

ABSTRACT CODE

Investigation of Pu(IV) Complexation by TcO_4^- Anion in perchloric media

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Technetium is an artificial radioelement arising primarily from the nuclear industry with the accumulation of ⁹⁹Tc in spent fuel. Numerous liquid/liquid extraction studies have shown that Tc(+VII) is coextracted with the actinides U(VI) and Pu(IV) in the organic phase (e.g. tributyl phosphate: TBP). The formation of TcO_4^- complexes with metallic cations such as Pu(+IV), U(+VI), Th(+IV) or Zr(+IV) accounts for the presence of technetium coextracted in the organic phase. The following species have been identified in the organic phase during studies of nitric acid solutions: $\text{UO}_2(\text{TcO}_4)(\text{NO}_3) \cdot 2\text{TBP}$ and $M(\text{TcO}_4)(\text{NO}_3)_3 \cdot n\text{TBP}$, where $M=\text{Th}$ and Zr , and $n=1$ or 2 .

The authors investigated the complexation of plutonium at oxidation state (+IV) by the pertechnetate anion in aqueous solution (perchloric acid) using visible/NIR absorption spectrophotometry and liquid/liquid extraction by TBP.

Absorption spectrophotometry observations of a 2 mM solution of Pu(IV) in 2 M HClO_4 at TcO_4^- concentrations ranging from 0.2 mM to 1.8 M confirmed the complexation of Pu(IV) by the TcO_4^- anion. Chemometric techniques were used for quantitative processing of the spectrum evolution [1]. Although the mathematical treatment allowed us to rule out 1:1 and 1:2 stoichiometry for these complexes, it was not sufficient to discriminate between two

$(\text{Pu}(\text{TcO}_4)_3^+)$ and $(\text{Pu}(\text{TcO}_4)_4)$ complexes with 1:3 and 1:4 stoichiometry.

In order to identify the stoichiometry of these complexes (1:3 or 1:4), we examined the partitioning of trace amounts of Pu(IV) between an organic phase (30 vol% TBP) and an aqueous phase (2 M HClO_4) at TcO_4^- concentrations ranging from 15.9 mM to 0.78 M. Using TBP, a neutral extractant, we were able to demonstrate 1:3 stoichiometry for the complex over the TcO_4^- concentration range. The calculated β_3 equilibrium constant at 25°C was approximately 2.3.

Applying the van't Hoff law to the spectrophotometric measurements revealed that the entropy term ($-\Delta S$) controls the complexation reaction. The characteristic data for the formation of the 1:3 complex are the following: $\Delta H = 3.5$ kcal/mol and $-\Delta S = -4.3$ kcal/mol.

The study of Pu(IV) partitioning in largely excess TcO_4^- over a range of TBP concentrations suggests that the 1:4 limit complex (which is extractable by TBP) is probably solvated in the organic phase as both $\text{Pu}(\text{TcO}_4)_4 \cdot \text{TBP}$ and $\text{Pu}(\text{TcO}_4)_4 \cdot 2\text{TBP}$.

References

- [1] P. POCHON, Ph. MOISY, L. DONNET, C. de BRAUER and P. BLANC; Investigation of neptunium(VI) complexation by $\text{SiW}_{11}\text{O}_{39}^{8-}$ by visible/near infrared spectrophotometry and factor analysis; *Phys. Chem. Chem. Phys.* **2**, (2000) 3813-3818.