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Spectroscopic investigation of the complexation of U(VI) with 2-Phosphonobutane-1,2,4-tricarboxylic acid (PBTC) in the pH range of 2 to 10

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Cement-based materials are used for waste conditioning and as technical barriers in potential nuclear waste repositories. In order to adjust the physico-chemical and mechanical properties of concretes, several additives are added to the cement. Various polycarboxylates with phosphonic acid groups, of which 2-Phosphonobutane-1,2,4-tricarboxylic acid, PBTC, is the most prominent representative, are used as modern long-term retarders for the hardening of cement. Water ingress into a repository is considered a worst-case scenario. The concrete decomposes and the cement additives can be leached out, enabling complexation with radionuclides. Therefore, the prediction and modelling of aqueous complexation reactions between actinides and various inorganic and organic ligands, such as PBTC, is of significant interest. Although PBTC is already known in industrial applications as a strong complexing agent of various metal ions (e.g. Ca^{2+} , Zn^{2+} , Al^{3+} , Fe^{3+}), there are no studies on the complexation behaviour with radionuclides. In contrast to these well-investigated spherical ions, in case of the linear uranyl ion ($\text{UO}(\text{VI})$) ligand coordination is limited to the plane perpendicular to the $\text{O}=\text{U}=\text{O}$ axis. For this reason, the complexation of PBTC with U(VI) in the pH range from 2 to 12 in NaCl medium was investigated spectroscopically. The aim is the structural and thermodynamic characterization of possible U(VI)-PBTC complexes. Here we present some results of the structural investigations by NMR spectroscopy.

First, the protonation constants of the commercially available PBTC ligand were determined by ^{13}C - and ^{31}P -NMR spectroscopy in the pH range from 0.5 to 12.5 in 0.5 m NaCl. The obtained NMR signals of the uncomplexed PBTC further served as a reference for the shift of the signals of the PBTC complexed with U(VI). This complexation was investigated with an U(VI) concentration of 50 mM and different metal-to-ligand ratios (U(VI)-to-PBTC ratio = 1:0.5 / 1:1 and 1:5) as well as a fixed ionic strength of 0.5 m NaCl. The results show, that at U(VI)-to-PBTC ratio $\geq 1:1$ one U(VI)-PBTC species dominates and this is the case over the whole investigated pH range. The ^{31}P - and ^{13}C -NMR spectra indicate that U(VI) is chelated by the phosphonate group and one of the carboxyl groups. Based on the NMR results various structural proposals of this U(VI)-PBTC complex were postulated and supported using DFT calculations.

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