 ROBL-CRG	Experiment title: Investigation of the aqueous phase in the ternary sorption system uranium(VI), Goethite, organic model compounds.	Experiment number: 20 - 01 - 675																		
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Shifts: 78	Local contact(s): André Roßberg	<i>Received at ROBL:</i>																		
Names and affiliations of applicants (* indicates experimentalists): A. Roßberg*, C. Lucks* Helmholtz-Zentrum Dresden-Rossendorf e.V., Institute of Radiochemistry, P.O. Box 510119, 01314 Dresden, Germany																				

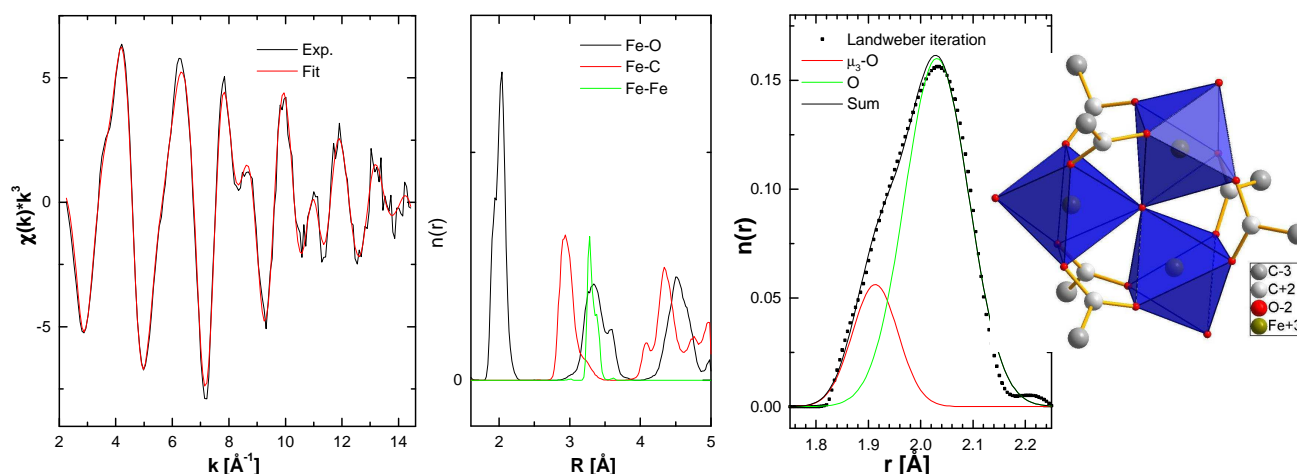
Experimental

The aim of this study was to investigate the structural influence of small organic (hydroxy)carboxylic acids on the sorption of U(VI) at the hematite/water interface. The system was divided in three subsystems which were investigated: solution phase of U(VI)/Fe(III) complexes with several (hydroxy)carboxylic acids, U(VI)-hematite sorption complexes, and U(VI) sorption complexes in the presence of hematite and (hydroxy)carboxylic acids as ternary systems. Due to the partly incomplete and unreliable results in the literature for the aqueous U(VI) complexes with acetic(ac)-, succinic-, and tartaric acid the molecular structures of all present complexes were determined including their pH speciation by using EXAFS, FT-IR and UV-Vis. For malic-, malonic-, lactic-, and citric acid the structures of the most prominent (highest spectral activity in EXAFS, UV-Vis) complexes were determined. The structures of the sorption complexes in the binary system U(VI)-hematite were determined whereas the structures of the sorption complexes in the more complex ternary systems are still under investigation. The state of the art data analysis was done by partly self-developed methods and programs which cover explorative factor analysis (FA)¹, Monte-Carlo

modeling (MC) of EXAFS spectra² and Landweber iteration³ for solving ill posed problems.

Results

While several of the results were already shown at conferences and in annual reports of our institute we present here as an interesting methodological example the $\text{Fe}_3(\text{OH})_2\text{ac}_6^+$ complex⁴ which might be present in the aqueous phase of the ternary sorption system. The spectrum of the complex was isolated from the spectral mixtures of the EXAFS pH- series by FA. The starting structure for the MC was taken from a



crystal structure.

Fig. 1: Left – FA isolated EXAFS (black) with MC reproduction (red) and corresponding Fe-O, Fe-C, and Fe-Fe RPDF. Right – U-O RPDF of the first shell determined by Landweber iteration. Inset – structure of the $\text{Fe}_3(\mu_3\text{-O})\text{ac}_6^+$ complex.

The FA extracted spectrum is shown in Fig. 1 together with the MC result. The MC calculated radial pair distribution function RPDF accounts for all spectral features in the EXAFS as can be seen by the good reproduction (Fig. 1). The Landweber iteration enables a more detailed analysis of the first O shell of this complex. The resulting Fe-O RPDF shows clearly the asymmetry at the left side which is expected due to the presence of a central $\mu_3\text{-O}$ atom. While this central O is up to now only reported for the solid structure, the developed methods enabled for the first time the investigation and the EXAFS spectroscopic proof of this special atomic arrangement for the aqueous medium. Due to this result the proposed stoichiometry $(\text{Fe}_3(\text{OH})_2\text{ac}_6^+)^4$ of this complex is $\text{Fe}_3(\mu_3\text{-O})\text{ac}_6^+$.

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