



Contribution ID: 701

Type: Poster

Np(VI) and Pu(VI) complex formation with malonate ions in low acid solutions

Tuesday, 15 May 2018 18:30 (15 minutes)

Carboxylic acids of different composition are the most frequently encountered components of a variety of natural media. They are active complexing agents for actinide ions in higher oxidation states and sometimes, depending on actinide ion pair redox potential, can play reductant role. Taking into account that actinide elements in higher oxidation states have an increased solubility in the solutions of pH range (what is often closed to the environmental media), it is became clear the importance of the understanding of their behaviour under such conditions. In the present work we have studied interaction of Np(VI) and Pu(VI) with anion of malonic acid ($\text{CH}_2(\text{COO})_2^{2-} = \text{L}_2^-$).

Synthesis of Pu(VI) solid compounds from aqueous solutions and their characterization also require special data on the behavior of Pu(VI) and Pu(V) in the presence of complexing agents. There is very limiting information on this topic for both Pu and Np. Some data were reported on complexation of the neptunyl ion with aromatic polycarboxylates, particularly, phthalate. Earlier we published new data on Np(VI) and Pu(VI) complexation with phthalate in neutral aqueous solutions. In this study we have gained additional information on the complexation and reduction of Pu(VI) and also on the disproportionation of Pu(V) in malonate solutions. For comparison, the behavior of Np(VI) was also examined.

Complexation of PuO_2^{2+} in solutions containing malonate anions was studied by spectrophotometry. Mono- and bimalonate complexes are formed. The monomalonate complex was isolated as $\text{PuO}_2\text{L}\cdot 3\text{H}_2\text{O}$. It was found to be isostructural with $\text{UO}_2\text{L}\cdot 3\text{H}_2\text{O}$. Isolated plutonium solid complex forms rhombic crystals with the unit cell parameters $a = 9.078(2)$, $b = 7.526(2)$, and $c = 6.2005(15)\text{\AA}$, space group $\text{Pmn}2_1$. The electronic absorption spectrum of the monomalonate complex is characterized by a strong band at 843nm. In malonate solutions, Pu(VI) is slowly reduced to the pentavalent state even in the cold.

In contrast to Pu(VI), Np(VI) is noticeably reduced by the malonate ions even at room temperature, making it possible to examine the kinetic features of the reaction $\text{An(VI)} \rightarrow \text{An(V)}$. In this work we have performed a series of experiments to examine the effect of the temperature, Np concentration, and solution composition on the reaction kinetics. Kinetic curves illustrating the general picture of the temperature dependence of the process of neptunium reduction are measured. Calculations have been performed showing that they (kinetic curves) are not described by first- or second-order reaction equations. A mechanism of neptunium(VI) reduction is proposed, the rate-determining stage of which is the intramolecular reduction of neptunium(VI) with the formation of the monomalonate complex Np(V) and the radical ion. The proposed mechanism is confirmed experimentally. The activation energy of the process is estimated. It is concluded that the synthesis of $\text{NpO}_2\text{L}\cdot 3\text{H}_2\text{O}$, a crystalline analogue of the previously described uranyl and the plutonium compound prepared in the course of this work, seems impossible in view of the high rate of reduction of Np(VI) by malonate ions even in the cold. The results obtained will be useful in determining the optimum conditions for the synthesis of crystalline compounds of penta- and hexavalent plutonium and neptunium.

Primary authors: Prof. BESSONOV, Alexei A. (A.N. Frumkin Institute of Physical chemistry and Electrochemistry Russian academy of sciences (IPCE RAS)); Prof. KULYUKHIN, Sergey

Presenter: Prof. BESSONOV, Alexei A. (A.N. Frumkin Institute of Physical chemistry and Electrochemistry)

Russian academy of sciences (IPCE RAS))

Session Classification: Poster TAN

Track Classification: Chemistry of Actinide and Trans-actinide Elements