Complexation Constants of Plutonium(IV) with Aldrich Humic Acid

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Humic acids are natural organic polyelectrolytes that form complexes with metal ions in natural groundwaters. The complexes influence the migration behavior of actinides, e.g., in the vicinity of a nuclear waste repository. For plutonium, it has previously been shown [1] that in Gorleben groundwater, reduction of Pu(VI) to Pu(V) occurs almost instantaneously, followed by the reduction of the latter to a mixture of Pu(IV) and Pu(III) within about a day at pH 1.7. At higher pH values, the reduction becomes faster [2]. We have started an experimental program aiming at the determination of the complex formation constants of Pu(IV) with Aldrich humic acid at different pH values. So far, logß values and loading capacities (LC) have been determined by ultrafiltration at pH values of 1.8, 2.5, and 3.0. It has been assumed that the complexation reaction is

$$[Pu(OH)_2]^{2+} + HA(z) \rightarrow Pu(OH)_2HA(z)$$

with z=2 [3]. The complexation with humic acid is decribed by the charge neutralization model [4]:

$$[HA(z)]_t = \frac{(HA)\cdot(PEC)}{z} \qquad (1)$$

Here, (HA) is the concentraion of humic acid in [g/L], (PEC) is the proton exchange capacity in [eq/g], and z is the charge of the plutonium ion. The loading capacity is defined as:

$$LC = \frac{[PuHA(z)]}{[HA(z)]_t} \qquad (2)$$

The complexation constant is then obtained as

$$ß_{LC} = \frac{[PuHA(z)]}{[Pu^{z+}]_f \cdot (([HA(z)]_t \cdot LC) - [PuHA(z)])} \qquad (3)$$

where [PuHA(z)] is the concentration of Pu humate [mol/L] and $[Pu^{z+}]_f$ is the concentration of the free Pu [mol/L].

For the experiments, ^{239}Pu is used. The 4+ oxidation state is produced electrochemically [5] and verified by UV-VIS spectroscopy. The concentrations are varied between 10^{-8} and 10^{-5} mol/L. Aldrich humic acid was used with concentrations between 0.01 and 25 mg/L.

According to the results of the kinetic study [6] an equilibration time of one week was chosen. After that, the free plutonium-ion concentration was determined by ultrafiltration and subsequent liquid scintillation counting (LSC). The loading capacity LC was determined from plots of [PuHA(z)] / $[HA(z)]_t$ vs. $[M^{z+}]_t$ / $[HA(z)]_t$ for the different pH values, see Figure 1. The loading capacities result as 3.3% at pH 1.8; 4.5% at pH 2.5; 9.2% at pH 3. The $logß_{LC}$ values calculated with these LC values are 6.5-7.9 at pH 1.8; 6.7-8.3 at pH 2.5; 6.4-8.4 at pH 3, see Figure 2.

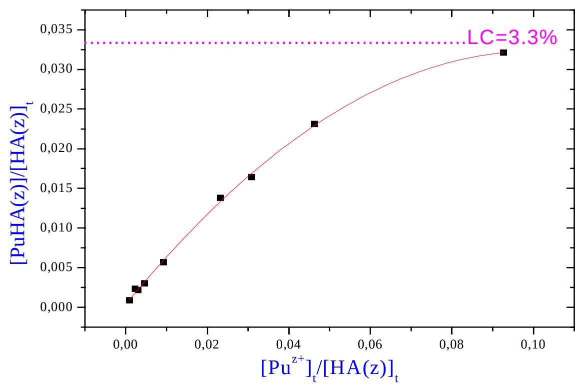

Figure 1: Determination of loading capacity at pH 1.8

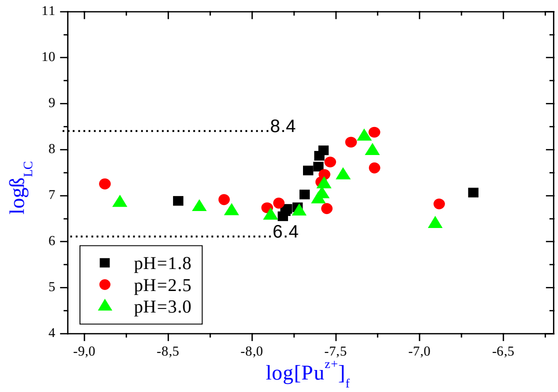

Figure 2: Humate complexation of Pu(IV) studied by UF; logß values calculated and plotted as a function of the free Pu(IV) conc. at different pH values (1.8, 2.5, 3.0)

The scatter in the $logß_{LC}$ values is unusually large with two orders of magnitude. This may be due to some kind of co-precipitation effect as the humic acid at these low pH values forms a precipitate. Therefore, these studies will be continued with fulvic acid which is soluble at all pH values.

References:

[1] B. Kuczewski et al.; Institut für Kernchemie, Universität Mainz, Jahresbericht 2001, C5.
[2] B. Kuczewski et al.; Institut für Kernchemie, Universität Mainz, Jahresbericht 2002, C3.
[3] C. Bitea et al.; Institut für Kernchemie, Universität Mainz, Jahresbericht 2002, C4.
[4] Kim, J. I. and Czerwinski, K. R.; Radiochim. Acta, 73, 5 (1996)
[5] D. Cohen. et al.; J. Inorg. Nucl. Chem., 18, 207 (1961)
[6] N.L. Banik et al.; Institut für Kernchemie, Universität Mainz, this report.