

Spectroscopic Study of the Uranium(IV) Complexation by Organic Model Ligands in Aqueous Solution.

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Risk assessments predicting the transport of actinides under environmentally relevant conditions require basic knowledge of their interaction with complexing ligands, their sorption and redox behavior, their solubility, as well as their ability to form colloids. Both the speciation and the mobility of actinides in aquatic systems strongly depend on their oxidation state. Under reducing conditions as prevalent in deep underground nuclear waste repositories and in the depth of flooded uranium mines, actinide species occur in lower oxidation states. For instance, in contrast to uranium(VI) which is mobile, uranium(IV) is much less mobile due to the low solubility of uranium(IV) hydrous oxide ($\text{UO}_2 \cdot x\text{H}_2\text{O}$). However, in the presence of inorganic and organic ligands uranium(IV) may become mobile by formation of soluble complexes. Thus, the speciation of tetravalent uranium in aqueous solution has to be studied to predict its migration behavior in natural environments.

Data for the complexation of uranium(IV) with inorganic and organic ligands are scarce. In the present study, the model ligands citric acid and glutaric acid as well as mandelic acid and glycolic acid were chosen for the uranium(IV) complexation. These ligands stand for a variety of organic ligands in aqueous systems. The complex formation constants for the uranium(IV) complexation were determined applying UV-Vis absorption spectroscopy. Thereby, the hydrogen ion concentration and the ionic strength were varied.

For instance, the complexation of uranium(IV) with citric acid has been investigated in dependence on hydrogen ion concentration (1 M, 0.5 M, 0.1 M and 0.05 M). Thereby, the formation of 1:1 and 1:2 complexes was detected in the citrate media. The stability constants for 1:1 and 1:2 uranium(IV) citrate complexes of the type $\text{M}_p\text{H}_q\text{L}_r$ were determined with $\log \beta_{101} = 13.5 \pm 0.2$ und $\log \beta_{102} = 25.1 \pm 0.2$. The obtained $\log \beta$ fit well in the known series of $\log \beta$ determined for the complexation of further tetravalent actinides (e.g., Pu(IV), Np(IV), Th(IV)) by citric acid.