

Stability constants of U(VI) and U(IV)-humic acid complexes

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Conditional stability constants have been determined for U(IV) and U(VI) Boom Clay humic acid (BCHA) and Aldrich humic acid (AHA) complexes, under anaerobic and carbonate free conditions. The constants are needed for nuclear waste repository performance assessment purposes. The U(IV) constants were obtained by developing an approach based on the solubility product of amorphous $U(OH)_4$. The U(VI) constants were obtained by applying the Schubert ion-exchange approach.

Introduction

A nuclear waste repository may be constructed underground in the Belgian Boom Clay (BC) geological formation. BC is highly impervious but contains relatively large amounts of interstitial humic acid (BCHA). Mobile and immobile fractions are present, capable, in principle, of exerting opposing effects on metal transport due to the formation of metal humate complexes.¹ The mobile and immobile forms exhibit similar complexing tendencies, but the immobile form is more abundant. Clearly, radionuclide humic acid stability constants are needed for repository performance assessment purposes.

This particular study was undertaken to obtain U(IV) and U(VI)–BCHA constants. Various U(VI) HA values can be found in the literature, see for example the fluorescence study by SAITO and co-workers,² and the references contained therein. Unfortunately, the reported constants are generally conditional, and relate to pH values less than 7.0, for example CZERWINSKI et al.³ reported for Gorleben humic acid (HA), $\log \beta = 6.16 \pm 0.13$ at pH 4.0.³ BC interstitial water has a pH of approximately 8.2. The U(IV)–HA value is particularly important because many possible far-field conditions, such as Boom Clay, are reducing. The solubility of crystalline UO_2 in Boom Clay conditions has been measured by CACHOIR et al.⁴ The solubility was found to vary between $3 \cdot 10^{-8}$ and $1.5 \cdot 10^{-6}$ mol·dm⁻³.

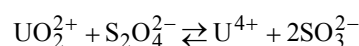
The experiments were conducted using purified Aldrich humic acid AHA and BCHA extracted from the clay at the underground research facility at Mol in Belgium, at a depth of 223 m.¹ The extract was concentrated using the diethyl-amino-ethyl cellulose procedure of MILES et al.⁵ The U(IV) constants were obtained by developing an approach based on the “solubility product” of the solid phase precipitated under alkaline conditions and assumed to be $U(OH)_4$ (am). The U(VI) constants were obtained by employing the “classical” Schubert ion-exchange approach.⁶ The

experiments were performed at pH values of relevance to environmental conditions, with O_2 and CO_2 excluded. For comparative purposes U(IV) and U(VI)–AHA constants were also determined using similar conditions.

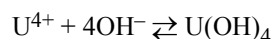
Solubility product approach for U(VI) constants

The solubility product approach involved three stages: (1) precipitation and ageing of amorphous $U(OH)_4$, (2) equilibration with BCHA or AHA, and (3) supernatant activity measurements.

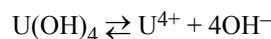
In the first stage uranyl nitrate [$UO_2(NO_3)_2$] solution, containing a tracer amount of ²³³U, was treated with sodium dithionite ($Na_2S_2O_4$) under alkaline conditions in the absence of air and carbonate. The yellow U(VI) solution was reduced to U(IV) and grey/brown amorphous $U(OH)_4$ precipitated. The precipitates were aged for 2 weeks. The reactions can be represented as:



and



Uranium(IV) hydroxide is very sparingly soluble. The dissolution can be represented as the reverse of the formation reaction, i.e.:



The solubility product (K_{sp}) is given by:

$$K_{sp} = [U^{4+}][OH^-]^4 \quad (1)$$

Under hydrolyzing conditions in the absence of HA, speciation studies show that the total U(IV) concentration in solution ($[U]_{sol}$) can be expressed as:

$$[U]_{sol} = [U^{4+}] + [U(OH)^{3+}] + [U(OH)_2^{2+}] + [U(OH)_3^+] + [U(OH)_4] \quad (2)$$

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Hence:

$$\begin{aligned}
 [U]_{\text{sol}} &= [U^{4+}] + \beta_I[U^{4+}][OH^-] + \beta_{II}[U^{4+}][OH^-]^2 + \\
 &+ \beta_{III}[U^{4+}][OH^-]^3 + \beta_{IV}[U^{4+}][OH^-]^4 = \\
 &= [U^{4+}]\{1 + \beta_I[OH^-] + \beta_{II}[OH^-]^2 + \\
 &+ \beta_{III}[OH^-]^3 + \beta_{IV}[OH^-]^4\} = [U^{4+}]A
 \end{aligned} \quad (3)$$

where β_I , β_{II} , β_{III} and β_{IV} are the stability constants of the various hydrolysis products, and A is a pH dependent constant, known as the side reaction coefficient.⁷

After ageing, the precipitates were treated with HA. Since U^{4+} may react with humic acids to form binary and ternary (i.e., mixed) complexes,⁸ the dissolved uranium concentration ($[U]_{\text{sol}}$) in the presence of HA may be expressed as:

$$\begin{aligned}
 [U]_{\text{sol}} - [U^{4+}]A &= [UHA] + [U(OH)[HA]] + \\
 &+ [U(OH)_2HA] + [U(OH)_3HA] + [U(OH)_4HA]
 \end{aligned} \quad (4)$$

Hence, the total humate complex concentration is given by:

$$\begin{aligned}
 [U]_{\text{sol}} - [U^{4+}]A &= \beta[U^{4+}][HA] + \\
 &+ \beta_1[U^{4+}][HA][OH^-] + \\
 &+ \beta_2[U^{4+}][HA][OH^-]^2 + \beta_3[U^{4+}][HA][OH^-]^3 + \\
 &+ \beta_4[U^{4+}][HA][OH^-]^4
 \end{aligned} \quad (5)$$

Rearrangement of Eq. (5) allows an experimental stability constant (β_{exp}) to be defined, i.e.:

$$\begin{aligned}
 \frac{[U]_{\text{sol}} - [U^{4+}]A}{[U^{4+}][HA]} &= \beta + \beta_1[OH^-] + \beta_2[OH^-]^2 + \\
 &+ \beta_3[OH^-]^3 + \beta_4[OH^-]^4 = \beta_{\text{exp}}
 \end{aligned} \quad (6)$$

From Eq. (1)

$$[U^{4+}] = \frac{K_{sp}}{[OH^-]^4}$$

Therefore:

$$\beta_{\text{exp}} = \frac{[U]_{\text{sol}} - \left(\frac{K_{sp}}{[OH^-]^4}\right)A}{\left(\frac{K_{sp}}{[OH^-]^4}\right)\left([HA]_{\text{total}} - \left([U]_{\text{sol}} - \left(\frac{K_{sp}}{[OH^-]^4}\right)A\right)\right)} \quad (7)$$

β_{exp} values were calculated using Eq. (7) from the measured supernatant activities, the HA concentrations and pH values. The K_{sp} value was obtained by determining the solubility of the precipitate in the absence of HA.

Schubert ion-exchange approach for U(VI) constants

The standard Schubert method was applied by placing ^{233}U tracer in contact with a cation exchange resin (Na form), in the presence and absence of varying amounts of HA. Appropriate D and D_0 values, i.e., the distribution coefficients ($[U]_{\text{resin}}/[U]_{\text{solution}}$), in the presence and absence of HA, were derived from supernatant activity measurements. β_{exp} values were calculated using the Schubert relationship, given by:

$$\log \beta_{\text{exp}} = \log_{10} A \left(\frac{D_0}{D} - 1 \right) - n \log[HA] \quad (8)$$

A is again the side reaction coefficient term, included to take account of competition from hydroxide ions, and n is the stoichiometric ratio of HA to U(VI) in the complex.⁶

Experimental

Determination of the U(IV)-HA stability constants using the solubility product approach

A concentrated solution of BCHA, known to contain traces of carbonate, was taken and purified by addition of hydrochloric acid ($5 \text{ mol}\cdot\text{dm}^{-3}$), and purged with N_2 to remove CO_2 . The precipitate formed was centrifuged off and dried in a desiccator. A working stock solution was then produced by dissolving the purified BCHA in dilute carbonate free NaOH solution. This stock ($904 \text{ mg carbon}\cdot\text{dm}^{-3}$) was successively diluted to produce a range of concentrations. Samples of amorphous $\text{UO}_2\cdot 2\text{H}_2\text{O}$ were precipitated in NALGENE vials by mixing 2.5 cm^3 of carbonate free NaOH ($0.4 \text{ mol}\cdot\text{dm}^{-3}$), 5.0 cm^3 $\text{Na}_2\text{S}_2\text{O}_4$ solution ($0.10 \text{ mol}\cdot\text{dm}^{-3}$) and 2.5 cm^3 $\text{UO}_2(\text{NO}_3)_2$ solution ($0.01 \text{ mol}\cdot\text{dm}^{-3}$, containing ^{233}U tracer solution giving $\sim 12 \text{ MBq}\cdot\text{dm}^{-3}$). The solutions were prepared using N_2 purged, boiled, de-ionized water and the mixtures were prepared in a N_2 atmosphere glove box. After two weeks the aged precipitates were centrifuged, washed with $\text{Na}_2\text{S}_2\text{O}_4$ solution ($0.05 \text{ mol}\cdot\text{dm}^{-3}$) and re-centrifuged. The supernatants were then decanted off, and the washed precipitates treated with different amounts of BCHA and AHA. Controls were set up with deionized water and a solution of sodium dithionite ($0.01 \text{ mol}\cdot\text{dm}^{-3}$) to determine if dithionite was causing a change in the solubility of U(IV). The AHA experiments used AHA diluted to $1000 \text{ mg carbon}\cdot\text{dm}^{-3}$ with deionized and deoxygenated water and adjusted to the required pH with HCl or NaOH. Experiments were performed at pH values of 8.6, 7.5 and 6.4. The BCHA experiments were designed for multiple repetitions at constant pH used HEPES buffer ($0.1 \text{ mol}\cdot\text{dm}^{-3}$). Humic acid addition ($x \text{ cm}^3$) was followed by $\text{Na}_2\text{S}_2\text{O}_4$ solution (2.5 cm^3 ; $0.20 \text{ mol}\cdot\text{dm}^{-3}$),

HEPES buffer (2.5 cm³, 0.4 mol·dm⁻³, pH 8.2) and sufficient H₂O to produce a final volume of 10 cm³, i.e., (5-x) cm³.

In the experiments undertaken to determine the solubility product, the HA was omitted. The solutions used in these experiments were filtered through 0.45, 0.2, 0.1, 0.02 µm and 100k, 10k and 1k MWCO filters to determine whether U(IV) colloids were present. After 2 weeks equilibration an aliquot of each supernatant was filtered off (0.45 µm) and the specific activity (dpm·cm⁻³) determined using liquid scintillation counting (LSC). The pH and E_h values were monitored throughout.

Determination of the U(VI)-BCHA and U(VI)-AHA stability constants using the Schubert ion-exchange procedure

A number of plastic (NALGENE) vials were taken and cation-exchanger, in the Na form, placed in each (10 mg; BioRad AG50W X2; 100–200 mesh). An aliquot (15 cm³) of one of the BCHA solutions was then added, followed by HEPES buffer (5.0 cm³; 0.41 mol·dm⁻³; pH 8.0) and finally ²³³U tracer solution (0.50 cm³; ~6 kBq·cm⁻³). Each vial contained 2.21·10⁻⁷ mol·dm⁻³ U(VI) in 20.5 cm³. A control experiment was also conducted replacing the BCHA solution with the same volume of water. The resulting mixtures were equilibrated for 2 weeks at room temperature with intermittent shaking. The whole experiment was conducted inside a N₂ atmosphere glove box (<1 ppm O₂). Afterwards a filtered (0.45 µm) sample of each supernatant was taken (1.0 cm³) and placed in a counting vial, containing 15 cm³ of Ecoscint cocktail. The ²³³U activity was determined using liquid scintillation counting. Quenching problems were avoided by the use of a wide counting channel in which the counting efficiency for ²³³U was 100%.

The experiments were performed in triplicate. Essential details of the mixtures and the results are given in Table 1. A second set of experiments at pH 8.4 was then conducted using acid precipitated AHA instead of BCHA. A similar procedure was followed using a 1000 mg·dm⁻³ purified AHA solution for the initial working stock. The details of the mixtures and results are given in Table 2.

Results and discussion

U(IV) solubility product determinations

The calculation of the side reaction coefficient, the A term, is simplified if the dominating uranium species, in the absence of HA, are known at the experimental pH values. Therefore, calculations were performed using the

thermodynamic constants published by NECK and KIM⁹ (Table 3), to determine the speciation of uranium(IV) from pH 6 to 9. These calculations are shown in Fig. 1. The calculations were performed using the speciation programme CHESS,¹⁰ for an initial concentration of U(IV) of 1·10⁻⁷ mol·dm⁻³, which was similar to that used in the experiments. The figure clearly shows that the dominant uranium(IV) species is U(OH)₄, which consequently dominates the A term. The A term was,

Table 1. Results of the Schubert experiment, using Na form cation-exchange resin (10 mg), with purified BCHA (15 cm³; proton capacity 4.0·10⁻³ mol·g⁻¹), HEPES buffer (pH 8.0; 0.41 mol·dm⁻³; 5.0 cm³) and ²³³U tracer (0.5 cm³). $A = 1.50·10^5$

Log[BCHA]	Supernatant, dpm·cm ⁻³	D	Log[(D_0/D)-1] A	Log β
-2.28	768.7	0.106	5.04	7.32
-2.58	765.1	0.111	5.02	7.60
-2.88	713.7	0.191	4.77	7.65
-3.18	706.3	0.203	4.74	7.92
-3.48	648.5	0.311	4.54	8.02
-4.08	526.6	0.614	4.19	8.27
-4.38	420.2	1.023	3.89	8.27
-4.99	244.8	2.472	2.90	7.88
-5.29	222.2	2.825	2.26	7.54
				Mean: 7.94
				(s.d.: 0.33)

Total activity present = 850 dpm·cm⁻³; $D_0 = 2.95$.

Table 2. Results of the Schubert experiment, using Na form cation-exchange resin (10 mg), with purified AHA (15 cm³; proton capacity 5.3·10⁻³ mol·g⁻¹), HEPES buffer (pH 8.4; 0.41 mol·dm⁻³; 5.0 cm³) and ²³³U tracer (0.5 cm³). $D_0 = 2.95$; for $A = 4.22·10^4$

Log[AHA]	Supernatant, dpm·cm ⁻³	D	Log[(D_0/D)-1] A	Log β
-2.41	830.8	0.023	6.73	9.14
-2.71	799.9	0.063	6.29	9.00
-3.01	717.9	0.184	5.80	8.82
-3.32	715.3	0.188	5.79	9.11
-3.62	612.7	0.387	5.45	9.06
-3.92	557.0	0.526	5.29	9.21
-4.22	462.2	0.839	5.03	9.24
-4.52	355.2	1.393	4.67	9.19
-4.82	313.5	1.711	4.49	9.30
-5.12	223.5	2.803	3.34	8.47
-5.42	242.7	2.502	3.88	9.30
				Mean: 9.13
				(s.d.: 0.25)

Total activity present = 850 dpm·cm⁻³; $D_0 = 2.95$.

therefore, calculated for the



reaction equation using log $\beta = 46$, which was further adjusted to 48.5 to take account of the experimental

ionic strength ($I=0.2$). The required activity coefficients were calculated using the DAVIES equation,¹¹ i.e.,

$$\log \gamma = -0.51z^2 \left(\frac{\sqrt{I}}{1+1.5\sqrt{I}} \right) - 0.3I$$

where I is the ionic strength and z is the charge on the ion, e.g., at pH 10.17:

$$A = \{1 + \sum \beta_4 [\text{OH}^-]^4\} = \\ = 1 + (3.47 \cdot 10^{48} \cdot (1.48 \cdot 10^{-4})^4) = 1.66 \cdot 10^{33}.$$

$$K_{sp} = [\text{U}^{4+}][\text{OH}^-]^4 = [\text{U}]_{\text{solution}}[\text{OH}^-]^4/A = \\ = 1.52 \cdot 10^{-8} \cdot (1.48 \cdot 10^{-4})^4 / 1.66 \cdot 10^{33} = 4.39 \cdot 10^{-57}$$

i.e., $\log K_{sp} = -56.4$. The details and results of the experiments conducted to determine the solubility product of $\text{UO}_2(\text{am})$, undertaken in the absence of HA, are summarized in Table 4.

Uranium(IV) oxide solubilities reported in the literature vary.⁹ The variation can be attributed to the stoichiometry of the solid and/or its degree of crystallinity. The solubility product determined in this study ($\log K_{sp} = -56.2$) agrees reasonably well with literature values for amorphous UO_2 , e.g.,

$\log K_{sp} = -53.45$ ($I=0$), -55.7 ($I=0$), -54.5 ($I=0$)⁹
and

-56.2 ($I=0$), -55.6 ($I=3.0$), -54.3 ($I=0.5$)¹²

which gave confidence in the use of the experimentally determined value to derive the U(IV)–HA $\log \beta$ values.

Control experiments showed that the addition of dithionite ($0.01 \text{ mol} \cdot \text{dm}^{-3}$) did not increase the solubility of uranium above that which was observed when deionized water alone was added. Hence, the possibility of significant complexation of dithionite with uranium(IV) was discounted. Further control experiments, in which HA free samples were filtered, did not show a decrease in the uranium concentration, demonstrating that uranium colloids were not significant.

Calculation of the U(IV)–BCHA stability constant

The U(IV)–BCHA results using the solubility product approach, are shown in Table 5. The presence of U(IV) was assumed based on the E_h evidence. The measured E_h values may be converted to the standard hydrogen electrode (E_{she}) scale by adding 204 mV. The term values were calculated using the constants from NECK and KIM⁹ (Table 1), but modified to be consistent with the ionic strength of the mixtures ($I=0.2$).

The experiments were conducted at various pH values. The effect of pH on the value of $\log \beta$ is shown in Fig. 2. The slope of 4 is a consequence of the dissolution step of UO_2 dissolving to form $\text{U}(\text{OH})_4$, and the inclusion of this term in the side reaction coefficient. The conditional $\log \beta$ values increased from 26.2 ± 0.7 at pH 6.9, to 30.2 ± 0.8 at pH 7.8 and 31.2 ± 0.6 at pH 8.15. The solubilities of uranium in the presence of BCHA measured in this study are slightly higher than in Reference 4 for comparable BCHA concentrations. This may be due to differences in the solid phase, i.e., crystalline as against amorphous, and/or the difference between the HA used which may have been caused by the method of preparing the solid HA and the subsequent solutions. In addition, the BCHA concentrations in the two studies are not exactly the same, and this study was done in the absence of carbonate.

U(IV) AHA study

The U(IV)–AHA results are presented in Tables 6, 7 and 8. The conditional $\log \beta$ values were $\log \beta = 29.0 \pm 1.3$ at pH 8.6, $\log \beta = 25.6 \pm 1.2$ at pH 7.5 and $\log \beta = 21.1 \pm 0.9$ at pH 6.4. The changes in the $\log \beta$ values with pH are shown in Fig. 3.

Table 3. Selected and estimated constants for uranium(IV) hydroxy species⁹

Species	Constant	$\log \beta$ (25 °C) ($I=0$)	$\log \beta$ (25 °C) ($I=0.2$)
$\text{U}(\text{OH})_4(\text{am})/\text{UO}_2 \cdot x\text{H}_2\text{O}(\text{am})$	$\log K_{sp}$	$-54.5 \pm 1.0^*$	
UOH^{3+}	$\log \beta_{11}$	$13.6 \pm 0.2^{**}$	11.1
$\text{U}(\text{OH})_2^{2+}$	$\log \beta_{12}$	$26.9 \pm 1.0^{**}$	24.4
$\text{U}(\text{OH})_3^+$	$\log \beta_{13}$	$37.3 \pm 1.0^*$	34.8
$\text{U}(\text{OH})_4(\text{aq})$	$\log \beta_{14}$	$46.0 \pm 1.4^*$	43.5

* Selected.

** Estimated.

Table 4. Data for measurement of solubility product of $UO_2(am)$

pH	$[OH^-]$	$[U]_{solution}$	A term	K_{sp}	$\log K_{sp}$
10.17	1.48E-04	1.52E-08	1.66E+33	4.38E-57	-56.4
8.90	7.94E-06	1.95E-08	1.38E+28	5.62E-57	-56.3
10.45	2.82E-04	7.93E-08	2.19E+34	2.29E-56	-55.6
8.18	1.51E-06	1.98E-08	1.82E+25	5.71E-57	-56.2
7.04	1.10E-07	4.94E-08	5.02E+20	1.42E-56	-55.8
6.97	9.33E-08	1.93E-08	2.63E+20	5.56E-57	-56.3
8.20	1.58E-06	9.63E-09	2.19E+25	2.78E-57	-56.6
				Mean:	-56.2
				S.D.:	0.31

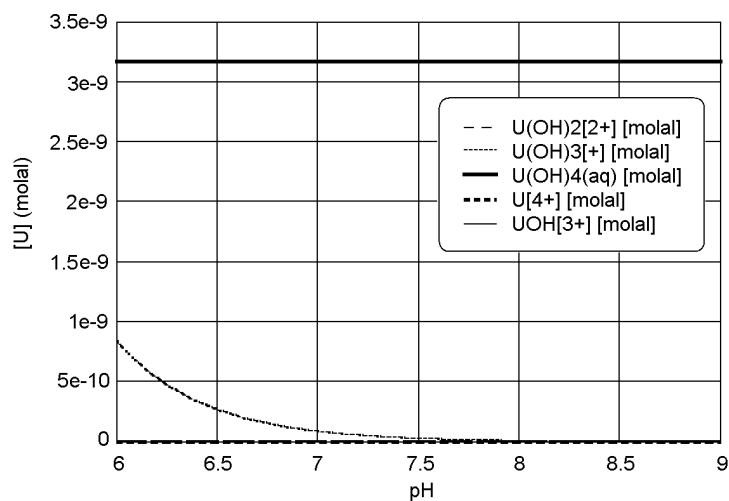


Fig. 1. Speciation of uranium(IV) from pH 6 to 9

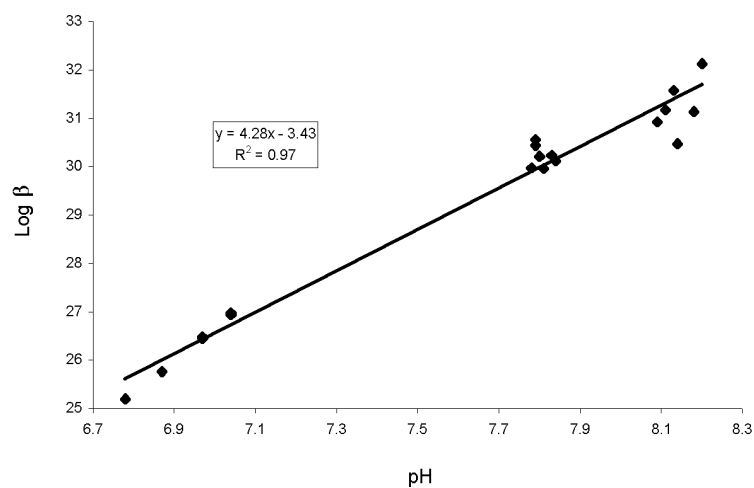


Fig. 2. Variation of U(IV)-BCHA $\log\beta$ values with pH

Table 5. U(IV)–BCHA data and derivation of conditional $\log\beta$ values, using the equilibrium constant expression incorporating the solubility product relationship for $[U^{4+}]$

$[HA]_{\text{total}}/M$	Log[HA]	pH	E_h	$[OH^-]$	$[U]_{\text{soln}}$	$[U^{4+}]$ i.e. $K_{sp}/[OH^-]_4$	A term	[UBCHA]	Log[UBCHA]	β	log β
2.15E-03	-2.67	7.84	-747	6.92E-07	7.67E-05	2.75E-32	6.62E+18	7.67E-05	-4.12	1.34E+30	30.1
1.08E-03	-2.97	7.83	-680	6.76E-07	5.29E-05	3.02E-32	6.04E+18	5.29E-05	-4.28	1.71E+30	30.2
4.30E-04	-3.37	7.80	-652	6.31E-07	2.64E-05	3.98E-32	4.58E+18	2.64E-05	-4.58	1.64E+30	30.2
3.23E-04	-3.49	7.79	-642	6.17E-07	4.39E-05	4.37E-32	4.18E+18	4.39E-05	-4.36	3.61E+30	30.6
2.15E-04	-3.67	7.81	-656	6.46E-07	7.00E-06	3.63E-32	5.02E+18	7.00E-06	-5.15	9.27E+29	30.0
1.08E-04	-3.97	7.78	-653	6.03E-07	4.62E-06	4.79E-32	3.81E+18	4.62E-06	-5.34	9.38E+29	30.0
4.30E-05	-4.37	7.79	-648	6.17E-07	4.62E-06	4.37E-32	4.18E+18	4.62E-06	-5.34	2.76E+30	30.4
Mean:		7.81								Mean:	30.2
										S.D.:	0.22
4.30E-05	-4.37	8.20	-688	1.58E-06	5.10E-06	1.00E-33	1.82E+20	5.10E-06	-5.29	1.35E+32	32.1
1.08E-04	-3.97	8.13	-687	1.35E-06	7.19E-06	1.91E-33	9.55E+19	7.19E-06	-5.14	3.76E+31	31.6
2.15E-04	-3.67	8.11	-684	1.29E-06	7.19E-06	2.29E-33	7.95E+19	7.19E-06	-5.14	1.51E+31	31.2
4.30E-04	-3.37	8.09	-680	1.23E-06	9.89E-06	2.75E-33	6.61E+19	9.89E-06	-5.00	8.55E+30	30.9
2.15E-03	-2.67	8.14	-681	1.38E-06	1.12E-05	1.74E-33	1.05E+20	1.12E-05	-4.95	3.01E+30	30.5
2.15E-03	-2.67	8.18	-693	1.51E-06	3.52E-05	1.20E-33	1.51E+20	3.52E-05	-4.45	1.38E+31	31.1
2.15E-03	-2.67	8.18	-701	1.51E-06	2.29E-05	1.20E-33	1.51E+20	2.29E-05	-4.64	8.94E+30	31.0
Mean:		8.15								Mean:	31.2
										S.D.:	0.56
2.69E-04	-3.57	7.04	-621	1.10E-07	1.08E-05	4.37E-29	4.25E+15	1.08E-05	-4.97	9.59E+26	27.0
2.69E-04	-3.57	7.04	-583	1.10E-07	9.85E-06	4.37E-29	4.25E+15	9.85E-06	-5.01	8.72E+26	26.9
5.38E-04	-3.27	6.97	-607	9.33E-08	1.34E-05	8.32E-29	2.24E+15	1.34E-05	-4.87	3.07E+26	26.5
5.38E-04	-3.27	6.97	-612	9.33E-08	1.25E-05	8.32E-29	2.24E+15	1.25E-05	-4.90	2.86E+26	26.5
1.08E-03	-2.97	6.87	-614	7.41E-08	1.28E-05	2.09E-28	8.95E+14	1.28E-05	-4.89	5.77E+25	25.8
1.08E-03	-2.97	6.87	-599	7.41E-08	1.29E-05	2.09E-28	8.95E+14	1.29E-05	-4.89	5.81E+25	25.8
2.15E-03	-2.67	6.78	-604	6.03E-08	1.63E-05	4.79E-28	3.93E+14	1.63E-05	-4.79	1.60E+25	25.2
2.15E-03	-2.67	6.78	-622	6.03E-08	1.57E-05	4.79E-28	3.93E+14	1.57E-05	-4.80	1.54E+25	25.2
Mean:		6.90								Mean:	26.2
										S.D.:	0.67

U(VI) BCHA complexation study at pH 8.0

Preliminary experiments were performed using HCl and NaOH to produce suitable pH values. However, pH control was difficult, so subsequent experiments were performed using HEPES buffer. Comparisons of the two sets of results indicated that the complexation of U(VI) by humic acid was not affected by the presence of the HEPES buffer. The UO_2 –BCHA $\log\beta$ values obtained at pH 8.0 and ionic strength $I=0.1$, calculated using Eq. (1), are presented in Table 1. The ionic strength reflected the HEPES concentration. The BCHA concentrations were derived from the total organic carbon (TOC) data supplied with the extract. BCHA was assumed to be comprised of 50% organic carbon and to possess a pH independent maximum proton exchange capacity of $4.0 \cdot 10^{-3} \text{ mol} \cdot \text{g}^{-1}$.¹ Since carbonate was absent, U(VI)–carbonato species did not interfere, and the side reaction coefficient ($A=4.09 \cdot 10^3$) was calculated by:

$$A = 1 + \beta_{UO_2(OH)^+} [OH^-] + \beta_{UO_2(OH)_2} [OH^-]^2 + \beta_{UO_2(OH)_3} [OH^-]^3 + \beta_{UO_2(OH)_4} [OH^-]^4$$

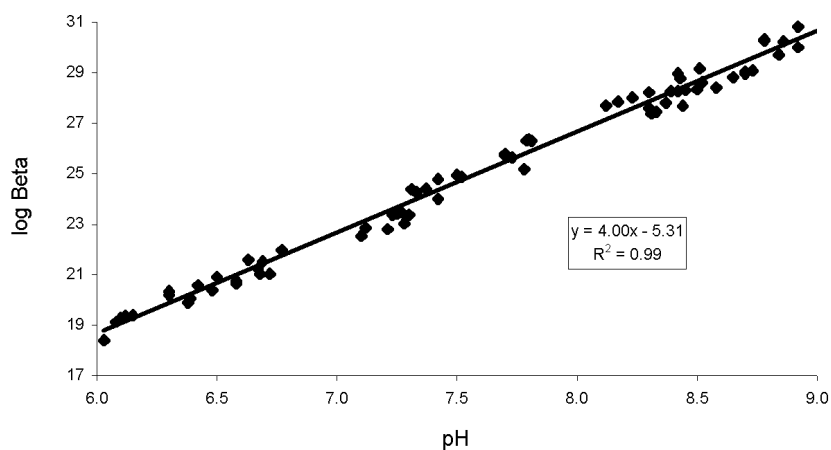
The β values for the hydroxy species were derived from the values in the HATCHES database¹³ but adjusted, to be consistent with the ionic strength conditions employed in the experiments, i.e., $I=0.1$. The final and originally derived values were as follows: $\log\beta_{UO_2(OH)^+} = 8.32$ (8.75), $\log\beta_{UO_2(OH)_2} = 15.21$ (15.85), $\log\beta_{UO_2(OH)_3} = 21.1$ (21.75) and $\log\beta_{UO_2(OH)_4} = 23.2$ (23.6). The thermodynamic HATCHES values ($I=0$) are in brackets. The experiments yielded a mean UO_2 –BCHA $\log\beta$ value of 7.93 at pH 8.0 with a standard deviation of 0.33.

Effect of pH on U(VI)–BCHA $\log\beta$ values

Further U(VI)–BCHA experiments were conducted, using the same overall approach, but at pH values of 5.9, 7.0, 7.2 and 8.1 still with $I=0.1$. The A term values were 2.98, 46.5, 96.3 and 7150, respectively. The effect on the resulting U(VI)–BCHA constants is displayed graphically in Fig. 4, the results are in Table 9. The log values of the constants increased from 4.42 at pH 5.9 to 5.49 at pH 7, 5.65 at pH 7.2 and 7.93 at pH 8.1.

Table 6. U(IV)-AHA data at pH 8.4 and derivation of conditional $\log\beta$ values, using the equilibrium constant expression incorporating the solubility product relationship for $[U^{4+}]$

[HA], M	Log[HA]	pH	DPM	[U] _{total}	[OH ⁻]	[U ⁴⁺]	A Term	[UHA]	Log[UHA]	β	Log β
2.65E-03	-2.58	8.23	882.1	8.76E-06	1.70E-06	3.13E-31	2.40E+20	8.76E-06	-5.06	1.06E+28	28.0
2.65E-03	-2.58	8.51	834.8	9.35E-06	3.24E-06	2.37E-32	3.16E+21	9.35E-06	-5.03	1.49E+29	29.2
2.65E-03	-2.58	8.78	891.9	9.99E-06	6.03E-06	1.97E-33	3.80E+22	9.99E-06	-5.00	1.92E+30	30.3
1.33E-03	-2.88	8.12	513.5	5.75E-06	1.32E-06	8.61E-31	8.71E+19	5.75E-06	-5.24	5.07E+27	27.7
1.33E-03	-2.88	8.42	610.4	6.84E-06	2.63E-06	5.43E-32	1.38E+21	6.84E-06	-5.16	9.55E+28	29.0
1.33E-03	-2.88	8.92	425.8	4.77E-06	8.32E-06	5.43E-34	1.38E+23	4.77E-06	-5.32	6.65E+30	30.8
1.33E-03	-2.88	8.30	333.0	3.73E-06	2.00E-06	1.64E-31	4.57E+20	3.73E-06	-5.43	1.72E+28	28.2
5.30E-04	-3.28	8.17	187.88	2.11E-06	1.48E-06	5.43E-31	1.38E+20	2.11E-06	-5.68	7.34E+27	27.9
5.30E-04	-3.28	8.78	196.99	2.21E-06	6.03E-06	1.97E-33	3.80E+22	2.21E-06	-5.66	2.12E+30	30.3
5.30E-04	-3.28	8.43	142.77	1.60E-06	2.69E-06	4.95E-32	1.51E+21	1.60E-06	-5.80	6.11E+28	28.8
3.98E-04	-3.40	8.92	19.87	2.23E-07	8.32E-06	5.43E-34	1.38E+23	2.23E-07	-6.65	1.03E+30	30.0
3.98E-04	-3.40	8.33	12.91	1.45E-07	2.14E-06	1.24E-31	6.02E+20	1.45E-07	-6.84	2.92E+27	27.5
3.98E-04	-3.40	8.42	36.64	4.11E-07	2.63E-06	5.43E-32	1.38E+21	4.11E-07	-6.39	1.90E+28	28.3
3.98E-04	-3.40	8.52	32.01	3.59E-07	3.31E-06	2.16E-32	3.46E+21	3.59E-07	-6.45	4.18E+28	28.6
2.65E-04	-3.58	8.37	13.69	1.53E-07	2.34E-06	8.61E-32	8.71E+20	1.53E-07	-6.81	6.73E+27	27.8
2.65E-04	-3.58	8.50	13.82	1.55E-07	3.16E-06	2.60E-32	2.88E+21	1.55E-07	-6.81	2.25E+28	28.4
2.65E-04	-3.58	8.70	10.96	1.23E-07	5.01E-06	4.12E-33	1.82E+22	1.23E-07	-6.91	1.12E+29	29.1
2.65E-04	-3.58	8.70	18.91	9.99E-08	5.01E-06	4.12E-33	1.82E+22	9.98E-08	-7.00	9.14E+28	29.0
2.65E-04	-3.58	8.31	18.57	9.61E-08	2.04E-06	1.50E-31	5.01E+20	9.60E-08	-7.02	2.42E+27	27.4
1.33E-04	-3.88	8.73	4.52	5.07E-08	5.37E-06	3.13E-33	2.40E+22	5.06E-08	-7.30	1.22E+29	29.1
1.33E-04	-3.88	8.65	5.21	5.84E-08	4.47E-06	6.53E-33	1.15E+22	5.83E-08	-7.23	6.74E+28	28.8
1.33E-04	-3.88	8.44	2.64	2.96E-08	2.75E-06	4.52E-32	1.66E+21	2.95E-08	-7.53	4.94E+27	27.7
1.33E-04	-3.88	8.58	3.87	4.34E-08	3.80E-06	1.24E-32	6.02E+21	4.33E-08	-7.36	2.63E+28	28.4
1.33E-04	-3.88	8.84	7.14	8.00E-08	6.92E-06	1.13E-33	6.60E+22	8.00E-08	-7.10	5.32E+29	29.7
5.30E-05	-4.28	8.39	6.41	7.19E-08	2.45E-06	7.16E-32	1.05E+21	7.18E-08	-7.14	1.89E+28	28.3
5.30E-05	-4.28	8.86	7.96	8.92E-08	7.24E-06	9.44E-34	7.93E+22	8.91E-08	-7.05	1.78E+30	30.3
5.30E-05	-4.28	8.30	3.26	3.66E-08	2.00E-06	1.64E-31	4.57E+20	3.65E-08	-7.44	4.20E+27	27.6
5.30E-05	-4.28	8.45	4.09	4.59E-08	2.82E-06	4.12E-32	1.82E+21	4.58E-08	-7.34	2.10E+28	28.3
Mean:		8.58				9.43E-32		1.98E-06			29.7
S.D.:		0.32				1.84E-31		3.10E-06			1.32

Fig. 3. Variation of U(IV)-AHA $\log\beta$ values with pH

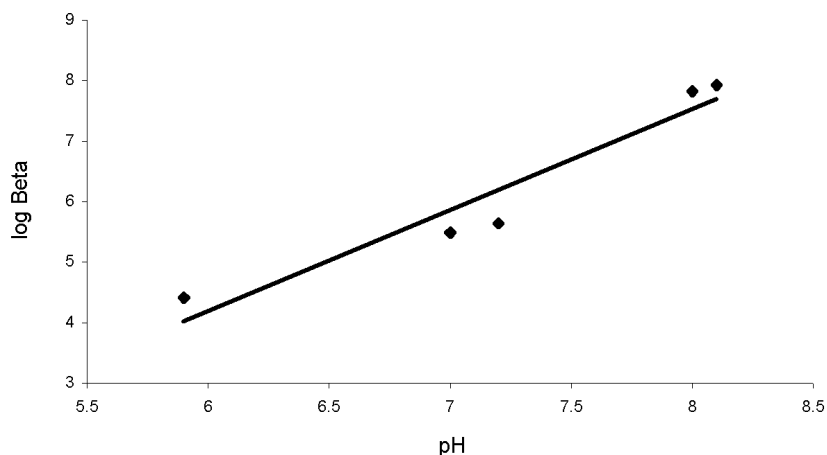


Fig. 4. Variation of U(VI)-BCHA $\log\beta$ values with pH

Table 7. U(IV)-AHA data at pH 7.4 and derivation of conditional $\log\beta$ values, using the equilibrium constant expression incorporating the solubility product relationship for $[U^{4+}]$

[HA], M	Log[HA]	pH	DPM	[U] _{total}	[OH ⁻]	[U ⁴⁺]	A term	[UHA]	Log[UHA]	β	Log β
2.65E-03	-2.58	7.80	793.2	1.00E-05	6.31E-07	1.64E-29	4.58E+18	1.00E-05	-5.00	2.31E+26	26.4
2.65E-03	-2.58	7.79	897.5	1.01E-05	6.17E-07	1.80E-29	4.18E+18	1.01E-05	-5.00	2.12E+26	26.3
2.65E-03	-2.58	7.81	728.4	8.16E-06	6.46E-07	1.50E-29	5.02E+18	8.16E-06	-5.09	2.07E+26	26.3
1.33E-03	-2.88	7.37	267.1	2.99E-06	2.34E-07	8.61E-28	8.78E+16	2.99E-06	-5.52	2.63E+24	24.4
1.33E-03	-2.88	7.50	285.6	3.20E-06	3.16E-07	2.60E-28	2.90E+17	3.20E-06	-5.49	9.31E+24	25.0
1.33E-03	-2.88	7.70	267.8	3.00E-06	5.01E-07	4.12E-29	1.83E+18	3.00E-06	-5.52	5.51E+25	25.7
1.33E-03	-2.88	7.70	301.5	3.38E-06	5.01E-07	4.12E-29	1.83E+18	3.38E-06	-5.47	6.20E+25	25.8
1.33E-03	-2.88	7.31	440.0	4.93E-06	2.04E-07	1.50E-27	5.06E+16	4.93E-06	-5.31	2.50E+24	24.4
5.30E-04	-3.28	7.33	111.62	1.25E-06	2.14E-07	1.24E-27	6.08E+16	1.25E-06	-5.90	1.90E+24	24.3
5.30E-04	-3.28	7.42	161.08	1.80E-06	2.63E-07	5.43E-28	1.39E+17	1.80E-06	-5.74	6.29E+24	24.8
5.30E-04	-3.28	7.52	77.02	8.63E-07	3.31E-07	2.16E-28	3.49E+17	8.63E-07	-6.06	7.54E+24	24.9
3.98E-04	-3.40	7.12	22.74	2.55E-07	1.32E-07	8.61E-27	8.84E+15	2.55E-07	-6.59	7.45E+22	22.9
3.98E-04	-3.40	7.42	20.29	2.27E-07	2.63E-07	5.43E-28	1.39E+17	2.27E-07	-6.64	1.05E+24	24.0
3.98E-04	-3.40	7.30	14.14	1.58E-07	2.00E-07	1.64E-27	4.61E+16	1.58E-07	-6.80	2.43E+23	23.4
3.98E-04	-3.40	7.25	24.04	2.69E-07	1.78E-07	2.60E-27	2.92E+16	2.69E-07	-6.57	2.61E+23	23.4
2.65E-04	-3.58	7.28	15.17	5.80E-08	1.91E-07	1.97E-27	3.84E+16	5.79E-08	-7.24	1.11E+23	23.0
2.65E-04	-3.58	7.23	18.36	2.06E-07	1.70E-07	3.13E-27	2.43E+16	2.06E-07	-6.69	2.48E+23	23.4
1.33E-04	-3.88	7.27	7.67	8.60E-08	1.86E-07	2.16E-27	3.50E+16	8.59E-08	-7.07	3.00E+23	23.5
1.33E-04	-3.88	7.10	4.26	4.78E-08	1.26E-07	1.04E-26	7.36E+15	4.77E-08	-7.32	3.48E+22	22.5
1.33E-04	-3.88	7.78	3.57	4.00E-08	6.03E-07	1.97E-29	3.81E+18	4.00E-08	-7.40	1.53E+25	25.2
1.33E-04	-3.88	7.21	2.94	3.30E-08	1.62E-07	3.76E-27	2.02E+16	3.29E-08	-7.48	6.61E+22	22.8
5.30E-05	-4.28	7.73	6.71	7.52E-08	5.37E-07	3.13E-29	2.41E+18	7.51E-08	-7.12	4.54E+25	25.7
Mean:		7.45				1.80E-27		2.32E-06			25.6
S.D.:		0.24				2.74E-27		3.23E-06			1.23

Table 8. U(IV)–AHA data at pH 6.4 and derivation of conditional $\log\beta$ values, using the equilibrium constant expression incorporating the solubility product relationship for $[U^{4+}]$

[HA], M	Log[HA]	pH	DPM	$[U]_{\text{total}}$	$[OH^-]$	$[U^{4+}]$	<i>A</i> term	[UHA]	Log[UHA]	β	Log β
2.65E-03	-2.58	6.63	724.4	8.12E-06	4.27E-08	7.85E-25	1.00E+14	8.12E-06	-5.09	3.91E+21	21.6
2.65E-03	-2.58	6.50	515.9	5.78E-06	3.16E-08	2.60E-24	3.08E+13	5.78E-06	-5.24	8.41E+20	20.9
2.65E-03	-2.58	6.30	614.9	6.89E-06	2.00E-08	1.64E-23	5.07E+12	6.89E-06	-5.16	1.59E+20	20.2
1.33E-03	-2.88	6.30	433.6	4.86E-06	2.00E-08	1.64E-23	5.07E+12	4.86E-06	-5.31	2.24E+20	20.4
1.33E-03	-2.88	6.69	179.5	2.01E-06	4.90E-08	4.52E-25	1.73E+14	2.01E-06	-5.70	3.36E+21	21.5
1.33E-03	-2.88	6.08	204.4	2.29E-06	1.20E-08	1.24E-22	7.12E+11	2.29E-06	-5.64	1.39E+19	19.1
1.33E-03	-2.88	6.67	111.9	1.25E-06	4.68E-08	5.43E-25	1.44E+14	1.25E-06	-5.90	1.74E+21	21.2
5.30E-04	-3.28	6.15	76.37	8.56E-07	1.41E-08	6.53E-23	1.32E+12	8.56E-07	-6.07	2.48E+19	19.4
5.30E-04	-3.28	6.10	95.71	1.07E-06	1.26E-08	1.04E-22	8.50E+11	1.07E-06	-5.97	1.96E+19	19.3
5.30E-04	-3.28	6.42	98.41	1.10E-06	2.63E-08	5.43E-24	1.49E+13	1.10E-06	-5.96	3.84E+20	20.6
5.30E-04	-3.28	6.12	97.76	1.10E-06	1.32E-08	8.61E-23	1.01E+12	1.10E-06	-5.96	2.41E+19	19.4
5.30E-04	-3.28	6.77	97.32	1.09E-06	5.89E-08	2.16E-25	3.59E+14	1.09E-06	-5.96	9.53E+21	22.0
3.98E-04	-3.40	6.38	22.42	2.51E-07	2.40E-08	7.85E-24	1.04E+13	2.51E-07	-6.60	8.05E+19	19.9
3.98E-04	-3.40	6.68	19.14	2.14E-07	4.79E-08	4.95E-25	1.58E+14	2.14E-07	-6.67	1.09E+21	21.0
3.98E-04	-3.40	6.03	18.01	2.02E-07	1.07E-08	1.97E-22	4.57E+11	2.02E-07	-6.70	2.57E+18	18.4
2.65E-04	-3.58	6.58	17.09	1.92E-07	3.80E-08	1.24E-24	6.36E+13	1.91E-07	-6.72	5.81E+20	20.8
2.65E-04	-3.58	6.48	18.17	2.04E-07	3.02E-08	3.13E-24	2.57E+13	2.04E-07	-6.69	2.46E+20	20.4
2.65E-04	-3.58	6.58	13.44	1.51E-07	3.80E-08	1.24E-24	6.36E+13	1.51E-07	-6.82	4.57E+20	20.7
1.33E-04	-3.88	6.72	4.42	4.96E-08	5.25E-08	3.43E-25	2.28E+14	4.95E-08	-7.31	1.09E+21	21.0
5.30E-05	-4.28	6.39	4.02	4.50E-08	2.45E-08	7.16E-24	1.14E+13	4.50E-08	-7.35	1.19E+20	20.1
Mean:		6.43				3.20E-23		1.89E-06			21.1
S.D.:		0.24				5.47E-23		2.47E-06			0.93

Figure 5 shows the speciation of uranium(VI) in the absence of HA from pH 5 to 9. The calculations were carried out using the programme CHESS.¹⁰ Over the pH range used in this study the principle uranium species changes from UO_2^{2+} (aq), to UO_2OH^+ (aq), to $UO_2(OH)_2^0$ (aq) and finally $UO_2(OH)_3^-$ (aq). The *A* term, used to calculate the $\log\beta$ values reflects this change and as a consequence the stability constant increases with a slope reflecting, but not exactly matching, the number of hydroxide ions involved in the hydrolysis reactions of the UO_2^{2+} ion. A number of other reasons, apart from the conditional nature of the derived $\log\beta$ values, have been advanced to explain the increase with pH, e.g., (1) unfurling giving access to stronger sites, (2) increasing participation of the phenolic OH ligands present, (3) increasing formation of mixed hydroxy complexes, e.g., $U(OH)_xHA$, or (4) increasing electrostatic effects due to the polyelectrolytic properties of HA. Unfortunately, the experiments reported here do not provide the evidence needed to distinguish between these possible explanations.

U(VI) Aldrich HA complexation study at pH 8.4

The U(VI)–AHA results are given in Table 2. The maximum AHA proton exchange capacity was assumed to be $5.3 \cdot 10^{-3}$ mol g^{-1} ,¹ and the *A* term was calculated to be $1.11 \cdot 10^6$, at *I*=0.1 and pH 8.4. An average $\log\beta$ value of 9.1 with a standard deviation of 0.25 was obtained. Further experiments, conducted at different pH values (see below), suggested that the increase in the value reflected the higher pH of the AHA experiment rather than intrinsic differences between U(VI)–BCHA and U(VI)–AHA reactions.

The BCHA and AHA Schubert plots based on Eq. (1) are shown in Fig. 6. The observed slopes of approximately one imply 1:1 U(VI) to HA stoichiometries, i.e., *n*=1 in Eq. (1).⁵ The intercepts provided further estimates of the $\log\beta$ values (BCHA=8.94, AHA=9.02), but because long extrapolations were involved, means of the individual values were considered to be more reliable. A summary of all the measured $\log\beta$ values is shown in Table 10.

Table 9. Data for U(VI) BCHA stability constant measurements at various pHs

[HA], M ⁻³	dpm	D	A term	log[(D ₀ /D)-1]A	Logβ
2.14E-03	600.0	0.417	2.98	1.26	3.93
1.07E-03	741.0	0.147	2.98	1.75	4.72
5.25E-04	520.2	0.634	2.98	1.04	4.32
2.63E-04	426.2	0.994	2.98	0.77	4.35
1.32E-04	361.2	1.353	2.98	0.55	4.43
6.61E-05	300.4	1.830	2.98	0.26	4.44
				Mean:	4.42
pH 5.9				s.d.:	0.26
1.91E-03	645.7	0.316	46.5	2.59	5.31
9.55E-04	604.3	0.407	46.5	2.46	5.48
4.79E-04	524.7	0.620	46.5	2.24	5.56
2.40E-04	425.1	0.999	46.5	1.96	5.58
1.17E-04	346.7	1.452	46.5	1.68	5.61
5.89E-05	255.6	2.325	46.5	1.10	5.33
				Mean:	5.49
pH 7				s.d.:	0.13
1.86E-03	583.3	0.457	96.3	2.72	5.45
9.33E-04	514.4	0.652	96.3	2.53	5.56
4.68E-04	471.3	0.804	96.3	2.41	5.74
2.34E-04	340.3	1.498	96.3	1.97	5.60
1.15E-04	249.0	2.414	96.3	1.33	5.27
5.75E-05	292.2	1.909	96.3	1.72	5.96
				Mean:	5.65
pH 7.2				s.d.:	0.24
3.80E-03	800.6	0.062	7150	5.52	7.94
1.91E-03	645.7	0.316	7150	4.77	7.49
9.55E-04	664.3	0.279	7150	4.83	7.85
4.79E-04	523.0	0.625	7150	4.42	7.74
2.40E-04	455.1	0.868	7150	4.23	7.85
1.17E-04	409.2	1.077	7150	4.09	8.02
5.89E-05	360.8	1.356	7150	3.92	8.15
2.95E-05	241.4	2.522	7150	3.08	7.61
4.27E-03	802.7	0.059	7150	5.54	7.91
2.14E-03	725.7	0.171	7150	5.06	7.73
1.07E-03	616.0	0.380	7150	4.68	7.65
5.25E-04	515.7	0.648	7150	4.40	7.68
2.63E-04	469.0	0.812	7150	4.27	7.85
6.61E-05	321.5	1.644	7150	3.75	7.93
3.31E-05	268.7	2.164	7150	3.41	7.89
8.32E-06	216.9	2.918	7150	1.89	6.97
4.17E-06	250.8	2.390	7150	3.22	8.60
				Mean:	7.93
pH 8.1				s.d.:	0.46

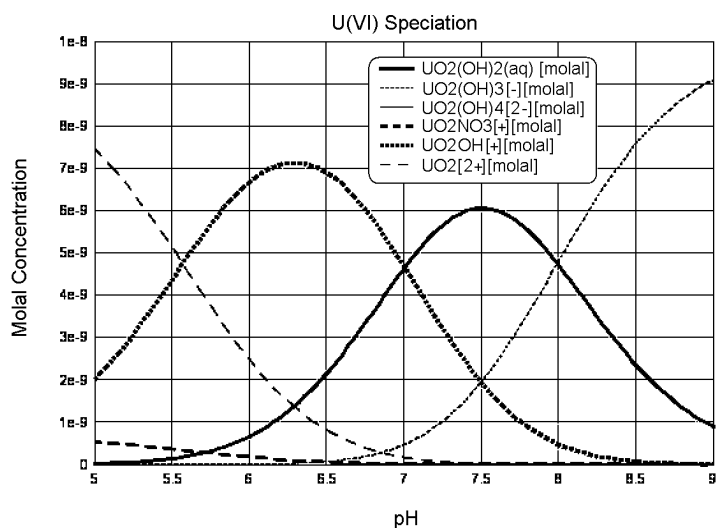


Fig. 5. Speciation of U(VI) from pH 5 to 9

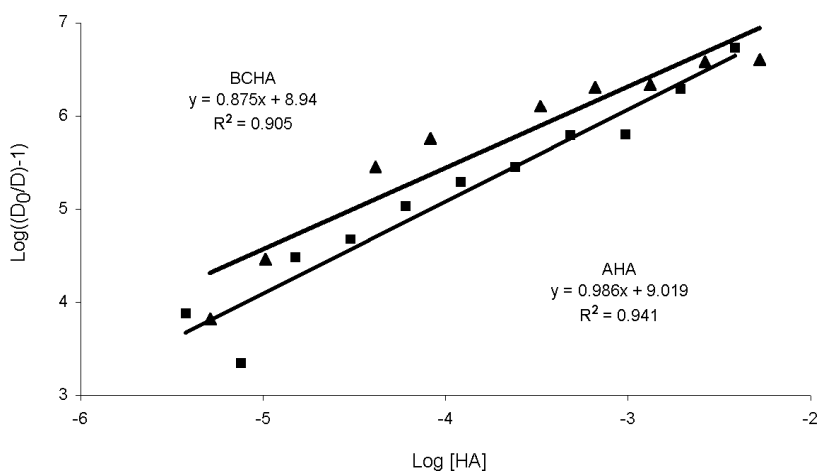


Fig. 6. Schubert plots used to investigate the U(VI)–BCHA and AHA stoichiometries; near-unit slopes are consistent with 1 U : 1 HA

Table 10. Summary of $\log\beta$ values

Humic	pH	U(IV) $\log\beta$	U(VI) $\log\beta$
BCHA	8.0		7.94 ± 0.33
AHA	8.4		9.13 ± 0.25
BCHA	5.9		4.42 ± 0.26
BCHA	7.0		5.49 ± 0.13
BCHA	7.2		5.65 ± 0.24
BCHA	8.1		7.93 ± 0.46
BCHA	7.8	30.2 ± 0.22	
BCHA	8.2	31.2 ± 0.56	
BCHA	6.9	26.2 ± 0.67	
AHA	8.6	29.7 ± 1.32	
AHA	7.5	25.6 ± 1.23	
AHA	6.4	21.1 ± 0.93	

Conclusions

Under the anaerobic, carbonate free, conditions used the graphically derived $\log\beta$ values for the BCHA complexes at pH 8.2, were (from Fig. 4) U(VI)-BCHA = 7.91 (s.d. = 0.39) and (from Fig. 2) U(IV)-BCHA = 31.66 (s.d. = 0.33). The AHA constants were generally similar to the BCHA constants.

Compared with the Schubert approach, the solubility product method has certain merits, e.g., the complication of the resin solid phase is avoided because the insoluble precipitate itself generates a solid liquid distribution, also the pH does not have to be controlled only known and the maintenance and measurement of the redox state of the system is facilitated. It is envisaged that the same approach will be used to obtain Pu-BCHA constants.

*

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