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Rapid characterization of novel uranyl complex redox behavior at the mineral-fluid interface via quantum mechanical models and electrochemistry

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Understanding the redox behavior, thermodynamics, and redox kinetics of actinides is paramount to understanding their mobility within the environment. For the simple uranyl complex, these properties are well documented within the literature. However, less common and newly synthesized complexes of uranium do not receive the same thorough treatment due to the resources required to reach a similar understanding. One of the most efficient ways to study this electrochemical behavior is through the use of powder microelectrodes (cavity microanalysis), allowing for rapid characterization of solids in direct contact with the electrode surface. A drawback of this method, is that electrochemical responses often represent a highly complex system in which redox transition, diffusion, adsorption/desorption, and a myriad of other processes occur simultaneously. To analyze these processes individually can require exhaustive experimental design and represent a bottleneck in an otherwise efficient analytical tool. This work explores the use of atomistic theoretical approaches to aid in the interpretation of experimental electrochemical results with a focus on the mobility of such contaminants in aquatic environments. Complexation and adsorption of uranyl leads to differing voltammetric responses in electrochemistry, evident in the wide-ranging standard reduction potentials of different uranyl complexes. Peaks in voltammetry related to redox transitions are shifted by the difference in binding energy, bonding, and ligands between uncommon uranyl complexes (like uranyl peroxides) and simple uranyl complexes. The change in Gibbs free energy (δG) of adsorption and complexation as calculated using computational models is shown to correlate with the measured redox transitions in electrochemistry. These changes in δG can then be converted to electrochemical potentials using the Nernst equation, allowing for the accurate prediction of electrochemical potentials via modeling. Our results show that the switching potential of uranyl peroxides can be predicted to within 0.1 V of electrochemical measurements and identifies the primary interactions occurring at the solid/electrolyte/electrode interface (complexation, adsorption, and reduction). This methodology not only streamlines the process of experimental design and is applicable to a wide range of environmental contaminants, but also offers a more detailed understanding of electrochemical results at the molecular level.