COMPLEX FORMATION OF URANIUM(VI) WITH FRUCTOSE AND GLUCOSE PHOSPHATES

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The uptake of heavy metals into plants is commonly quantified by the soil-plant transfer factor. Up to now little is known about the chemical speciation of actinides in plants. To compare the obtained spectroscopic data of uranium complexes in plants with model compounds, we investigate the complexation of uranium with relevant bioligands of various functionalities. A very important class of ligands are phosphate esters, which serve as phosphate group and energy transmitters as well as energy storage mediums in biological systems. Heavy metal ions bound to the phosphate esters can be transported into living cells and than deposited.

Therefore, in our study we present the results of uranium complexation with glucose-6-phosphate (G6P), and fructose-6-phosphate (F6P) obtained by time-resolved laser-induced fluorescence spectroscopy (TRLFS). The experiments were performed at a fixed uranyl concentration (10^{-5} M) as a function of the ligand concentrations (10^{-5} to 10^{-3} M) in a pH range from 2 to 4.5.

For the glucose phosphate system we observed, using increasing ligand concentrations, a decreased fluorescence intensity and a small red shift of the emission bands. From this we conclude that the complexed uranyl glucose phosphate species either show only minor or no fluorescence properties. The TRLFS spectra of the glucose phosphate samples indicated the presence of only one species with fluorescence properties. This species has a lifetime of approximately 1.5 µs and was identified as the free uranyl ion.

An opposite phenomenon was observed for the fructose phosphate system: There was no decrease of fluorescence intensity. However, a strong red shift of the spectra was observed illustrating the fluorescence properties of the uranyl fructose phosphate complex. The TRLFS spectra of the fructose phosphate system showed a second lifetime (<1µs) belonging to the complexed species.

The concentration of the free uranyl ion was determined on the basis of the measured fluorescence spectra. These data were used to calculate the corresponding concentrations of the uranyl sugar phosphate complexes and the non-complexed ligands. The complex formation reaction is assumed to be:

$x\ lig + UO_2^{2+} \Leftrightarrow UO_2(lig)_x^{(2-y)+} + y\ H^+$ (lig = sugar phosphate)

Applying the mass action law and transformation to the logarithmic scale, we obtain:

$$\log \frac{[UO_2(lig)_x^{(2-y)+}]}{[UO_2^{2+}]} = x \log[lig_{noncomplexed}] - y \log[H^+] + \log K$$

From this we conclude, that 1:1 uranyl sugar phosphate species $UO_2(ROPO_3)$ (R is either glucose or fructose) has formed. Using these data complex formation constants for the complexes were calculated to be in the range of logK=3.7 for G6P and 3.2 for F6P.