



Spectroscopic insights into U(IV) speciation in aqueous solution

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This work is focused on uranium as the major component of the nuclear fuel cycle. It is important to predict its environmental behavior for, e.g., the safety assessment of a future repository or the remediation of the various legacies of uranium mining and milling. Typically, diluted to highly saline aquifer systems under reducing conditions with carbonates, silicates, phosphates, chlorides and sulfates as important complexing agents are to be considered. However, predictions for U(IV) speciation often suffer from a sparsely populated thermodynamic data base [1], often due to a missing spectroscopic evaluation of species stoichiometry and structure.

This work combines absorption and fluorescence spectroscopies to reveal the speciation of U(IV) in solution in concentrations down to 10^{-6} M uranium. The set-up for time-resolved laser-induced fluorescence was optimized to allow the determination of fluorescence decay times of U(IV) in perchloric as well as in chloric acid with 2.5 ± 0.4 ns at room temperature and 152 ± 8.3 ns at liquid nitrogen temperature. By decreasing the temperature we gained an improved fine structure with a band splitting of the main peak at 410 nm and a redshift could be observed.

By evaluation of UV-vis based titration series ($\text{pH} = 0$ – 2 , $[\text{U}] = 5 \times 10^{-5}$ M, $[\text{SO}_4]$ from 0 to 1.9×10^5 M) in the U(IV) sulfate system, complex formation constants for USO_4^{2+} and $\text{U}(\text{SO}_4)_2(\text{aq})$ could be derived, yielding 6.9 ± 0.3 and 11.8 ± 0.5 , respectively, when extrapolated to infinite dilution. This log K values for the 1:1 complex is close to the NEA recommendation of 6.58 whereas our value for the 1:2 complex is about one order of magnitude higher than that selected in [1]. The NEA recommendations are exclusively based on liquid-liquid extraction experiments, with higher ionic strengths (up to 2 M) and U(IV) concentrations (up to 0.1 M) as applied in this work.

The potential of direct U(IV) spectroscopy for speciation analysis at environmentally relevant uranium concentrations was proven in this study. Eventually, all acquired information will increase confidence in respective U(IV) reactive transport modelling.

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[1] R. Guillaumont et al. (2003). "Update on the chemical thermodynamics of uranium, neptunium, plutonium, americium and technetium.", vol. 5 of Chemical Thermodynamics." Elsevier: 960 pp.