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DFT approach of uranyl species originating from acid mine drainage and its interaction with ion exchange resin

Authors: Alexandre Carvalho Bertoli, Hélio Anderson Duarte, Heitor Avelino de Abreu

*Address: Departamento de Química, Universidade Federal de Minas Gerais - UFMG
Av. Pres. Antônio Carlos, 6627 - Pampulha, Belo Horizonte - MG, 31270-901, Brasil
bertolialexandre@yahoo.com.br*

Abstract: Acid drainage, commonly referred to as acid mine drainage (AMD), has become an economic and environmental burden. It is a very ubiquitous problem in areas where there has been a history of coal or hard rock mining. This phenomenon is generally associated with heavy metals as a uranium mine localized in the southeast of Brazil, in the state of Minas Gerais (Poços de Caldas Municipality). The study and identification of uranium complexes from such acid water are imperative not only from the point of view of its economic value but it is important for understanding actinide separation and predicting actinide transport in the environment, particularly with respect to the safety of nuclear waste repositories [1]. The uranyl, UO_2^{2+} , ion has received considerable interest due to its importance for environmental chemistry of radioactive elements and its role as a benchmark system for larger actinides. Many useful insights into structures and intrinsic stabilities of actinide complexes can be gained from quantum-chemical calculations are it through ab initio wave function theory or density functional theory (DFT). As for the latter, hybrid DFT and small-core relativistic effective core potentials (ECPs) or all-electron relativistic treatments have proven fairly robust in describing the thermochemistry of actinides. Therefore, it is a challenge to evaluate the thermodynamic properties of the hydrolyzed UO_2^{2+} species and the interactions with SO_4^{2-} ions and an amino exchanger group, present in ion exchange resins [2]. DFT computations were performed using the Gaussian 09 program package. Full geometry optimizations and frequency computations were performed using the B3LYP hybrid functional; the Stuttgart–Dresden triple-valence basis sets together with the corresponding effective small-core potential (SDD) were used for uranium and the Pople triple-zeta basis sets, 6-311G(d,p), for hydrogen and oxygen. A thermodynamic study aims to provide a theoretical discussion on the complexes, in order to obtain the parameters that determine their chemical properties. The heats of formation values (ΔG) of the complexes were obtained using a thermodynamic cycle. The calculation of relative energy ($\Delta\Delta G_{(\text{aq})}$) was performed to identify the most stable species. The following structures were calculated UO_2OH^+ , $\text{UO}_2(\text{OH})_2$, $\text{UO}_2(\text{OH})_3^-$, $(\text{UO}_2)_2(\text{OH})^{3+}$, $(\text{UO}_2)_2(\text{OH})_2^{2+}$, $(\text{UO}_2)_3(\text{OH})_4^{2+}$, $(\text{UO}_2)_3(\text{OH})_5^+$ and $(\text{UO}_2)_3(\text{OH})_7^-$, reported previously based on experimental evidences [3]. The formation reaction energies of the different species from the UO_2^{2+} and H_2O were estimated. The relative formation energies follow



XIX SBOQT

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the order: UO_2OH^+ (20.99 kcal/mol) > $(\text{UO}_2)_2(\text{OH})^{3+}$ (21.67 kcal/mol) > $(\text{UO}_2)_2(\text{OH})_2^{2+}$ (41.73 kcal/mol) > $(\text{UO}_2)_3(\text{OH})_5^+$ (51.14 kcal/mol) > $\text{UO}_2(\text{OH})_2$ (56.63 kcal/mol) > $(\text{UO}_2)_3(\text{OH})_4^{2+}$ (81.71 kcal/mol) > $\text{UO}_2(\text{OH})_3^-$ (93.23 kcal/mol) > $(\text{UO}_2)_3(\text{OH})_7^-$ (180.20 kcal/mol). The interaction of these species with the SO_4^{2-} and benzyltriethylammonium ion exchange their relative energies will be also presented. Sulfate ions are present in the acid rock drainage that occur in the mining areas of uranium and may affect the chemical speciation of the uranyl in aqueous solution. From experimental data it is observed that the ion exchange resins work well, in a wide range of pH, for the removal of uranium. According to our results, we can suggest the formation of ionic pairs due to a strong electrostatic attraction between the sulphate oxygens coordinated to the UO_2^{2+} ions and the quaternary ammonia of the resin. This mechanism is probably predominant, although not the only one, since these functional groups can participate in covalent, hydrogen bonds and weak Van der Waals forces [4].

Key-words: Uranyl, Hydrolysis, Ionic exchange, Acid drainage.

Support: INCT-ACQUA, GPQIT, FAPEMIG, CNPQ.

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