



Hydration of the pertechnetate anion. DFT study

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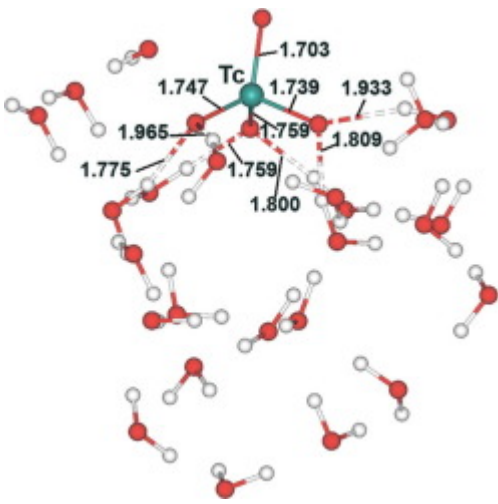
Highlights

- $[\text{TcO}_4(\text{H}_2\text{O})_n]^-$ and $[\text{TcO}_4(\text{H}_2\text{O})_{n-m}]^-[\text{H}_3\text{O}]^+_m$ ($n=1-50$, $m=1-4$) clusters have been simulated with DFT.
- First hydration shell of TcO_4^- is asymmetric and contains no more than 7 water molecules.
- Only three of the four oxygen atoms of TcO_4^- form hydrogen bonds with water molecules.
- In a two-phase system TcO_4^- tends to concentrate at the aqueous/organic interface.
- In highly acidic solutions hydration of TcO_4^- leads to the formation of ortho-acid $(\text{HO})_5\text{TcO}$.

Abstract

The long-lived radionuclide ^{99}Tc ($t_{1/2} = 2.11 \times 10^5$ years) is one of abundant and problematic fission products in the nuclear fuel cycle with the yield of >6 % for thermal neutron fission of uranium-235. During the reprocessing of the spent nuclear fuel (SNF) in PUREX process, ^{99}Tc is stabilized as pertechnetate ion TcO_4^- . Owing to long half-life of ^{99}Tc and high environmental mobility, TcO_4^- is rather environmentally hazardous radioactive pollutant. Preferentially it is to be removed at the head-stage operations when the used fuel rods are dissolved in highly concentrated nitric acid. The lack of reliable knowledge on the structure and thermodynamics of aqua complexes that the pertechnetate anion forms in aqueous solutions hampers the development of technologies for $^{99}\text{TcO}_4^-$ separation from SNF. To fill this gap, in this paper we used DFT simulation of clusters $[\text{TcO}_4(\text{H}_2\text{O})_n]^-$ and $\{[\text{TcO}_4(\text{H}_2\text{O})_{n-m}]^-[\text{H}_3\text{O}]^+_m\}$ ($n = 1 - 50$, $m = 1 - 4$). We have shown that unlike NO_3^- , SO_4^{2-} , and other hydrophilic anions, the pertechnetate anion does not form a dense hydration shell in aqueous solutions. Its first hydration shell contains not more than 7 water molecules. Only three of four oxygen atoms of the anion in this shell form hydrogen bonds with water molecules. The energy of hydrogen bonds $[\text{O}_3\text{TcO} \cdots \text{H}-\text{O}-\text{H}]$ is significantly lower ($10-15 \text{ kJ mol}^{-1}$) than the energy of the hydrogen bond in the water dimer ($\approx 20 \text{ kJ mol}^{-1}$). The hydration shell of HTcO_4 preserves the same asymmetric structure in acidic solution up to acid concentration of $3 - 4 \text{ mol L}^{-1}$. This suggests that during extraction in two-phase system the pertechnetate anion will predominantly concentrates at the water/organic interface, displacing more hydrophilic anions from it. When acid concentration in solution is above 4 mol L^{-1} , water molecules are attached to the technetium atom with formation of ortho-pertechnetic acids $\text{O}_2\text{Tc}(\text{OH})_3$ and $\text{OTc}(\text{OH})_4$.

Graphical abstract



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Keywords

Pertechnetate; hydration; DFT; spent nuclear fuel processing

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