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Complexation of protactinium(V) with nitrilotriacetic acid

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Protactinium, as a ^{235}U decay product, is naturally present in the environment as ^{231}Pa isotope (alpha emitter with a half-life of 32,400 years). Over the years, this isotope is accumulated in uranium tailings and stocks of yellow cake. Modelling the behavior of this element in the geosphere requires thermodynamic and structural data relevant to environmental conditions. The present work concerns a study of the complexation of Pa(V) with nitrilotriacetic acid (NTA, $\text{N}(\text{CH}_2\text{COOH})_3$), a chelating agent that can be regarded as a model for polyaminocarboxylic acids.

Because of the strong tendency of Pa(V) towards hydrolysis and polymerization, speciation studies have been conducted with the element at ultra-trace scale ($C_{\text{Pa}} < 10^{-10}\text{M}$) [1,2]. A systematic study using liquid-liquid extraction with a β -diketone as extractant has been performed at constant ionic strength and temperature. Under these experimental conditions, the variations of the distribution coefficient of $^{233}\text{Pa}(\text{V})$ as a function of NTA and proton concentrations provides information on the stoichiometry of the complexes Pa-NTA in aqueous phase and also on their mean charge (slope method). Results indicate the formation of two successive complexes that are likely to be $\text{PaO}(\text{NTA})$ and $\text{PaO}(\text{NTA})_2^{3-}$. The formation of complexes (1:1) and (1:2) are observed with actinides at oxidation states +3 and +4. In contrast, only (1:1) complexes are formed with actinides +5 and +6. In addition, capillary electrophoresis inductively coupled plasma mass spectrometry experiments have been performed with several actinides ($^{239}\text{Pu}(\text{IV})$, $^{243}\text{Am}(\text{III})$, $^{231}\text{Pa}(\text{V})$) at tracer scale. $\text{Pu}(\text{IV})$ and $\text{Am}(\text{III})$ namely are known to form complexes of charge -2 ($\text{Pu}^{\text{IV}}(\text{NTA})_2^{2-}$) [3] and -3 ($\text{Am}^{\text{III}}(\text{NTA})_2^{3-}$) [4]. Comparison of electrophoretic mobility for the complexes $\text{Am}(\text{III})$, $\text{Pu}(\text{IV})$ and $\text{Pa}(\text{V})$ with NTA, confirms the charge -3 for the maximum stoichiometry complex.

The formation constants of $\text{PaO}(\text{NTA})$ and $\text{PaO}(\text{NTA})_2^{3-}$ have been deduced from solvent extraction experiments. The value obtained for the (1:1) complex is similar to those relative to actinides + 6 whereas the formation constant of the (1:2) complex is close to the ones observed for the actinides at the oxidation state +3. Thus, these results emphasize the distinctive feature of protactinium chemistry as compared to the other actinides.

To complete the results already obtained, a structural study by X-ray absorption spectroscopy (XAS) and density functional theory (DFT) calculations is currently being processed to determine the coordination geometry and the interatomic distances of the formed complexes. Preliminary results on the structural study performed with the maximum stoichiometry complex will be also presented.

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