Supporting Information

Potentiometric and Multinuclear NMR Study of the Binary and Ternary Uranium(VI)-α-Hydroxycarboxylate/ Glycine-Fluoride Systems

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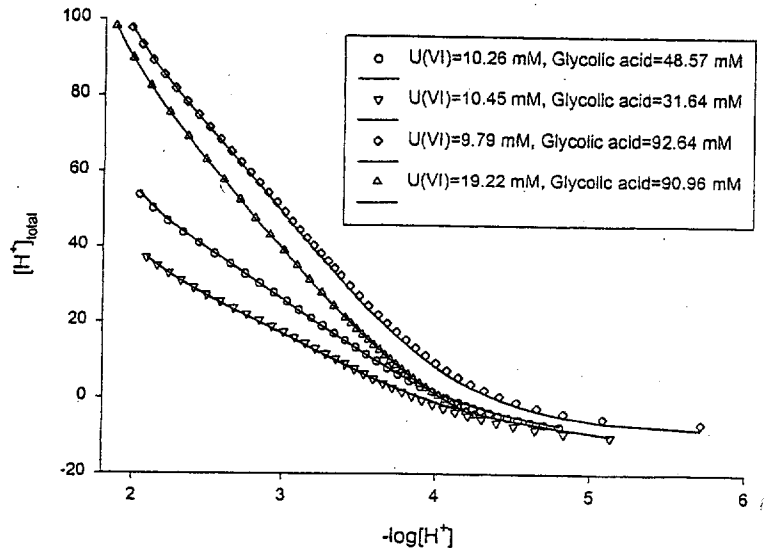
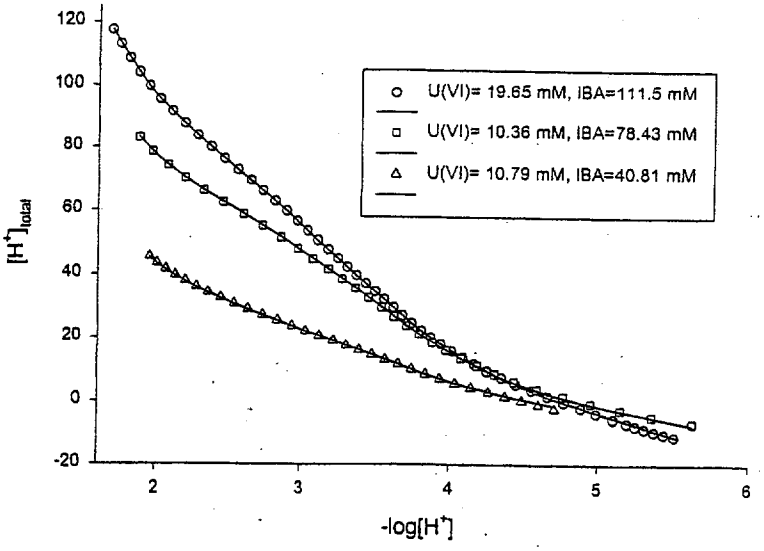
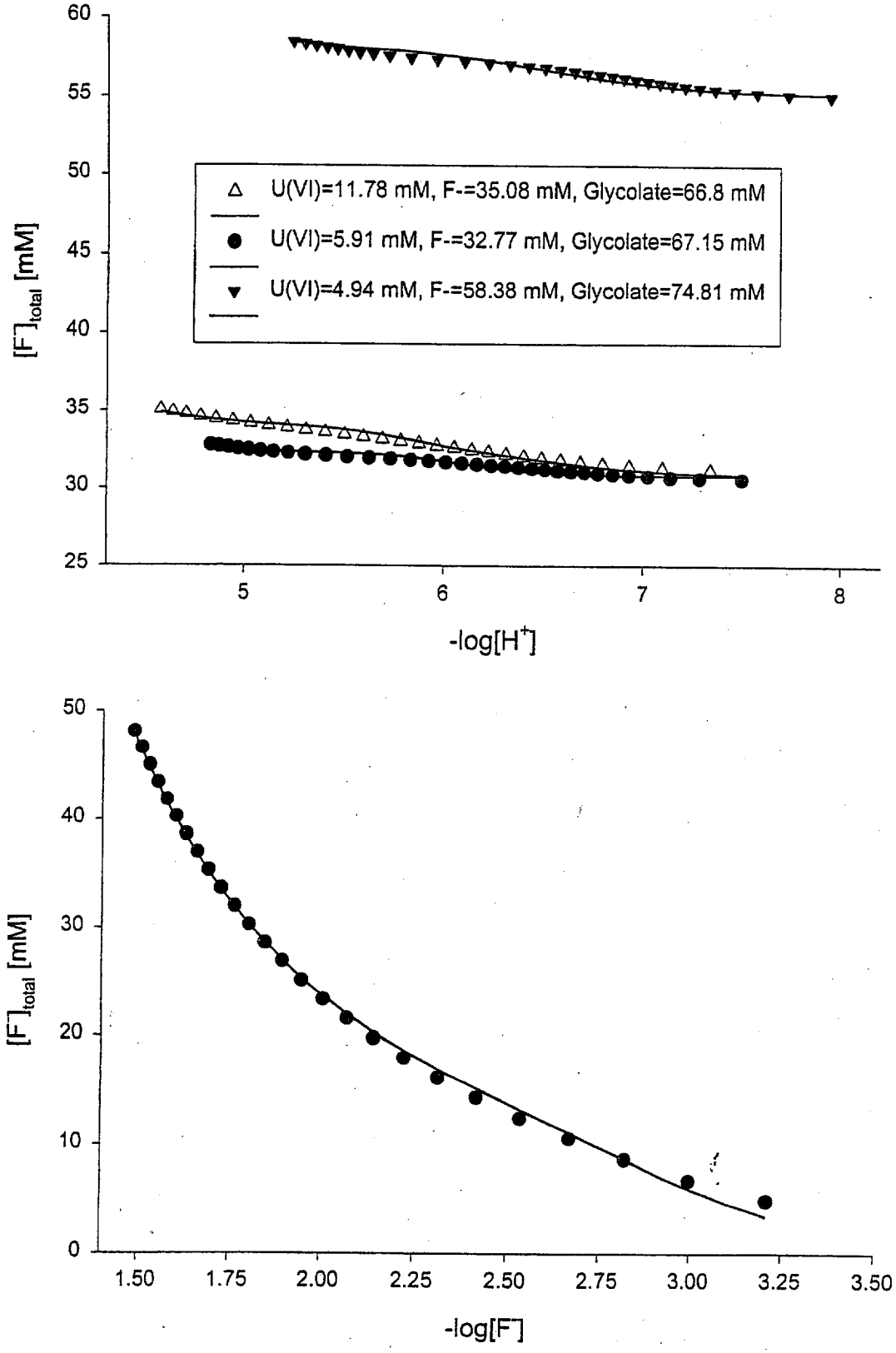
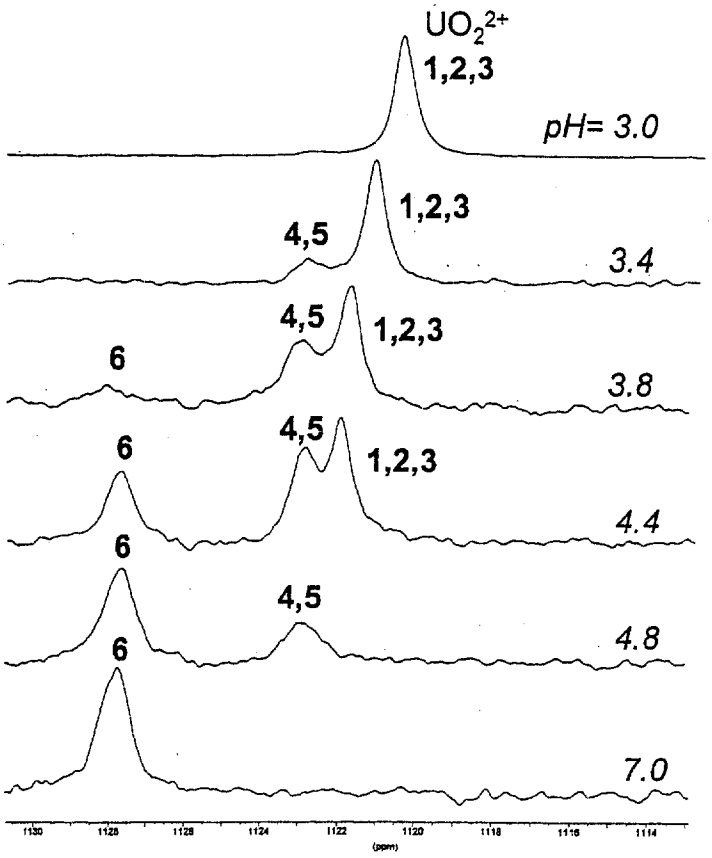


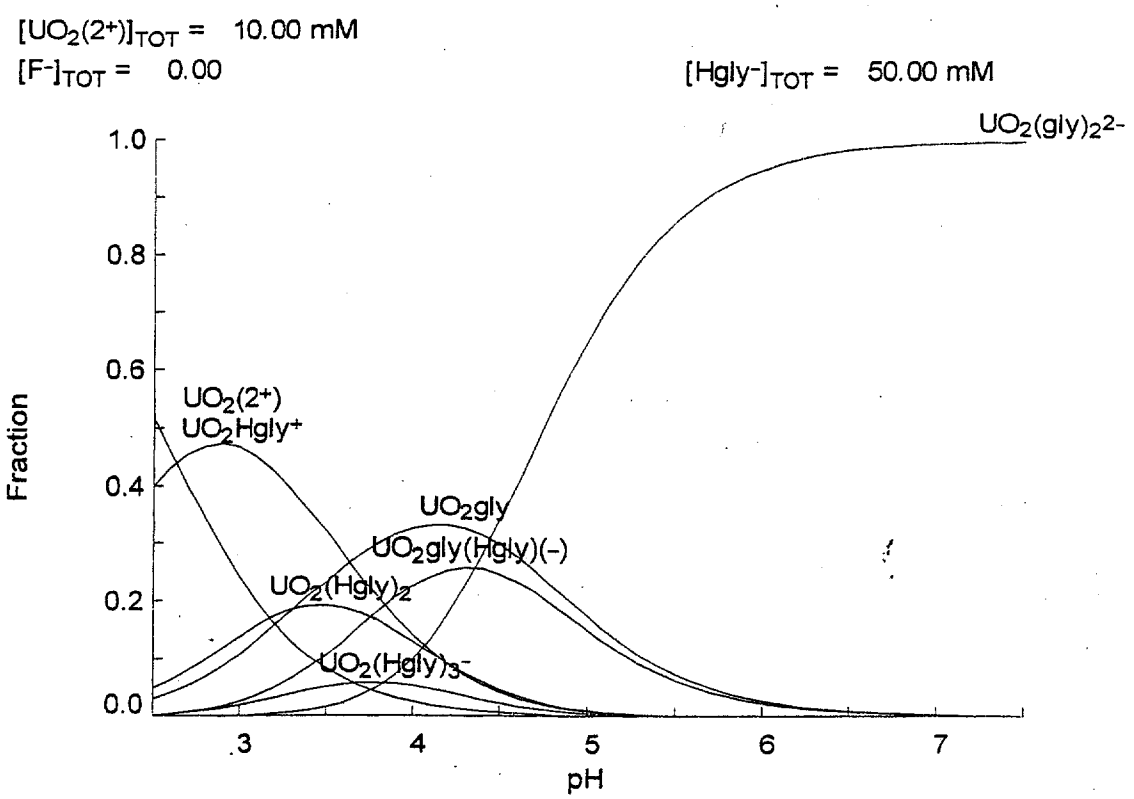


S1. Titration curves for the binary systems investigated at various uranium(VI) and glycolic acid and α-hydroxyisobutiric acid (IBA) concentrations. The solid lines are the theoretical curves calculated from the equilibrium constants in Table 1.

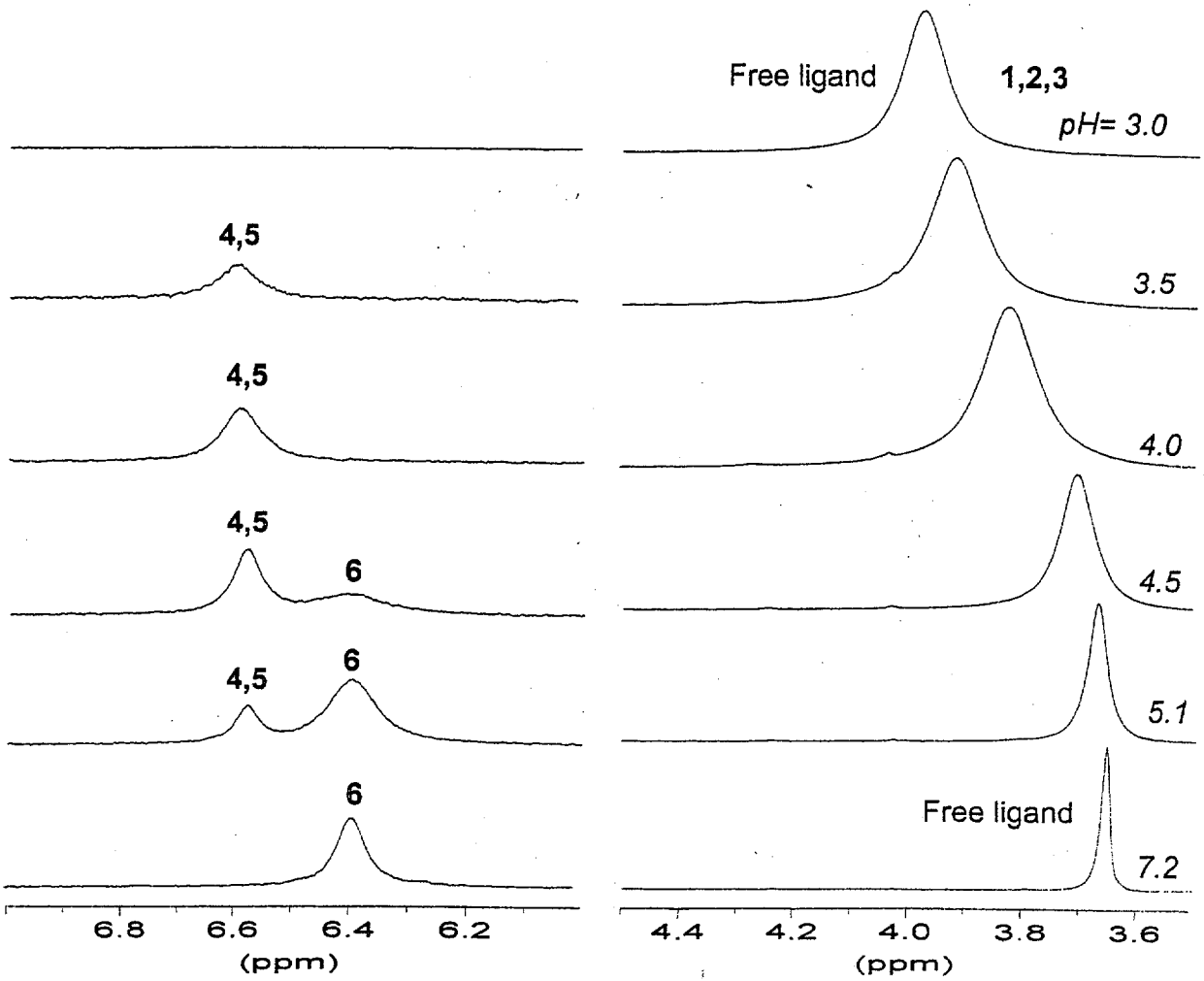


S2. Titration curves for the ternary systems investigated at various uranium(VI), fluoride, glycolic acid (top) and α-hydroxyisobutiric acid (IBA) (bottom) concentrations. The solid lines are the theoretical curves calculated from the equilibrium constants in Table 1.

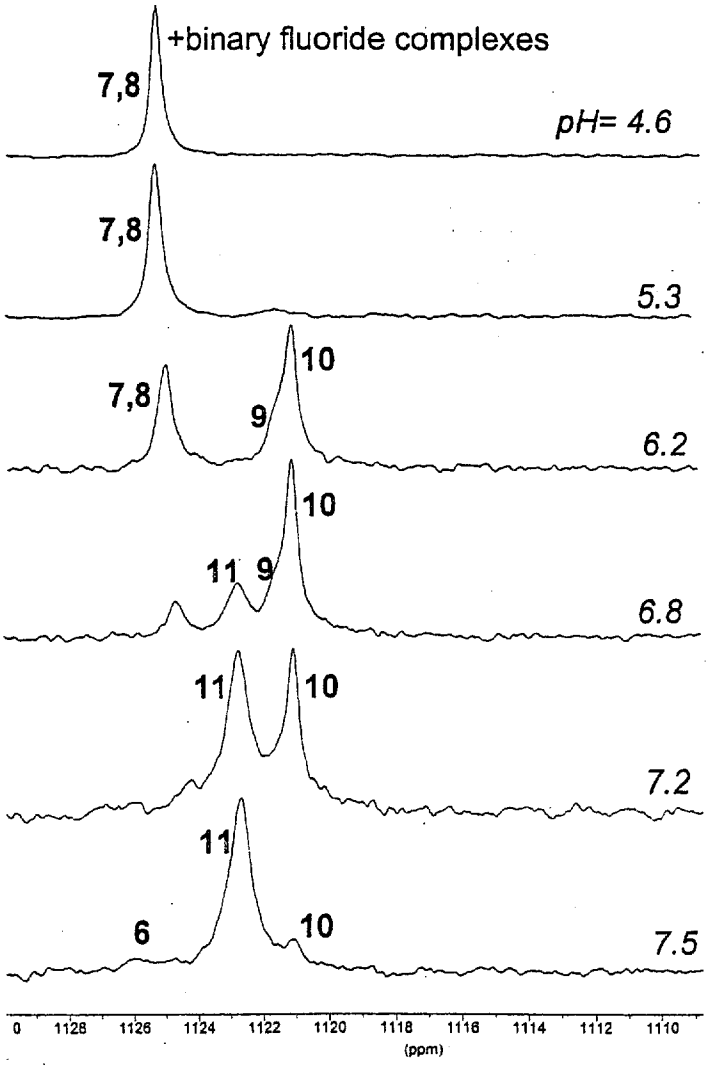




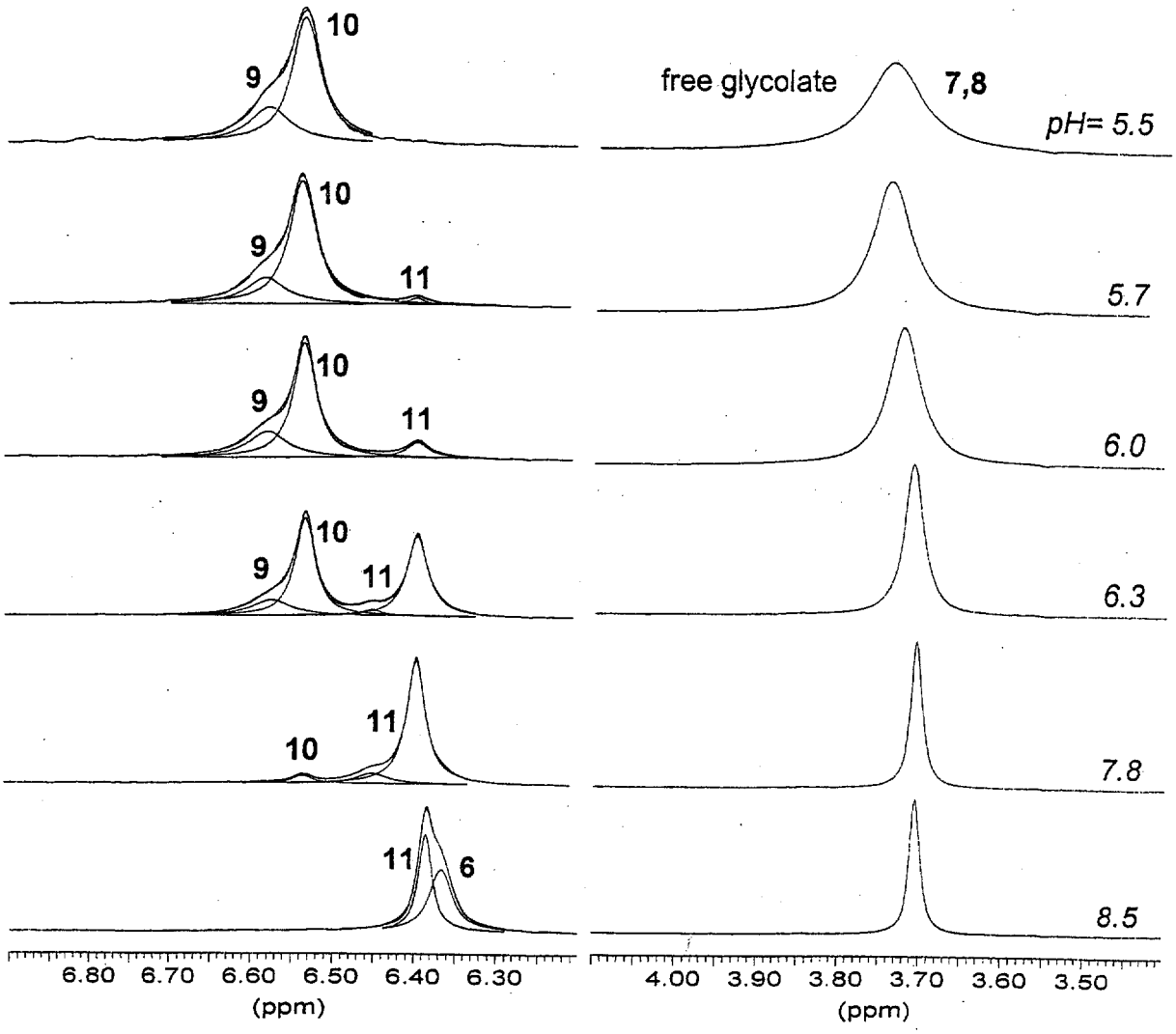
S3. pH dependent ^{17}O NMR spectra (54.2 MHz, $[UO_2^{2+}]$=10mM, [Glycolic acid]=50 mM, at 268 K, $[Na^+]$= 1M) and equilibrium uranium(VI) distribution diagram as a function of pH for the binary U(VI)-glycolate system. (Hgly=HO-CH_2COO^-, gly= O-CH_2COO^{2-})



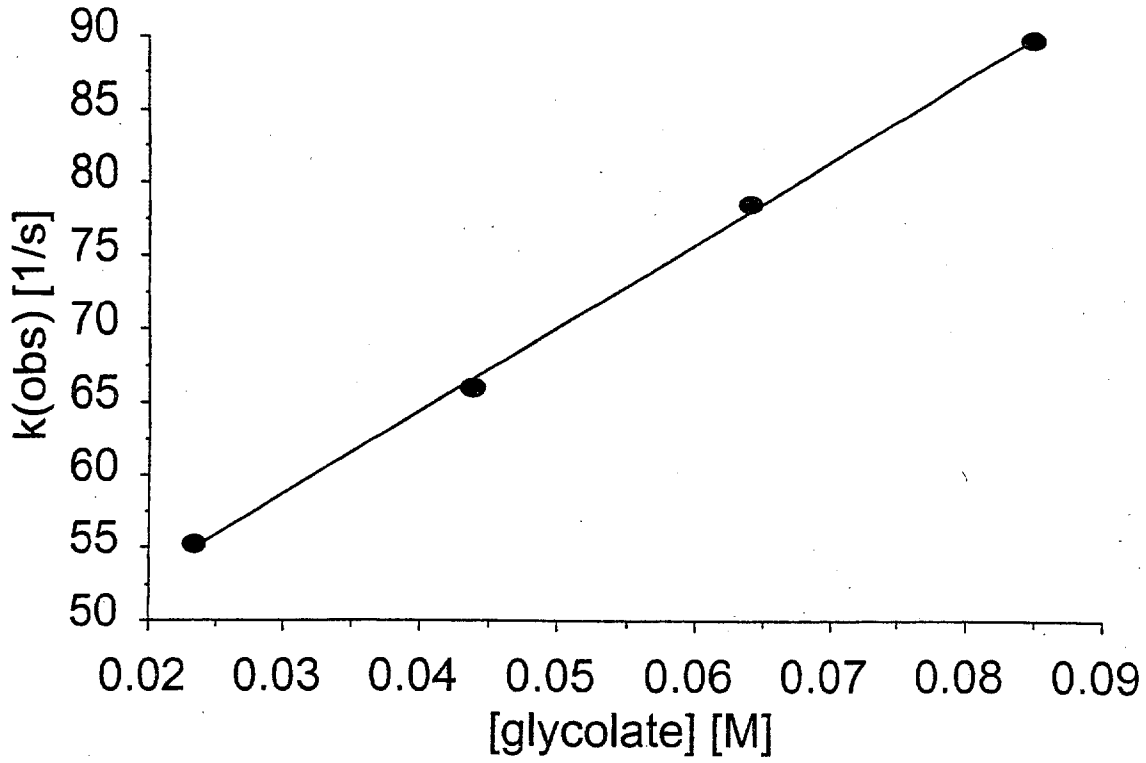
S4. pH dependent ^{1}H NMR spectra for the binary U(VI)-glycolate system (500.1 MHz, $[UO_2^{2+}]$=10mM, [Glycolic acid]=100 mM, in D_2O $[Na^{+}]$= 1M, at 268 K).

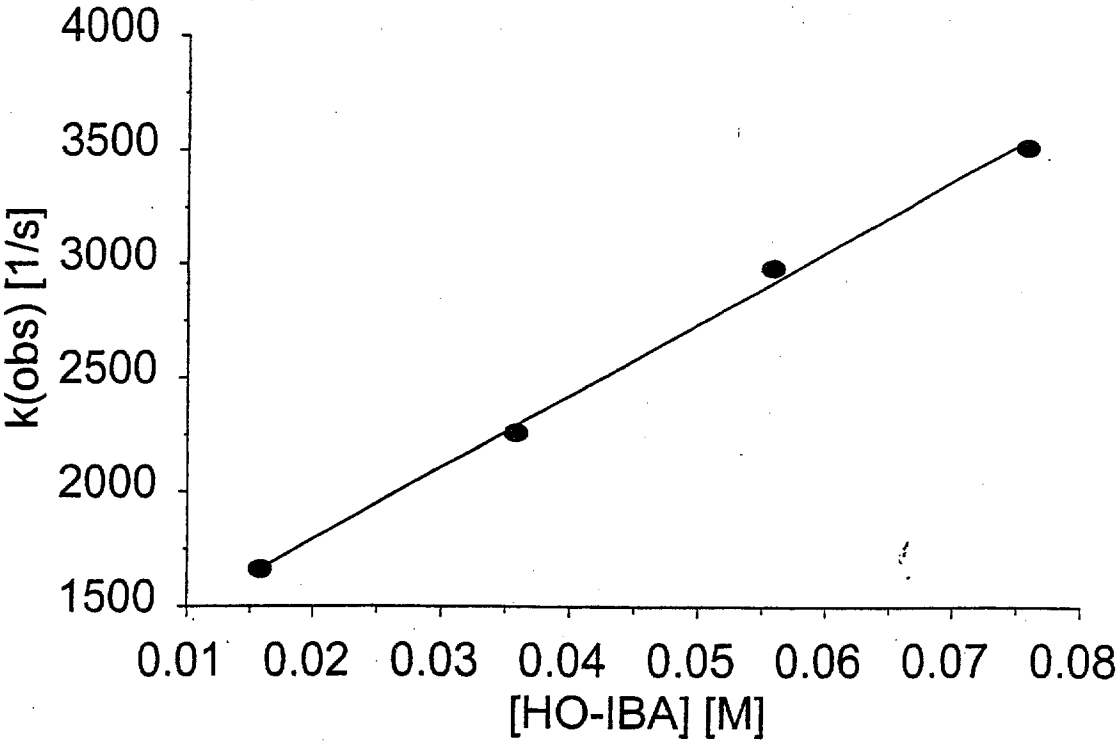


S5. pH dependence of the ^{17}O NMR spectra for the ternary U(VI)-glycolate-fluoride system (67.8 MHz, $[UO_2^{2+}]$=20mM, $[F^-]$= 100 mM, [Glycolic acid]=300 mM, at 268 K, $[Na^+]$= 1M)

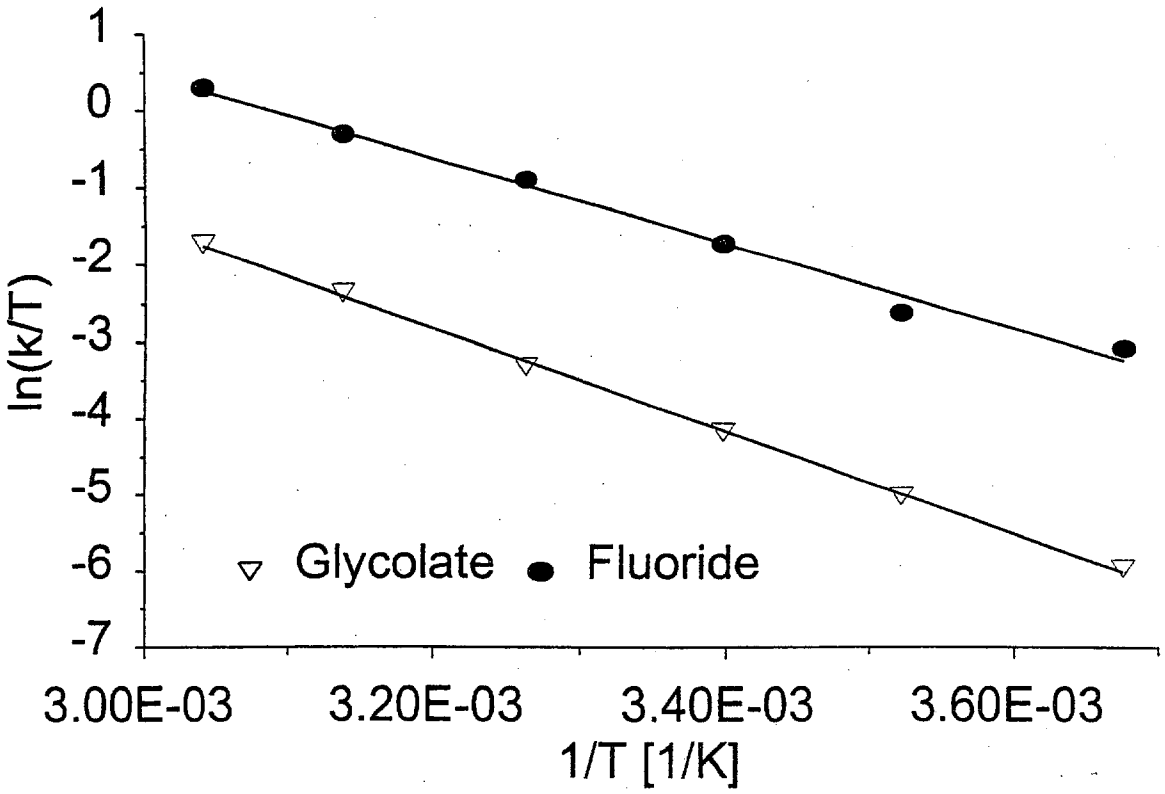


S6. pH dependent ^{1}H NMR spectra and deconvoluted peaks for the ternary U(VI)-glycolate-fluoride system (500.1 MHz, $[UO_2^{2+}]$=10mM, $[F^-]$= 50 mM, [Glycolic acid]=100 mM, in D_2O $[Na^+]$= 1M, at 268 K).

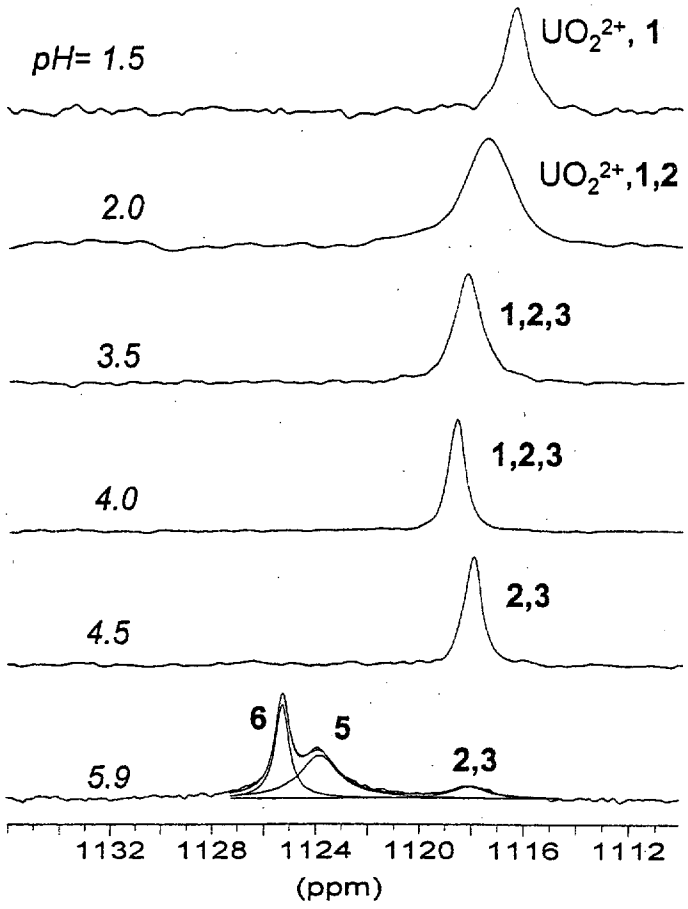




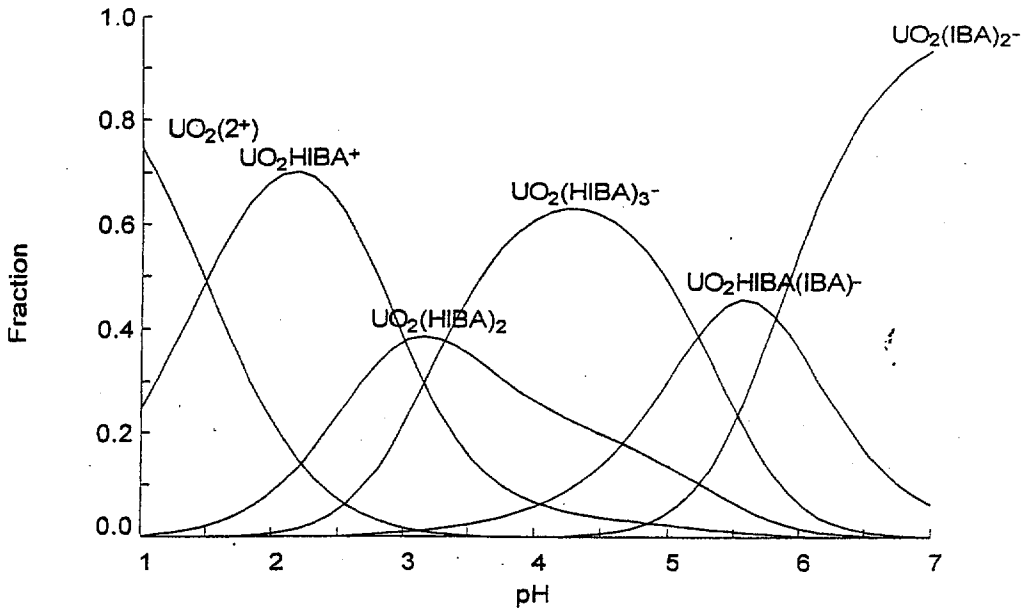
S7. Plots of the observed rate constants against the equilibrium glycolate and α-hydroxy-isobutyrate (HO-IBA) (bottom) concentration for **6** in the binary glycolate (top) and for $UO_2F_3^-$ in the ternary α-hydroxy-isobutyrate-fluoride systems.



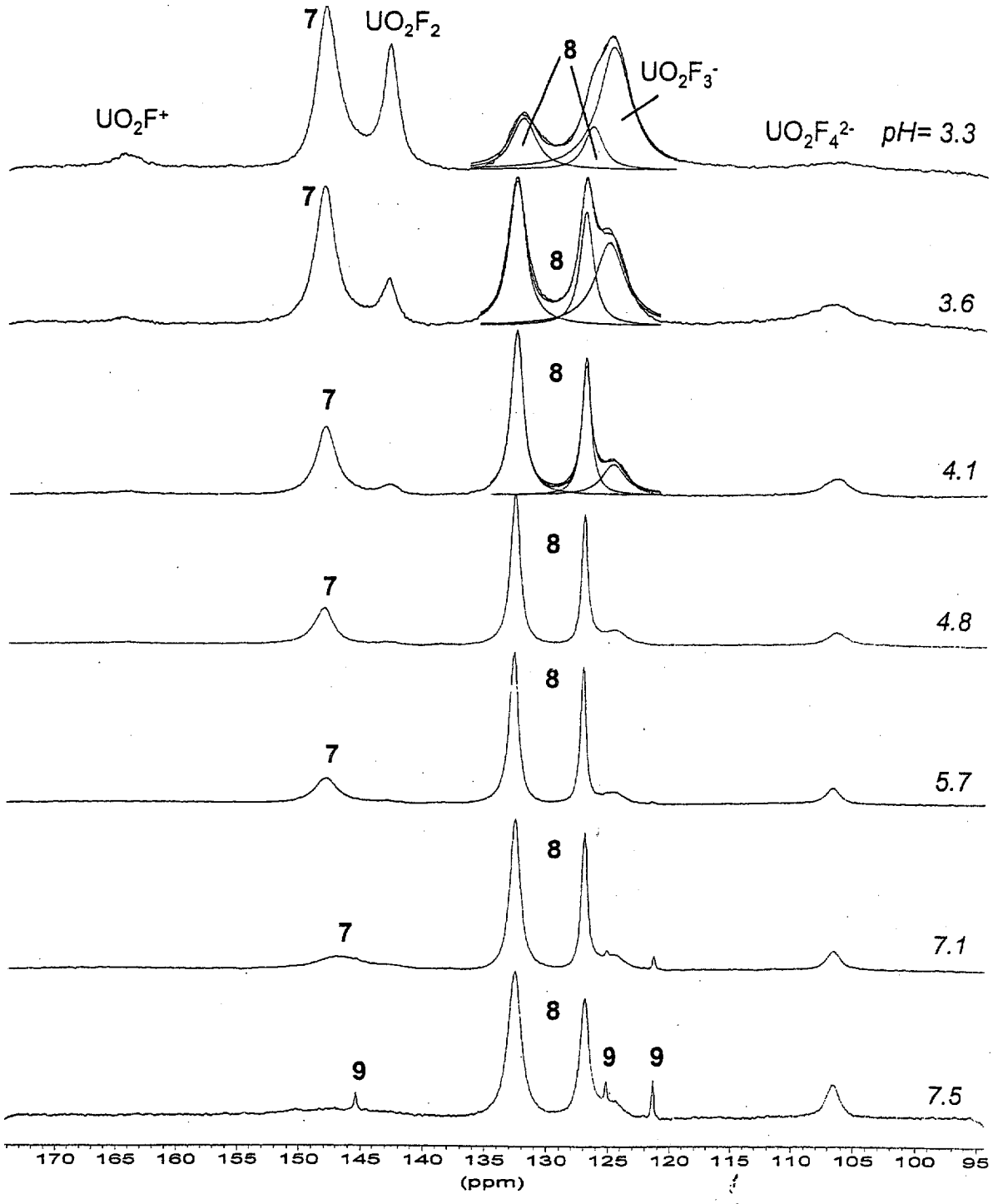
S8. Eyring plot of the temperature dependence of the rate constant for the exchanges between $UO_2(glyc)_2F^{3-}$ (11) and free fluoride and free glycolate measured by ^{19}F and ^{1}H NMR experiments, respectively.



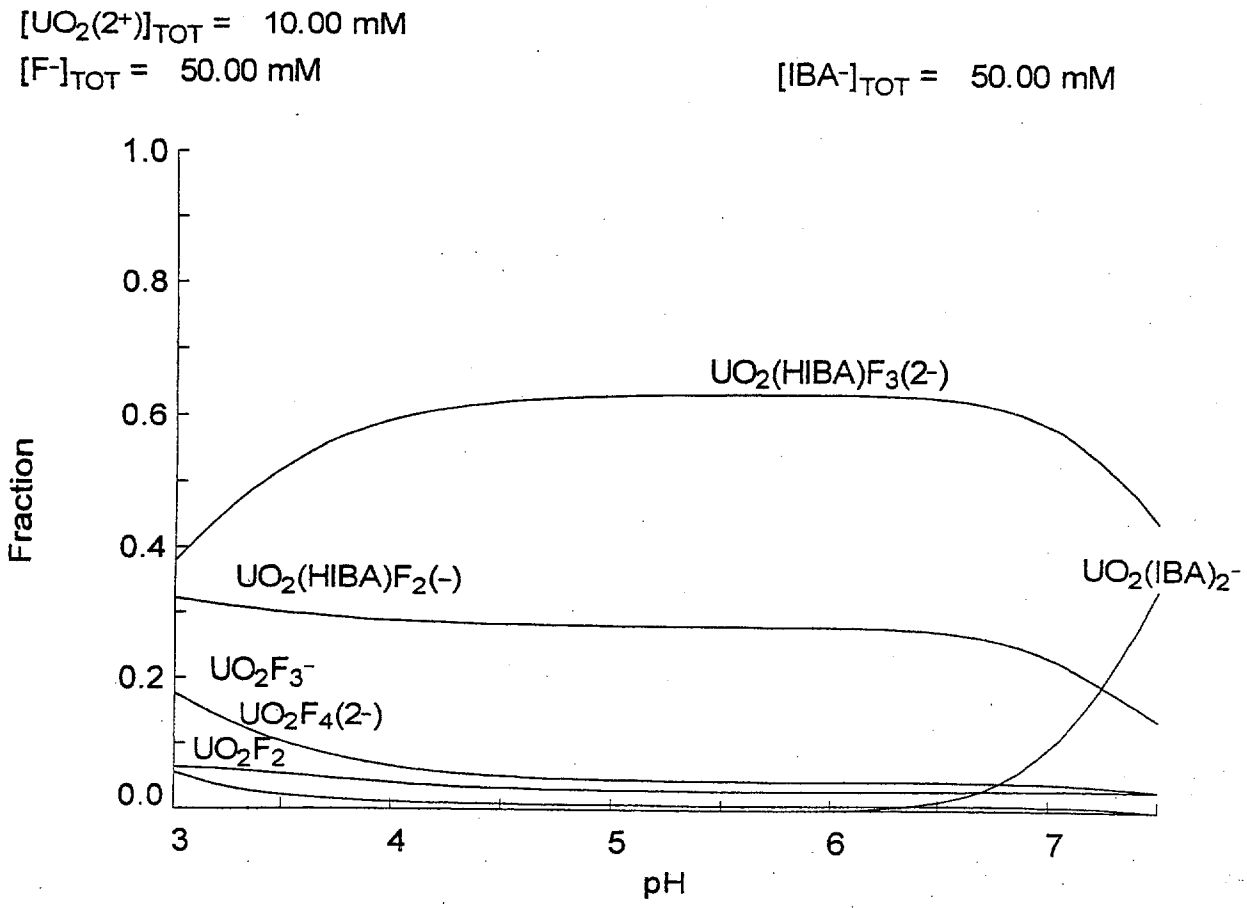
$[UO_2(2+)]_{TOT}$ = 10.00 mM
$[F^-]_{TOT}$ = 0.00
$[IBA^-]_{TOT}$ = 100.00 mM



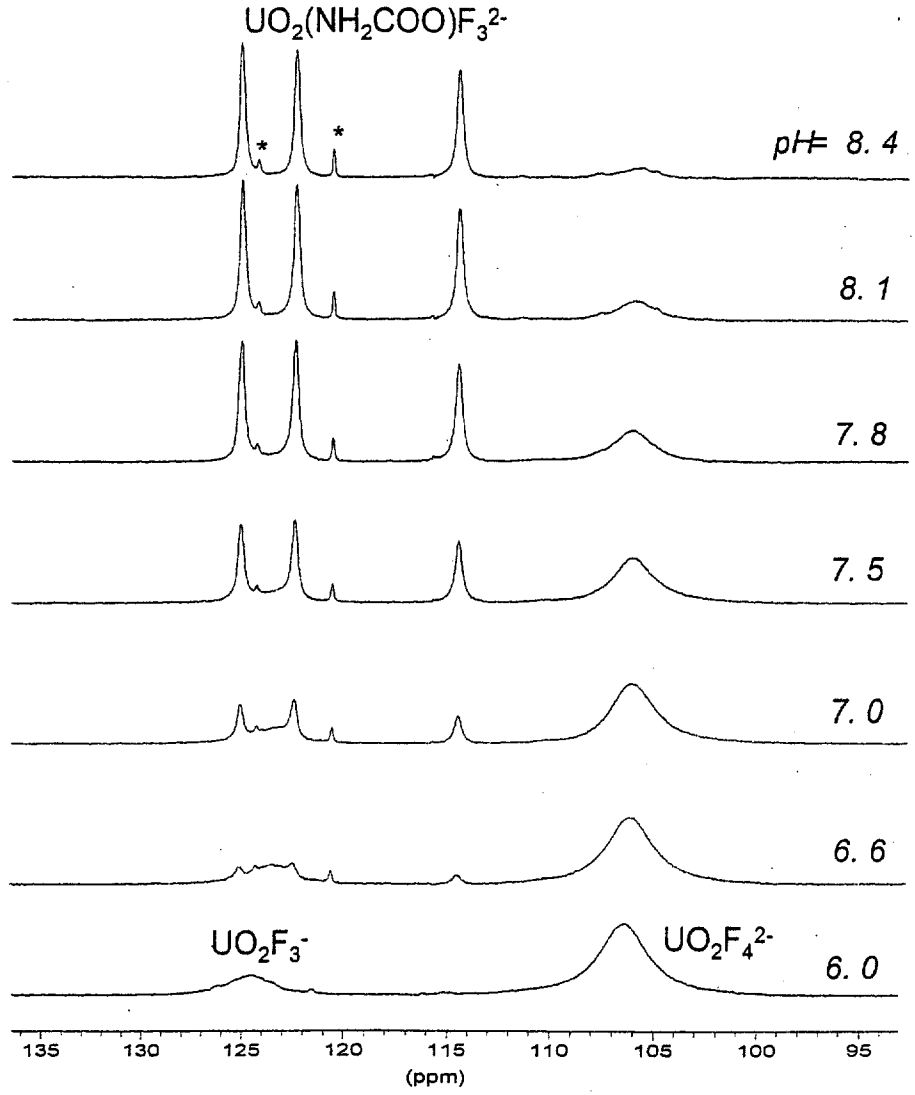
S9. pH dependent ^{17}O NMR spectra (54.2 MHz, $[UO_2^{2+}]$=10mM, [α-hydroxyisobutyric acid]=100 mM, at 268 K, $[Na^+]$= 1M) and equilibrium uranium(VI) distribution diagram as a function of pH for the binary U(VI)-α-hydroxyisobutyrate system.
(HIBA=HO-$C(CH_3)_2COO^-$, IBA= O-$C(CH_3)_2COO^{2-}$)

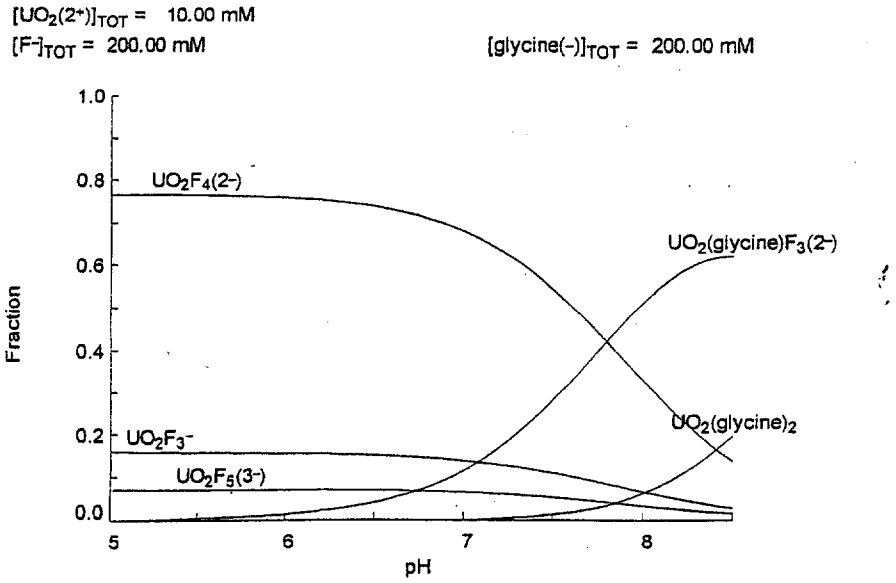


S10. pH dependent ^{19}F NMR spectra and deconvoluted peaks for the ternary U(VI)-α-hydroxyisobutyrate-fluoride system (470.5 MHz, $[UO_2^{2+}]$=10mM, [α-hydroxyisobutyric acid]=50 mM, $[F^-]$=50 mM, at 268 K, $[Na^+]$= 1M).

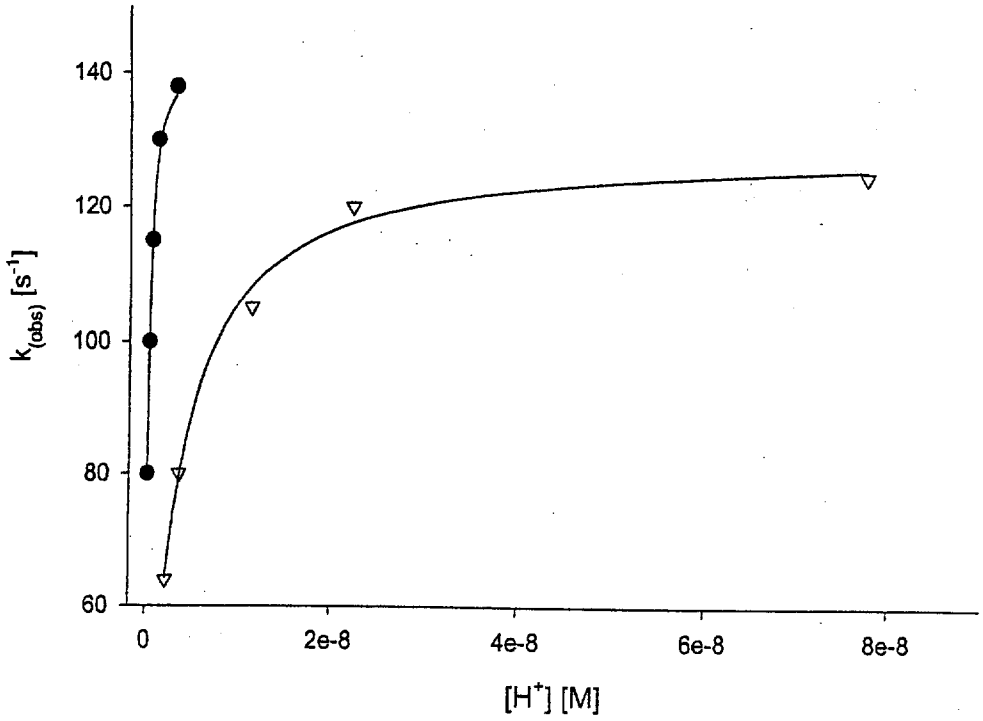


S11. Equilibrium uranium(VI) distribution diagram as a function of pH for the ternary U(VI)-α-hydroxyisobutyrate-fluoride system, $[UO_2^{2+}]$=10mM, [α-hydroxyisobutyric acid]=50 mM, $[F^-]$=50 mM. (**HIBA**= $HO\text{-}C(CH_3)_2COO^-$, **IBA**= $O\text{-}C(CH_3)_2COO^{2-}$)

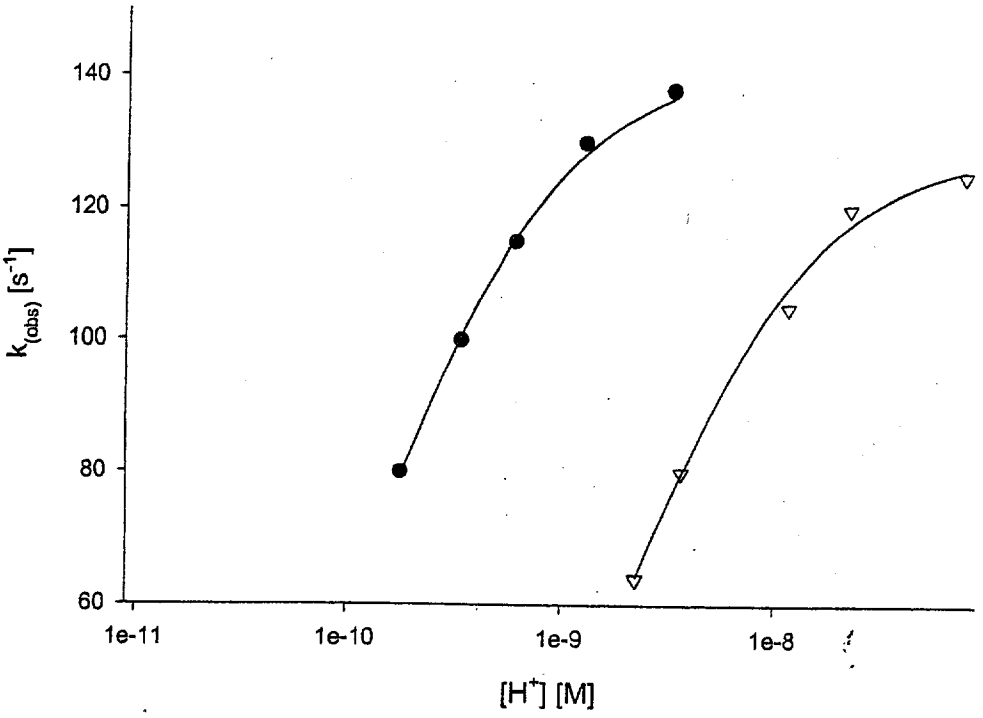




S12. pH dependence of the ^{19}F NMR spectra and equilibrium uranium(VI) distribution diagram as a function of pH for the ternary U(VI)-glycine-fluoride system (470.5 MHz, $[UO_2^{2+}]$=10mM, [glycine]=200 mM, $[F^-]$=200 mM, at 268 K, $[Na^+]$= 1M). Peaks marked by stars indicate the presence of small amount of $UO_2CO_3F_3^{3-}$.

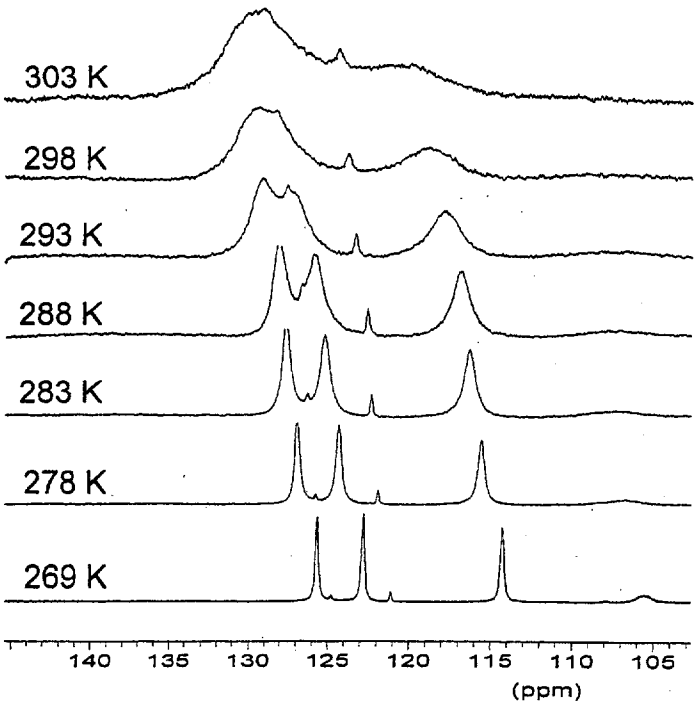


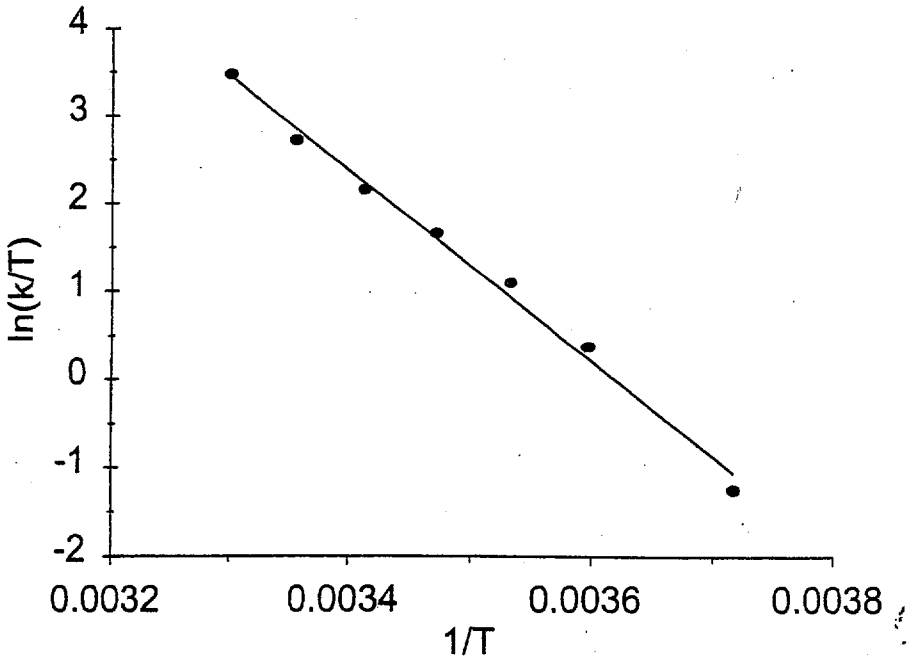
a.)



b.)

S13. a.) Proton concentration dependence of the pseudo first order rate for glycine exchange in the ternary $UO_2(H_2N\text{-}CH_2\text{-}COO)F_3^{2-}$ complex at 268 K (● in D_2O, o in H_2O), b.) the same plot using logarithmic scale.





S14. Temperature dependent ^{19}F NMR spectra in the ternary uranium(VI)-glycine-fluoride system (470.5 MHz, $[UO_2^{2+}]$=10mM, [glycine]=300 mM, $[F^-]$=200 mM) and Eyring plot of the temperature dependence of the rate constant for the glycine exchange based on the line shape analysis of the spectra.