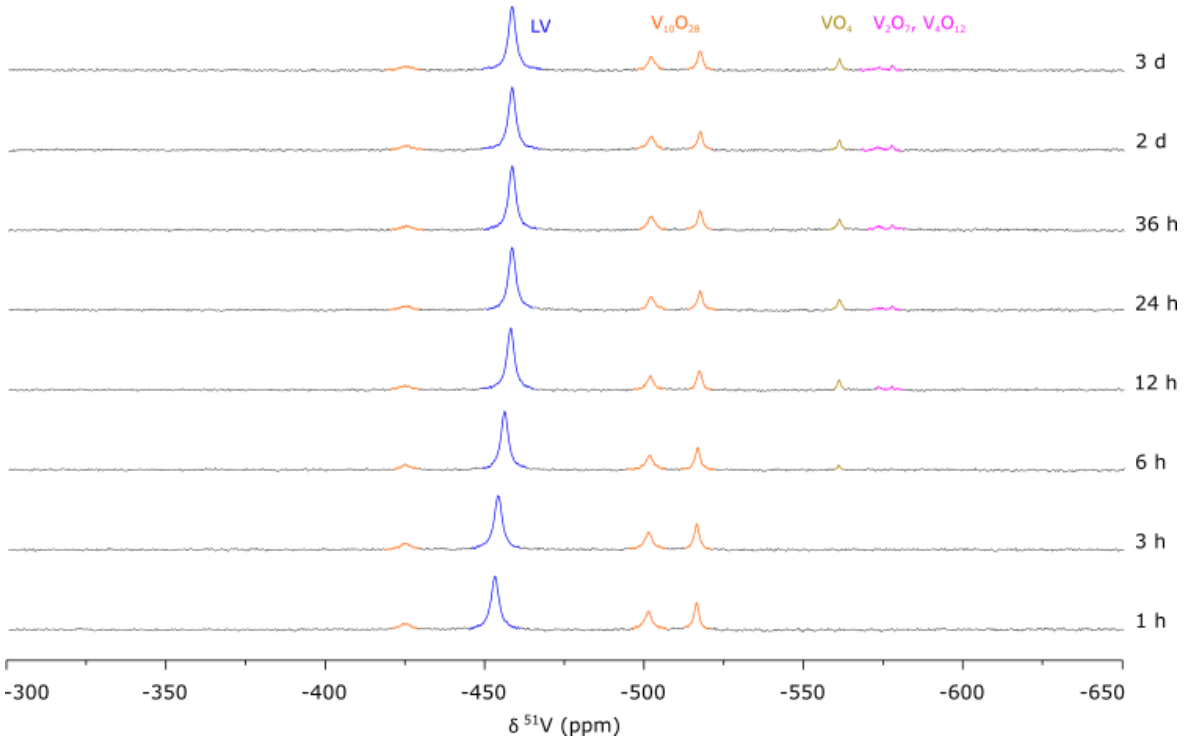

Figure S11: ^{51}V NMR spectra monitoring speciation of a V/L mixture over time (see figure S10). Conditions; [V] = 12 mM, [L] = 6 mM, pH = 7-8. No changes were observed after 3 days, and no signals were observed at δ > -300 ppm.

Uranium

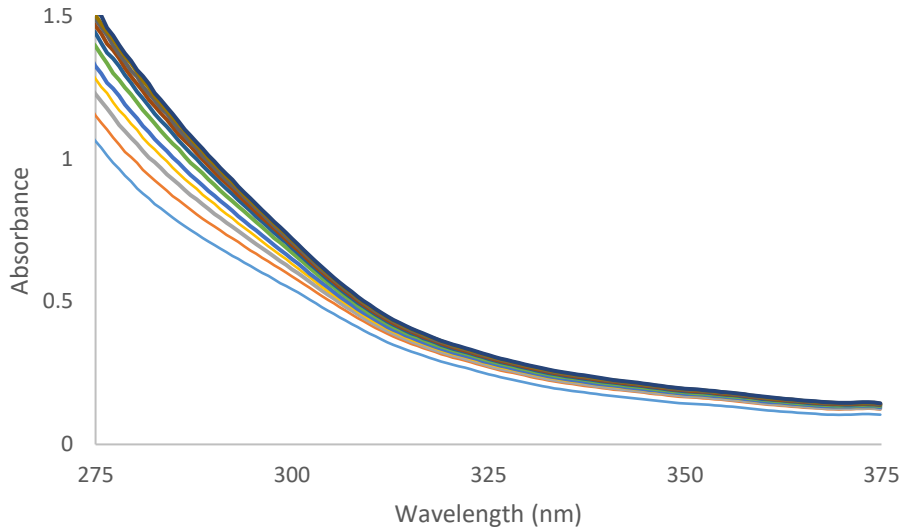

Figure S12: Spectra monitoring the formation of **4** over time. Conditions: [UO_2] = 0.200 mM, [L] = 0.500 mM, [CO_3] = 1.200 mM, [Ca] = 2.50 mM, pH = 7. The number of spectra shown has been reduced for clarity (t = 0.1s to t = 8.0 s)

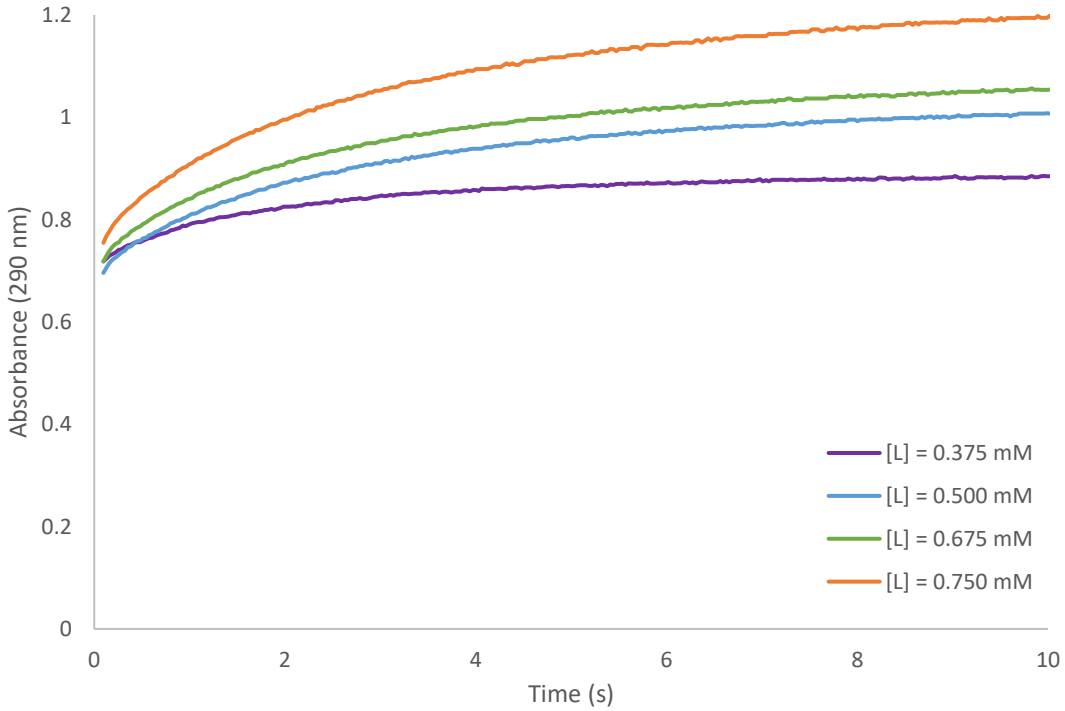

Figure S13: Sample curves from stopped-flow kinetic experiments showing the effect of ligand concentration. Conditions: [UO_2] = 0.200 mM, [carbonate] = 1.600 mM, [Ca] = 2.50 mM, pH = 7.

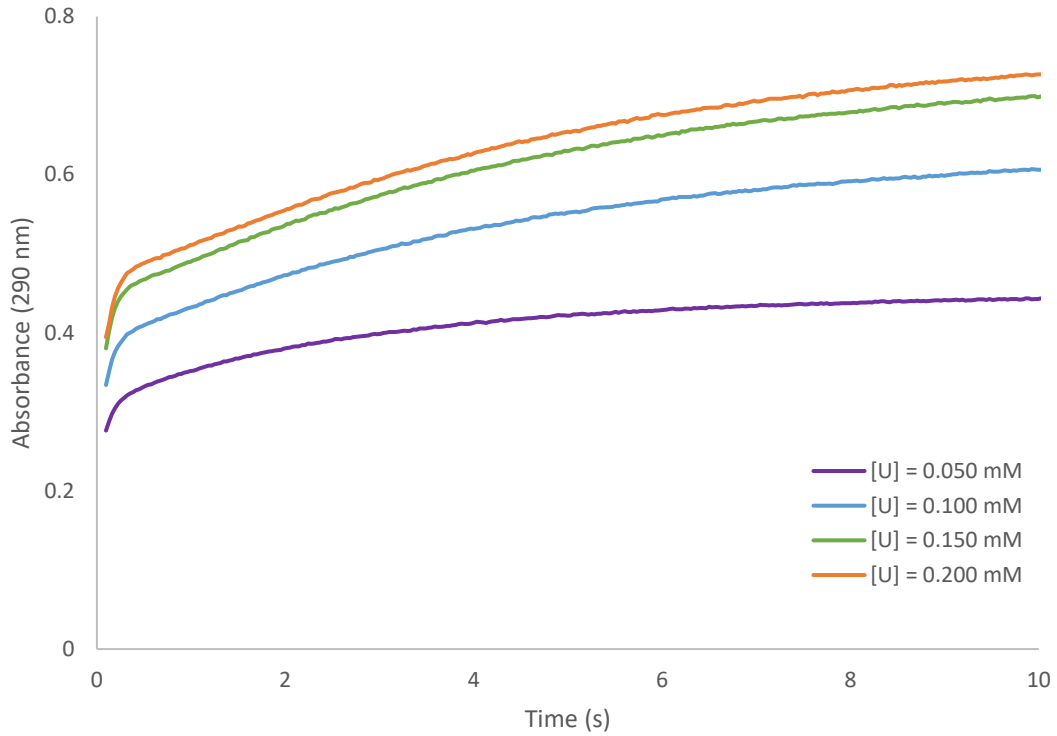

Figure S14: Sample curves from stopped-flow kinetic experiments showing the effect of uranyl concentration. Conditions: [L] = 0.500 mM, [carbonate] = 25×[UO_2], [Ca] = 25×[U], pH = 7.

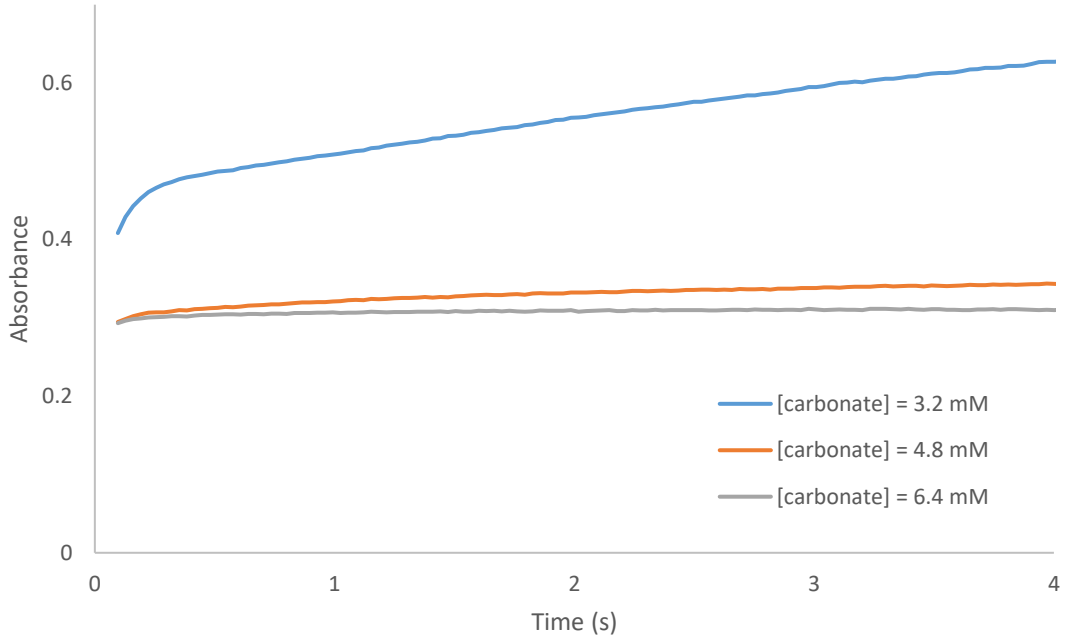

Figure S15: Sample curves from stopped-flow kinetic experiments showing the effect of carbonate concentration. Note that two distinct slopes are only visible at the lowest [carbonate]. Conditions: [UO_2] = 0.200 mM, [Ca] = 2.50 mM, pH = 7.

Iron

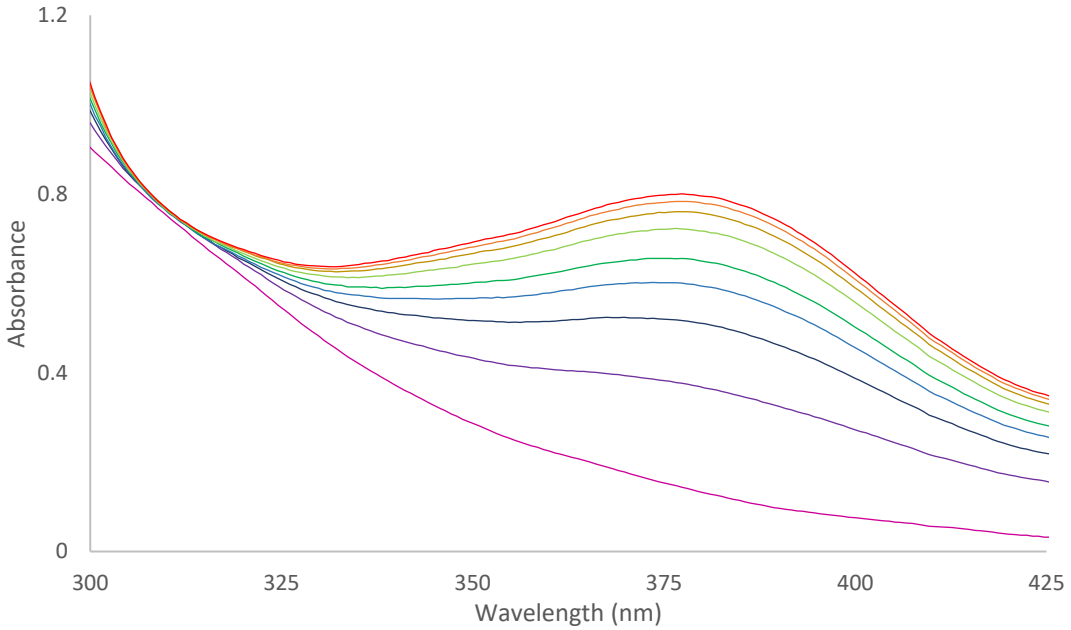

Figure S16: Spectra monitoring the formation of **3** over time. Conditions: [Fe] = 0.200 mM; [L] = 0.500 mM. The number of spectra shown has been reduced for clarity (t = 0.2 s to t = 20.0 s)

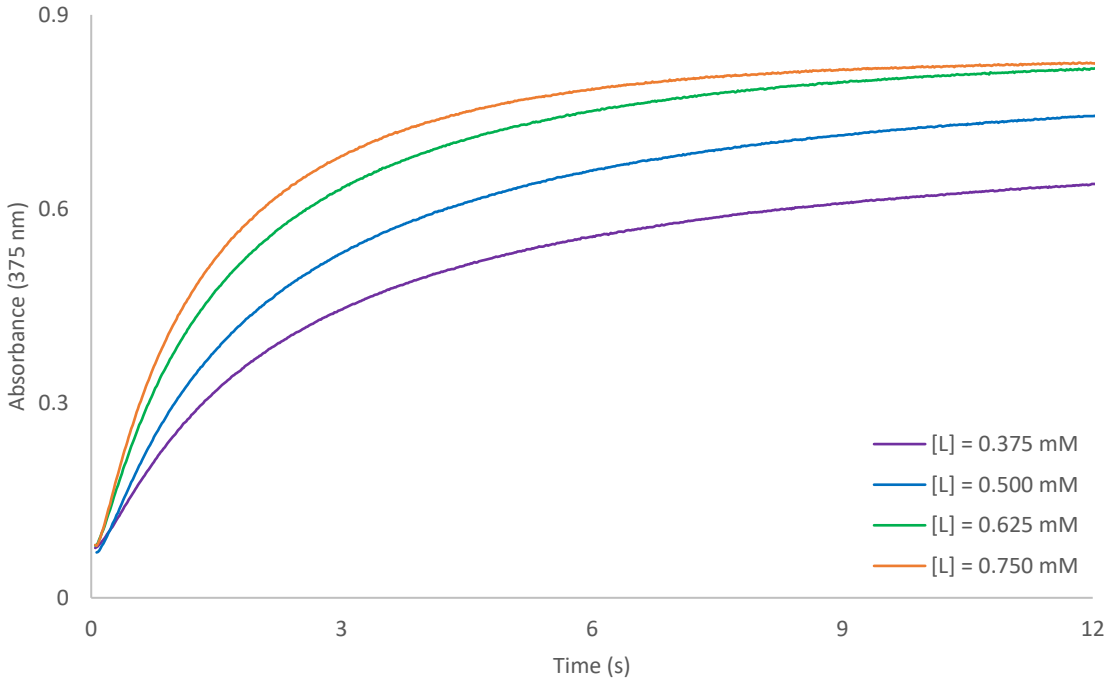

Figure S17: Sample curves from stopped-flow kinetic experiments showing the effect of ligand concentration. Conditions: [Fe] = 0.200 mM, pH = 4.5.

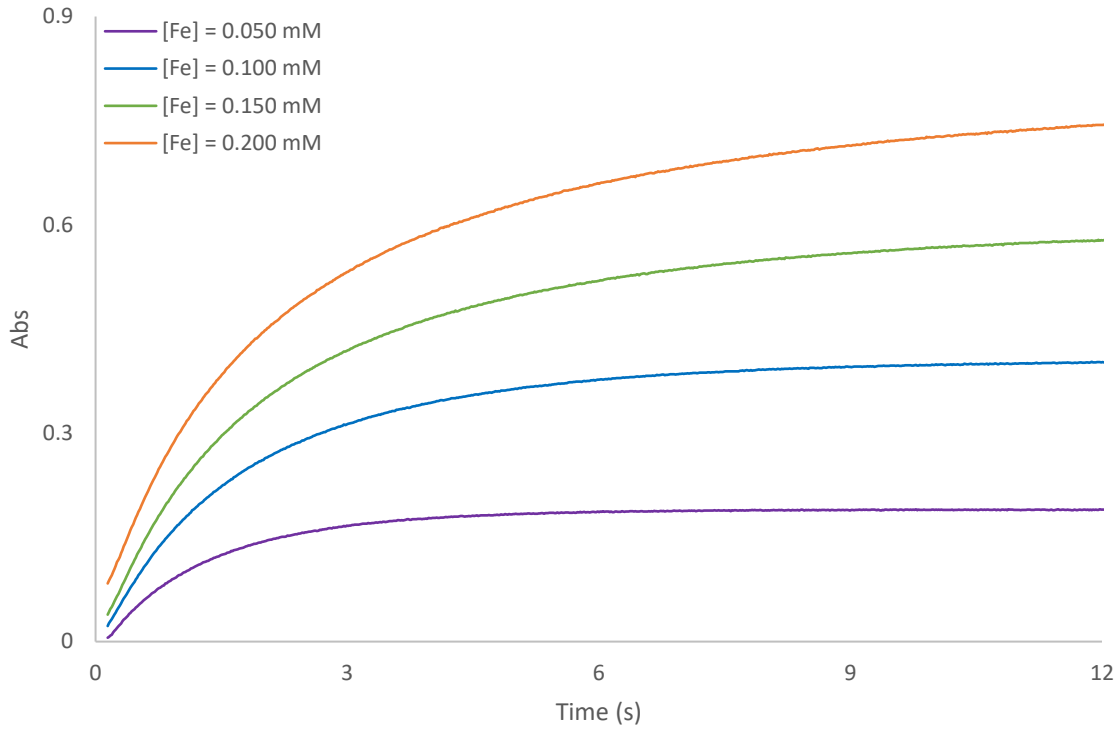

Figure S18: Sample curves from stopped-flow kinetic experiments showing the effect of iron concentration. Conditions: [L] = 0.500 mM, pH = 4.5.

Speciation diagrams

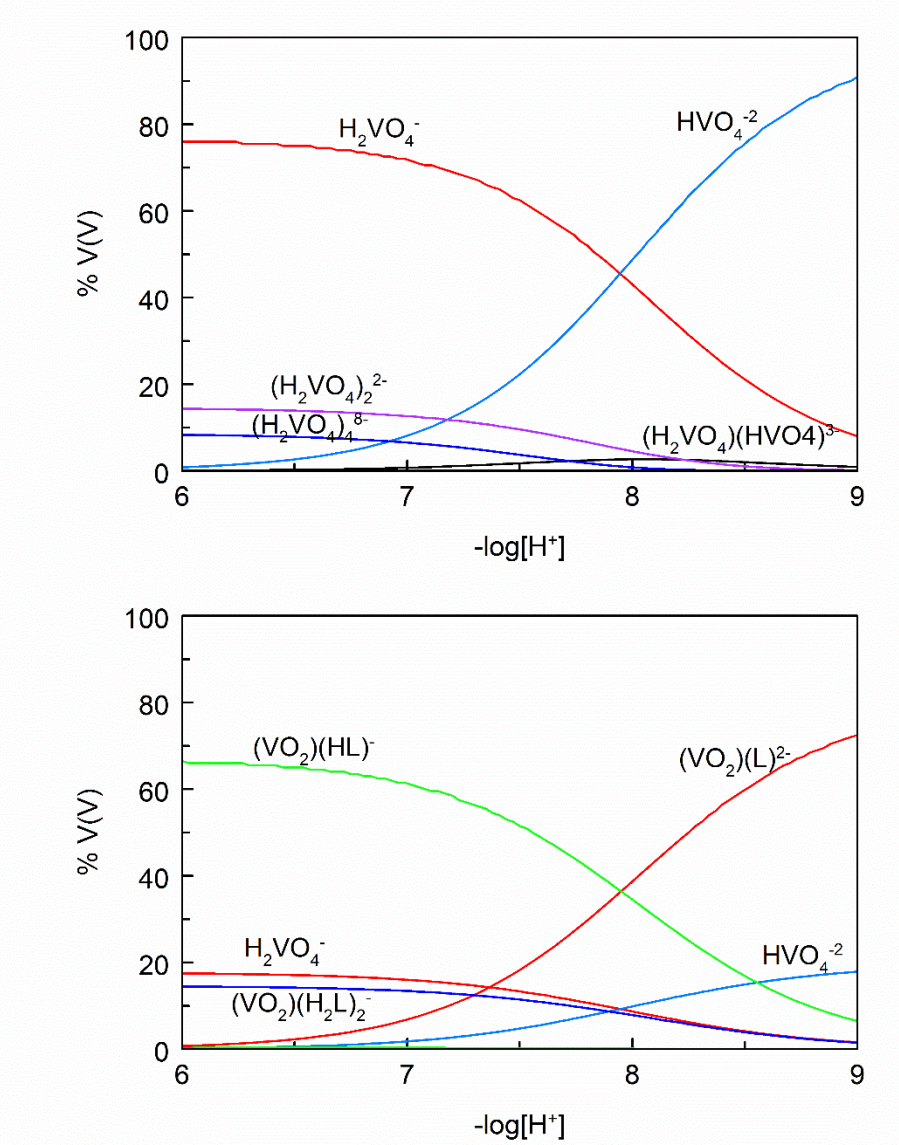

Figure S19: Speciation of 0.2 mM V(V) in the absence (upper) and presence of 0.5 mM glutaroimide-dioxime (lower), for the stopped-flow experiments monitoring the formation of 1:1 V/L complex. The equilibrium constants of V(V) alone are taken from L.Pettersson and K.Elvingson, *Vanadium Compounds*, 1998, vol. 711, pp. 30–50. The V/L complexation constants are taken from an unpublished thermodynamic study from our group.

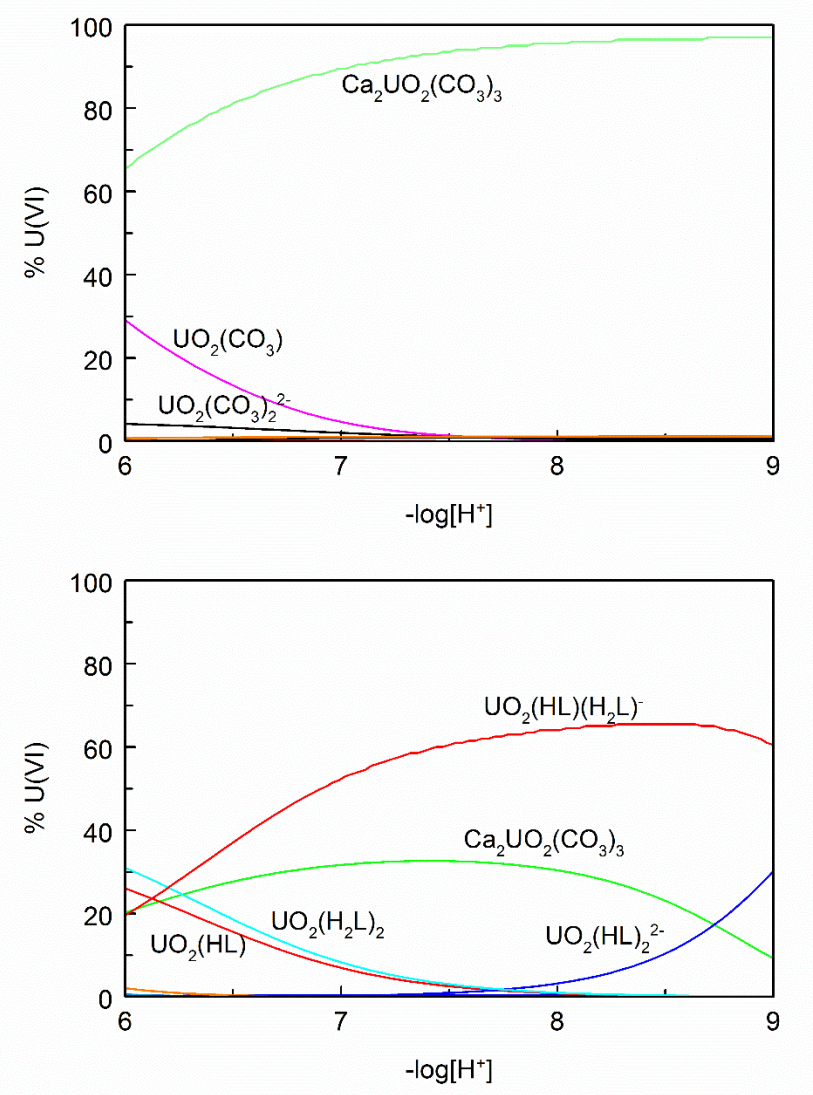

Figure S20: Speciation of 0.2 mM U(VI) in the absence (upper) and presence of 0.5 mM glutaroimide-dioxime (lower). $C_{carbonate}$ = 0.6 mM, C_{Ca} = 2.5 mM. The hydrolysis constants of U(VI) are taken from I. Grenthe et al., "Chemical Thermodynamics of Uranium". The U/L complexation constants are taken from ref.11 of the main text.

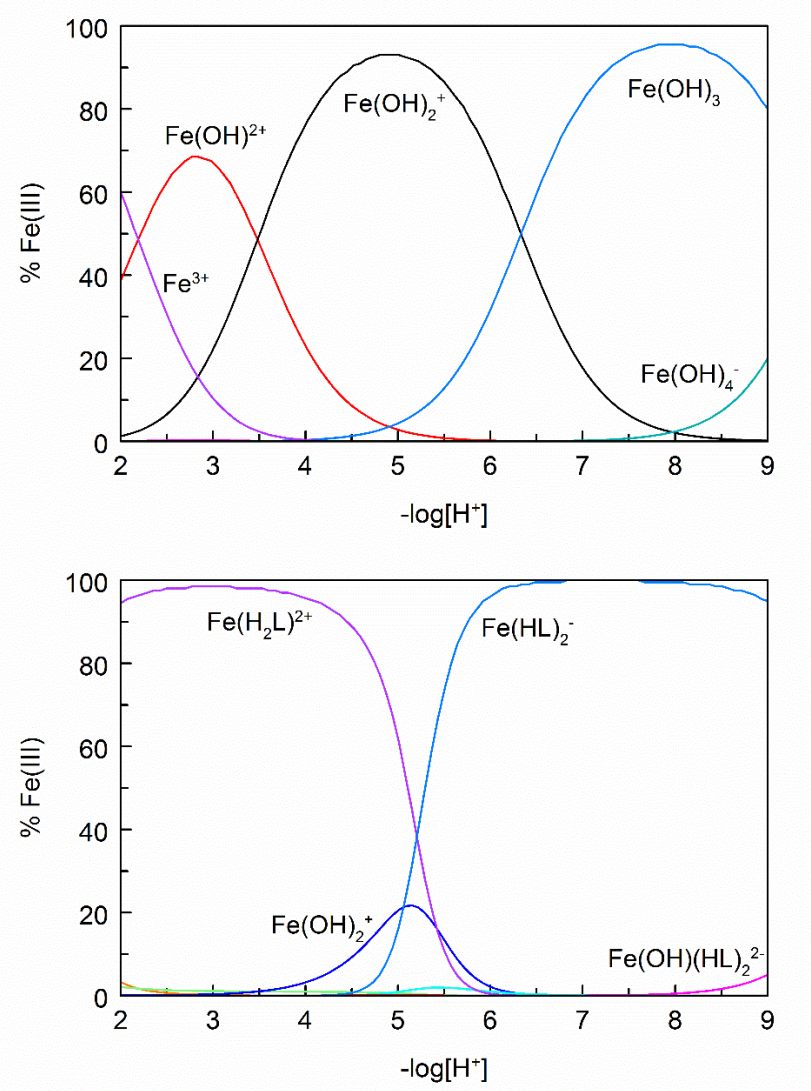

Figure S21: Speciation of 0.2 mM Fe(III) in the absence (upper) and presence of 0.5 mM glutaroimide-dioxime (lower). In the absence of glutaroimide-dioxime, $Fe(OH)_3$ that is formed will precipitate, driving the equilibrium to forming more $Fe(OH)_3$, and so the speciation and mass balance are only accurate up to pH = 4. The hydrolysis constants of Fe(III) are taken from C.F.Baes, Jr. and R.E.Mesmer, "The Hydrolysis of Cations". The Fe/L complexation constants are taken from ref.13 of the main text.