Estimation of Model VII humic binding constants for Pd\(^{2+}\), Sn\(^{2+}\), U\(^{4+}\), NpO\(_2\)^{2+}, Pu\(^{4+}\), and PuO\(_2\)^{2+}

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Environmental impact statement

Understanding of the interactions between radionuclide cations and humic substances is important in the performance assessment of radioactive waste geological disposal options. Ultimately, any potential transport associated with humic substances (humic and fulvic acids) will be directly related to the capacity to bind a given radionuclide cation. Here we present the determination of several fulvic and humic acid binding constants for the chemical speciation model WHAM/Model VII. Modelling can be used to predict how partitioning may occur under a range of differing conditions and can help inform priorities for laboratory and field studies.
Summary

Using previously established procedures that utilise linear free energy relationships, we estimated binding constants for the Windermere Humic Aqueous Model VII (WHAM/Model VII) for several radionuclide cations (Pd$^{2+}$, Sn$^{2+}$, U$^{4+}$, NpO$_{2}^{2+}$, Pu$^{4+}$ and PuO$_{2}^{2+}$). This extends the number of cations that can be calculated with the model above the 40 included in the original Model VII work. When combined with equilibrium constants for inorganic species this allows the calculation of equilibrium distributions of chemical species under a wide range of conditions.

Introduction

Thermodynamic data are important for the modelling of potential chemical processes in both engineered parts of nuclear waste repository systems (the ‘near-field’) and in ground water and surface water systems that may affect transport to the biosphere (the ‘far-field’).

Significant efforts have been made in the collation of and assessment of thermodynamic data for the solubility and inorganic speciation of radionuclides, in particular the Nuclear Energy Agency’s Thermodynamic Data Base Project$^2$, which is now in its third decade. Whilst data for simple organic ligands have been collated, there has largely been an absence of the assessment of binding data for natural organic matter (humic and fulvic acids). There remains a large uncertainty associated with the importance of colloidal species for repository safety cases.$^3$ Overestimation of the effect of humic substances could lead to a safety case that necessitates over-engineering of a repository. In order to make more reliable safety predictions we need to improve confidence in model predictions, and this is not achieved by simply over-estimating effects. Furthermore, overestimates that may be conservative for near-field transport may have the opposite influence when considering bioavailability and toxicology issues that may affect the far-field.

The Windermere Humic Aqueous Model (WHAM$^4$) is a widely used chemical speciation code used in geochemical and ecotoxicological research and in regulation. The sub-model
dealing with natural organic matter binding has recently been updated (WHAM/Model VII)\(^5\) to include the most up to date information on humic and fulvic acid binding of protons and metal cations (40 cationic species). This also includes improved prediction of cation binding at higher pH due to increased numbers of available data and stricter data selection criteria than previously applied. Table 1 identifies those radionuclides present in significant quantities in the UK waste inventory and with half-lives longer than 10\(^5\) years, which may be relevant to radiological performance assessments for long-term geological disposal. WHAM/Model VII includes humic and fulvic acid binding data for some of these radionuclides such as \(\text{Be}^{2+}\), \(\text{Ca}^{2+}\), \(\text{Th}^{4+}\) and \(\text{UO}_2^{2+}\). In this work we have used previously described methods,\(^7\) involving linear free energy relationships, to estimate WHAM/Model VII binding constants, for the following radionuclide cations, \(\text{Pd}^{2+}\), \(\text{Sn}^{2+}\), \(\text{U}^{4+}\), \(\text{NpO}_2^{2+}\), \(\text{Pu}^{4+}\) and \(\text{PuO}_2^{2+}\). Previous models used relationships between organic binding parameters and the equilibrium constants for the first hydrolysis product (NICA-Donnan\(^8\)) or for complexation with lactic acid (Model VI\(^9\)) in the calculation/estimation of humic and fulvic binding constants. However, because of differences between models (i.e. NICA-Donnan, Models V, VI and VII), the binding parameters need to be calculated for each individual model. Furthermore, because the approach of Carbonaro and Di Toro\(^7\) involves the use of a range of simple ligands rather than a single ligand, this should give an improvement over using single values and ligands.

**Theory/methods**

The Windermere Humic Aqueous Model combines the WHAM inorganic speciation program\(^4\) with Humic Ion Binding Model VII\(^5\). The model is described in more detail in Tipping et al.\(^5\). The combination of the organic and inorganic codes is referred to here as WHAM/Model VII. The model uses a structured formulation of discrete, chemically-plausible, humic binding sites for protons, in order to allow the creation of regular arrays of bidentate and tridentate binding sites for metals. Metal ion binding at the type A (carboxylic acid type groups) and B (weaker acids, such as phenolic acids) sites is described with average intrinsic equilibrium
constants (\(K_{\text{MA}}\) and \(K_{\text{MB}}\), which are interrelated). High values of \(K_{\text{MA}}\) mean that the metal ion is strongly bound at the high abundance “weak” sites. A low density of strong binding sites are defined and are postulated to be associated with nitrogen groups (represented by \(\Delta LK_2\)) in the model (first proposed in Model VI\(^9\)). Experimental evidence for the association of cations with strong binding nitrogen sites has been reviewed by Tipping.\(^10\) High values of \(\Delta LK_2\) mean that the metal ion favours the low abundance “strong” sites. If \(\Delta LK_2\) is small, the strong sites are not favoured, and binding is predominantly due to binding at oxygen containing sites. The relative importance of the strong binding sites will be greater when cations are present at low concentrations. Such concentration windows are likely to be important when considering transport of radionuclides in the environment.

Estimating binding constants for oxygen containing sites

Irving and Rossotti\(^11\) observed that the linear free energy relationship (LFER) between thermodynamic constants for metal-ligand (\(\log K_{\text{ML}}\)) and proton-ligand (\(\log K_{\text{HL}}\)) complexation reactions could be defined by Equation 1:

\[
\log K_{\text{ML}} = \alpha \log K_{\text{HL}} + \beta
\] (1)

where \(\alpha\) is the slope, and \(\beta\) the intercept. Carbonaro and Di Toro\(^7\) referred to these parameters as the Irving–Rossotti slope and intercept, respectively. It was subsequently shown\(^12\) that in some cases plots of \(\log K_{\text{ML}}\) versus \(\log K_{\text{HL}}\) for complexes with monodentate ligands containing negatively-charged oxygen donor atoms (carboxylic acids, substituted-phenols, and hydroxide ion) are linear with an intercept nearly equal to zero \((\beta \approx 0)\). Consequently, the magnitude of the formation constant for metal–ligand complexation increases linearly with the basicity of the negatively-charged oxygen donor. The magnitude of \(\alpha_{\text{O}}\) indicates the relative preference of metal binding to negatively-charged oxygen donor atoms.\(^8\) Carbonaro and Di Toro\(^7\) showed that \(\alpha_{\text{O}}\) gave good correlations to the log \(K_{\text{MA}}\) binding parameters for humic acid (HA) and fulvic acid (FA) in WHAM V. These relationships
were recalculated by Tipping for WHAM/Model VII\(^5\) (Equations 2 and 3) by plotting fitted log 
\(K_{\text{MA}}\) for different metals (individual datasets) against \(\alpha_O\), the Irving–Rossotti slope.

\[
\text{HA log } K_{\text{MA}} = 3.51\alpha_O + 0.75 \quad (r^2 = 0.68) \tag{2}
\]

\[
\text{FA log } K_{\text{MA}} = 3.81\alpha_O + 0.37 \quad (r^2 = 0.80) \tag{3}
\]

In order to extend the WHAM database for long-lived radionuclide cations, we have compiled 
data to enable the calculation of \(\alpha_O\) and thus, the log \(K_{\text{MA}}\) values for several radionuclide 
cations. Data selection was consistent with the work of Carbonaro and Di Toro,\(^7\) i.e., the 
selected ligands were the same; thermodynamic constants were taken from the NIST Critical 
Database,\(^13\) where proton-ligand (\(K_{\text{HL}}\)) and metal-ligand (\(K_{\text{ML}}\)) complexation reactions are 
described according to \(K_{\text{HL}} = \{\text{HL}^+\}/(\{\text{H}^+\}\{\text{L}^-\})\) and \(K_{\text{ML}} = \{\text{ML}^{z-}\}/(\{\text{M}^{z+}\}\{\text{L}^-\})\); data up to ionic 
strengths of 1 mol L\(^{-1}\) were used; values were corrected to an ionic strength of \(I = 0.0\) mol L\(^{-1}\) 
using the Davies Equation\(^14\) with \(b = 0.3\); and constants with data spanning ±5°C from 25°C 
were used without temperature corrections. In addition to the NIST data, values for metal ion 
 bonding to ethanoic acid (for Sn\(^{2+}\), U\(^{4+}\) and Pu\(^{4+}\)) were estimated from the Drago equation 
(Equation 4) and associated parameters, as described in Martell and Hancock\(^12\) and 
references therein.

\[
\text{log } K_i = E_{\text{A}}^{\text{aq}}E_{\text{B}}^{\text{aq}} + C_{\text{A}}^{\text{aq}}C_{\text{B}}^{\text{aq}} + D_{\text{A}}D_{\text{B}} \tag{4}
\]

The parameters are defined as the tendency of a Lewis acid A or Lewis base B to undergo 
either electrostatic (\(E_{\text{A}}^{\text{aq}}\) and \(E_{\text{B}}^{\text{aq}}\)) or covalent (\(C_{\text{A}}^{\text{aq}}\) and \(C_{\text{B}}^{\text{aq}}\)) bonding. The parameters \(D_{\text{A}}\) 
and \(D_{\text{B}}\) correct for steric hindrance to solvation of the Lewis acid or base on complex 
formation, however, these terms have zero values for the ligands considered in this present 
work. Table 2 lists those values for species referred to in this work. The predictions are 
closely correlated with estimates, with an \(r\) squared of 0.85, based on data for 29 different 
metal complexes with ethanoate (figure shown in the supporting information).

\textit{Constants for strong binding sites}
The value for the affinity of cations to strong binding sites (\( \Delta LK_2 \)) is defined in WHAM/Model VII using a direct relationship with the equilibrium constant for complex formation with \( \text{NH}_3 \) (Equation 5),

\[
\Delta LK_2 = 0.58 \, K_{\text{NH}_3}
\]

Thus, only a single value is required for each cation (this approach is based on data fitting and the philosophy is explained in the previous work of Tipping\(^5,10\)). These data are directly available from the NIST database for \( \text{Pd} \), however, estimation is required in the cases of \( \text{Sn}^{2+} \), \( \text{U}^{4+} \), \( \text{NpO}_2^{2+} \), \( \text{Pu}^{4+} \), and \( \text{PuO}_2^{2+} \). Martell and Hancock\(^12\) established that there is a LFER for \( \text{NH}_3 \) complexation compared to pairs of ligands where one ligand has a saturated nitrogen donor, the other has a saturated oxygen and both contain two adjacent carboxylic acid chelating functional groups (Equation 6; where \( m \) is the slope, and \( c \) the intercept).

\[
K_{\text{NH}_3} = m (\log K_{1\text{IDA}} - \log K_{1\text{ODA}}) + c
\]

Thus estimation of \( \text{NH}_3 \) constants can be obtained for elements where complexation constant data are available for both oxydiacetic acid (ODA) and iminodiacetic acid (IDA). This procedure was used to determine constants for \( \text{NpO}_2^{2+} \) and \( \text{PuO}_2^{2+} \) (see supporting information for a figure showing the relationship). Values for other cations were calculated using Equation 4 and the variables cited in Martell and Hancock\(^12\).

**Results and discussion**

Figure 1 shows the Irving-Rossotti slopes for \( \text{Pd}^{2+} \), \( \text{Sn}^{2+} \), \( \text{U}^{4+} \), \( \text{NpO}_2^{2+} \), \( \text{Pu}^{4+} \) and \( \text{PuO}_2^{2+} \). The \( r^2 \) values and binding constants calculated from \( \alpha_0 \) are shown in Table 3. Data in parentheses are those obtained from only a two point plot. Other species, such as \( \text{Zr}^{4+} \), \( \text{Sn}^{4+} \), \( \text{Np}^{4+} \), \( \text{Np}^{3+} \) and \( \text{Pu}^{3+} \) were included in the data search, but were absent or did not fulfil the data selection criteria. Monovalent cations (e.g., \( \text{Cs}^+ \), \( \text{NpO}_2^+ \) and \( \text{PuO}_2^+ \)) were not included as the model only considers metal species that have appreciably greater affinities for humic functional groups. Monovalent cations are assumed to bind only non-specifically as counterions.\(^4,15\) Values for the strong binding parameters and the source of the \( K_{\text{NH}_3} \) constant
are shown in Table 3. The variables calculated for Equation 6 were \( m = 0.660 \) and \( c = -0.058 \), with an \( r \) squared of 0.934 (see supporting information for the figure used to derive these values).

It may be expected that similar actinide species may have analogous binding parameters. Model VII log \( K_{MA} \) values for Th\(^{4+}\) are 3.58 and 3.34 for humic and fulvic acid respectively, and \( \Delta LK_2 \) has a value of 0.23. Values for U\(^{4+}\) and Pu\(^{4+}\) (Table 3) show higher log \( K_{MA} \) values and much higher \( \Delta LK_2 \)s. However, the \( \Delta LK_2 \) disparities are predictable when the differences in variables for Equation 4 are considered (Table 2). Th\(^{4+}\) has a greater electrostatic contribution (\( E_A \)) and lower covalent contribution (\( C_A \)) than U\(^{4+}\) and Pu\(^{4+}\) (which have similar values). As the electrostatic term for ammonia complexation is negative, the result is a lower strong binding constant for Th\(^{4+}\). Thus, whereas U\(^{4+}\) and Pu\(^{4+}\) may be considered analogous, the data suggests that Th\(^{4+}\) should be considered in isolation. Model VII log \( K_{MA} \) values for UO\(_2\)\(^{2+}\) are 2.61 and 2.38 for humic and fulvic acid respectively, and \( \Delta LK_2 \) has a value of 1.16. Whilst the values derived here for NpO\(_2\)\(^{2+}\) and PuO\(_2\)\(^{2+}\) are slightly higher than those for UO\(_2\)\(^{2+}\), they are within the predicted margin of error for binding constants included in the uncertainty analysis within Model VII (±0.3).\(^{16}\) This suggests that these divalent oxycations may be analogous in their binding behaviour. It is worth noting here that WHAM/Model VII includes options to perform uncertainty analysis using the Monte Carlo statistical method.\(^{16}\)

To model aqueous speciation fully in WHAM, a comprehensive dataset of important inorganic equilibrium constants is required. To achieve this, we have compiled these data using a pragmatic procedure extracting the latest available data\(^{17-19}\) for each radionuclide cation. These data are tabulated in the supporting information including a brief outline of the procedure used for their compilation.

**Modelling example**
Figure 2 shows the results of speciation calculations for a simple solution containing NaCl ($\sim 0.2$ mol L$^{-1}$), PuO$_2^{2+}$ ($10^{-12}$ mol L$^{-1}$) and fulvic acid (1 mg L$^{-1}$) in both the absence and presence of carbonate ($\Sigma$[CO$_3^{2-}$]: $10^{-3}$ mol L$^{-1}$). Predictions show that in the absence of carbonates, binding to fulvic acid dominates up to a pH of $\sim$10, when the tri-hydroxyl species becomes dominant. In the presence of carbonates, fulvic acid still dominates but the di-carbonate complex is also present at a significant concentration. Above pH 10, the tri-hydroxyl species becomes dominant over the carbonate and organic species. This illustrates the capacity of the model to yield useful predictions under many different conditions.

Conclusions

Using previously established procedures we have estimated WHAM/Model VII binding constants for Pd$^{2+}$, Sn$^{2+}$, U$^{4+}$, NpO$_2^{2+}$, Pu$^{4+}$ and PuO$_2^{2+}$. When combined with constants for inorganic species this allows the calculation of equilibrium distributions of chemical species under a wide range of conditions. This has vastly improved the applicability of the WHAM speciation model for radioactive isotope speciation and thus makes the model applicable to radiological performance assessment calculations. Whilst efforts should be made to enable determination of K$_{MA}$ values from laboratory data, estimates based on sound chemical principles provide a useful starting point to predicting behaviour of these cations in aqueous solutions in the presence of humic substances and there is a pressing need to perform such estimations. Models such as WHAM/Model VII allow comparison of different datasets for the same cation using a consistent framework. Furthermore, these simple procedures allow easy recalculation of constants should further data become available for these or other radionuclide cations.

Acknowledgements

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References


Tables

Table 1. Radionuclides with both half-lives greater than $10^5$ years and with more than 0.1 TBq of activity in UK quantified waste streams. Half-lives, activity and equivalent quantities in terms of mass and molar quantity are shown.

<table>
<thead>
<tr>
<th>Nuclide</th>
<th>Half life (My)</th>
<th>Activity (TBq) reported in 2010 UK inventory*</th>
<th>Equivalent as:</th>
</tr>
</thead>
<tbody>
<tr>
<td>$^{10}$Be</td>
<td>$1.60 \times 10^0$</td>
<td>$4.10 \times 10^{-1}$</td>
<td>Kg: 0.050; Moles: ($10^3$) 0.050</td>
</tr>
<tr>
<td>$^{36}$Cl</td>
<td>$3.02 \times 10^{-1}$</td>
<td>$1.13 \times 10^1$</td>
<td>Kg: 9.32; Moles: 0.259</td>
</tr>
<tr>
<td>$^{41}$Ca</td>
<td>$1.03 \times 10^{-1}$</td>
<td>$3.72 \times 10^0$</td>
<td>Kg: 1.19; Moles: 0.029</td>
</tr>
<tr>
<td>$^{93}$Zr</td>
<td>$1.53 \times 10^{-2}$</td>
<td>$7.30 \times 10^2$</td>
<td>Kg: 7882; Moles: 84.8</td>
</tr>
<tr>
<td>$^{95}$Tc</td>
<td>$2.13 \times 10^{-1}$</td>
<td>$2.98 \times 10^3$</td>
<td>Kg: 4768; Moles: 48.2</td>
</tr>
<tr>
<td>$^{103}$Pd</td>
<td>$6.50 \times 10^{-2}$</td>
<td>$2.96 \times 10^1$</td>
<td>Kg: 1562; Moles: 14.6</td>
</tr>
<tr>
<td>$^{126}$Sn</td>
<td>$1.00 \times 10^{-1}$</td>
<td>$2.25 \times 10^2$</td>
<td>Kg: 215; Moles: 1.71</td>
</tr>
<tr>
<td>$^{129}$I</td>
<td>$1.57 \times 10^{-1}$</td>
<td>$6.80 \times 10^1$</td>
<td>Kg: 104.5; Moles: 0.81</td>
</tr>
<tr>
<td>$^{135}$Cs</td>
<td>$2.30 \times 10^{-2}$</td>
<td>$1.97 \times 10^2$</td>
<td>Kg: 4637; Moles: 34.3</td>
</tr>
<tr>
<td>$^{229}$Th</td>
<td>$1.41 \times 10^{-4}$</td>
<td>$2.30 \times 10^{-1}$</td>
<td>Kg: 57093; Moles: 246</td>
</tr>
<tr>
<td>$^{232}$U</td>
<td>$1.59 \times 10^{-1}$</td>
<td>$1.60 \times 10^0$</td>
<td>Kg: 4.50; Moles: 0.019</td>
</tr>
<tr>
<td>$^{235}$U</td>
<td>$7.04 \times 10^{-2}$</td>
<td>$5.51 \times 10^1$</td>
<td>Kg: 6917; Moles: 29.4</td>
</tr>
<tr>
<td>$^{236}$U</td>
<td>$2.34 \times 10^{-1}$</td>
<td>$1.51 \times 10^0$</td>
<td>Kg: 631; Moles: 2.67</td>
</tr>
<tr>
<td>$^{238}$U</td>
<td>$4.47 \times 10^{-2}$</td>
<td>$1.70 \times 10^1$</td>
<td>Kg: 1.37 x $10^6$; Moles: 5776</td>
</tr>
<tr>
<td>$^{237}$Np</td>
<td>$2.14 \times 10^{-2}$</td>
<td>$9.80 \times 10^1$</td>
<td>Kg: 3772; Moles: 15.9</td>
</tr>
<tr>
<td>$^{242}$Pu</td>
<td>$3.74 \times 10^{-3}$</td>
<td>$6.41 \times 10^0$</td>
<td>Kg: 44.0; Moles: 0.182</td>
</tr>
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</table>

* NDA/DECC

Table 2. Drago equation parameters for those Lewis acids and bases referred to in this work (from reference 12). $D_A$ and $D_B$ values are not shown as the value for the two Lewis bases is zero.

<table>
<thead>
<tr>
<th>Lewis acid</th>
<th>$E_A$ or $E_B$</th>
<th>$C_A$ or $C_B$</th>
</tr>
</thead>
<tbody>
<tr>
<td>$\text{Sn}^{2+}$</td>
<td>5.65</td>
<td>0.700</td>
</tr>
<tr>
<td>$\text{Th}^{4+}$</td>
<td>8.44</td>
<td>0.771</td>
</tr>
<tr>
<td>$\text{U}^{4+}$</td>
<td>7.55</td>
<td>0.968</td>
</tr>
<tr>
<td>$\text{Pu}^{4+}$</td>
<td>7.90</td>
<td>0.950</td>
</tr>
<tr>
<td>Lewis base</td>
<td></td>
<td></td>
</tr>
<tr>
<td>$\text{CH}_3\text{OO}^-$</td>
<td>0.00</td>
<td>4.760</td>
</tr>
<tr>
<td>$\text{NH}_3$</td>
<td>-1.08</td>
<td>12.34</td>
</tr>
</tbody>
</table>

Table 3. Linear Free Energy Relationship analysis for metal complexes of several long-lived radionuclides, including derived WHAM/Model VII $\log K_{MA}$ values for humic and fulvic acid, and strong binding constants plus the source of the $\text{NH}_3$ stability constant data.

<table>
<thead>
<tr>
<th>Metal / species</th>
<th>n</th>
<th>Irving–Rossotti slope, $\alpha_O$</th>
<th>$r^2$</th>
<th>HA $\log K_{MA}$</th>
<th>FA $\log K_{MA}$</th>
<th>$\Delta LK_2$</th>
<th>Source of $K_{\text{NH}_3}$ data</th>
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</thead>
<tbody>
<tr>
<td>$\text{Pd}^{2+}$</td>
<td>4</td>
<td>0.860</td>
<td>0.929</td>
<td>3.77</td>
<td>3.65</td>
<td>5.57</td>
<td>NIST database</td>
</tr>
<tr>
<td>$\text{Sn}^{2+}$</td>
<td>2</td>
<td>(0.749)</td>
<td>-</td>
<td>3.38</td>
<td>3.22</td>
<td>1.47</td>
<td>Equation 4</td>
</tr>
<tr>
<td>$\text{U}^{4+}$</td>
<td>2</td>
<td>(0.952)</td>
<td>-</td>
<td>4.09</td>
<td>4.00</td>
<td>2.20</td>
<td>Equation 4</td>
</tr>
<tr>
<td>$\text{NpO}_2^{2+}$</td>
<td>5</td>
<td>0.635</td>
<td>0.988</td>
<td>2.98</td>
<td>2.79</td>
<td>1.33</td>
<td>Equation 6</td>
</tr>
<tr>
<td>$\text{Pu}^{4+}$</td>
<td>2</td>
<td>(0.948)</td>
<td>-</td>
<td>4.08</td>
<td>3.98</td>
<td>1.85</td>
<td>Equation 4</td>
</tr>
<tr>
<td>$\text{PuO}_2^{2+}$</td>
<td>4</td>
<td>0.580</td>
<td>0.994</td>
<td>2.79</td>
<td>2.58</td>
<td>1.32</td>
<td>Equation 6</td>
</tr>
</tbody>
</table>
Figure captions

Figure 1. Plots of log $K_{ML}$ for metal complex formation versus the corresponding ligand log $K_{HL}$ for a series of monodentate ligands containing negatively-charged oxygen donor atoms. Solid lines represent results from linear regression with intercepts forced through zero. Irving–Rossotti slopes for negatively-charged oxygen donor atoms, $\alpha_O$, and the $r^2$ values, are indicated on each plot. Circles represent data from the NIST database, squares represent data for ethanoic acid calculated using the Drago equation (Equation 4; Table 2).

Figure 2. Example speciation calculations for a simple aqueous solution containing $\text{PuO}_2^{2+}$ and fulvic acid, in both the absence (panel A) and presence (panel B) of carbonate. See text for discussion.

Figures

Figure 1.
Figure 2.

[Graph showing pH vs. Concentration (log mol L\(^{-1}\)) for different species including PuO\(_2\)-FA, PuO\(_2\)(OH\(_3\))\(^-\), PuO\(_2\)(OH\(_2\))(aq), PuO\(_2\)(OH\(_-\)), PuO\(_2\)(OH\(_2\))(aq), PuO\(_2\)(CO\(_3\))\(^2-\), PuO\(_2\)(CO\(_3\))\(^3-\), PuO\(_2\)(OH\(_+\)), PuO\(_2\)(CO\(_3\))(aq), PuO\(_2\)(CO\(_3\))(aq), PuO\(_2\)(OH\(_-\)), PuO\(_2\)(CO\(_3\))(aq).]