U(VI) – SO_4^{2-} complexation at elevated temperature – a combination of spectroscopy and thermodynamic modeling

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In order to evaluate the fate and transport of radionuclides in the environment, knowledge about complexation behaviour with inorganic ligands is mandatory. The complex stability constants ($\log_{10}K$) which are required for thermodynamic calculations are mostly determined at ambient conditions (293-303 K). However, high level radioactive waste is expected to considerably increase the temperature in the vicinity of waste disposal sites up to 373 K. The temperature dependence of the $\log_{10}K$ value can be calculated if all necessary thermodynamic parameters ($\log_{10}K(T_0)$, $\Delta_r S^\circ(T_0)$, $\Delta_r H^\circ(T_0)$, and the temperature dependence of $\Delta_r C_p^\circ$) are known. However, reliable thermodynamic data for most actinide complexes with inorganic ligands, e.g. SO_4^{2-} or CO_3^{2-} are still lacking. Theoretical approximations may be helpful to estimate $\log_{10}K$ values for higher temperatures, with the actual methods depending on the investigated temperature range and the chemical system.

In this study of the U(VI)–SO_4^{2-} system, we compare two approximation methods (constant enthalpy of reaction and Ryzhenko-Bryzgalin model - RBM) for the calculation of $\log_{10}K$ at different temperatures. Both models show an increase of $\log_{10}K$ with increasing temperature for both the 1:1 and 1:2 complex. However, at the lowest and highest temperatures, the RBM gives slightly higher values than the constant enthalpy approach.

These predictions are compared to experimentally determined $\log_{10}K$ values as $f(T)$. They are based on various spectroscopic techniques (TRLFS, fluorimeter, UV-vis, conventional Raman and surface-enhanced Raman) and yielded with increasing sulfate-concentrations a stepwise complexation from the free UO_2^{2+}, to the 1:1, 1:2 and 1:3 complex. This illustrated that a combination of different techniques is helpful for the distinct discrimination of the different complexes.