Quantitative Prediction of Uranium Speciation and Amidoxime Binding in Seawater from Advanced Simulation Techniques

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ABSTRACT:

The goal of this research project is to quantitatively predict the stability of uranium species and thermochemistry (free energy, entropy, and enthalpy) of uranium binding with amidoxime ligands in realistic seawater conditions. To achieve this goal, we pursue three specific objectives: i) determine the stable species of uranium and its solvation structure in realistic seawater conditions; ii) accurately predict the free energies (and thereby stability constants) of binding between uranium and amidoxime; iii) accurately predict the reaction enthalpies and entropies of binding between uranium and amidoxime. State-of-the-art simulation techniques including molecular dynamics, free-energy calculations, and the hybrid quantum mechanical/molecular mechanical approach will be employed to explicitly include water molecules and common seawater ions (such as Na^+, Cl^-, Mg^{2+}, and Ca^{2+}) in the simulations. This is motivated by the recent discovery that the neutral $Ca_2UO_2(CO_3)_3(aq)$ species is the dominant species in seawater instead of the previously thought $UO_2(CO_3)_3^{4-}$, due to the overwhelming abundance of Ca^{2+} ions in seawater. The quantum mechanical/molecular mechanical simulations will also yield free-energy profiles along certain reaction coordinates and therefore provide free-energy barriers of the binding-unbinding process. Experimental measurements will be used to validate and improve our predictions in all three objectives, so that a computational protocol will be established to predict binding free energies, entropies, and enthalpies for new ligands. This will allow us to address over the long-term exciting questions such as: (a) which new group or functionalized amidoxime could offer even better binding with uranium; (b) whether such groups could selectively bind with uranium over other metal ions in the seawater. Overall this project will lead to molecular-level insights into the complexation modes, binding mechanisms, and kinetics of the uranium extraction process in realistic seawater conditions, a key interest of the Fuel Resources program.