The impacts of EDTA on the solubility and speciation of uranium were evaluated as a function of ionic strength, redox conditions, and pH. EDTA is both a strong complexant of U(IV/VI) and, under many conditions, can act as a reducing agent towards U(VI). An accurate knowledge of this aquatic chemistry and, more generally, the thermodynamics of actinides are fundamental needs that support nuclear waste disposal concepts. The availability of complete and correct chemical and thermodynamic models helps provide reliable geochemical model calculations and source-term estimations for the safety assessment of nuclear waste repositories.

Uranium typically comprises the largest inventory in treated TRU and HLW radioactive waste and is the key component of spent fuel. In this context, understanding its chemistry is important in its own merit as well as being potentially useful as an analog of the An(VI) and An(IV) actinides. U(VI) is the most stable oxidation state of uranium under anoxic and oxidising conditions, whereas U(IV) prevails in strongly reducing environments, forming the sparingly soluble UO$_2$(am,hyd) in the absence of complexing ligands. EDTA is a strong complexing ligand used for decontamination purposes in nuclear reactors, clean-up operations and for the separation of radionuclides. Previous studies available in the literature have shown that both An(IV) and An(VI) form strong complexes with EDTA, eventually leading to significant increase in the solubility compared to EDTA-free systems [1-3]. However, most of these studies have been performed under acidic conditions, and accordingly the NEA–TDB review selected only binary U–EDTA complexes [3], both for +IV and +VI redox states. In the alkaline to hyperalkaline pH conditions, which are most relevant to nuclear waste repositories, the formation of ternary U–OH–EDTA complexes is also to be expected, as recently reported for the Pu(IV) system [4–5]. Additionally, such complexes can importantly affect the solubility and redox transitions between U(IV) and U(VI). In this context and based on a combination of solubility experiments and spectroscopic measurements, this work aims at evaluating the impact of EDTA on the solubility and redox phenomena of uranium and, ultimately, at developing complete and correct chemical and thermodynamic models for U(IV) and U(VI) in EDTA-containing systems, valid for dilute to concentrated salt systems and covering the entire pH range.

The solubility of U(IV) and U(VI) in the presence of EDTA was investigated from both undersaturation and oversaturation conditions. Experiments were performed in an inert gas atmosphere with < 2 ppm O$_2$ at $T = (22 ± 2)$ °C. Oversaturation solubility experiments were conducted with [U]$_0 = 10^{-3}$ M (either as +IV or +VI), whereas undersaturation solubility experiments were performed with approximately 3 mg of UO$_2$(am,hyd) or Na$_2$U$_2$O$_7$·H$_2$O(cr) per sample. In the case of UO$_2$(am, hyd), strongly reducing conditions (pH + pe < 2) were fixed in each independent solubility sample with SnCl$_2$. Background electrolyte solutions were prepared with [EDTA] = 0.001 and 0.01 M, constant ionic strength $I = 0.5$ and 5.0 M Na$_2$EDTA–NaCl–HCl–NaOH, and covering the pH$_m$ range 0–13 (with pH$_m$ = $–\log [H^+]$). Uranium concentration, pH$_m$ and $E_h$ values were monitored at regular time intervals. Thermodynamic equilibrium was assumed after repeated measurements with constant [U] and pH$_m$. After attaining equilibrium conditions, selected samples were characterized by UV–vis-NIR (supernatant solutions), XRD and quantitative chemical analysis (solid phases). Additionally, spectroscopic measurements were performed with U(IV) as a function of EDTA concentration in 0.5 M HCl (see Figure 1), and as a function of pH at constant EDTA concentration to identify the changes in the aqueous speciation. The results obtained on the impact of EDTA on the aqueous speciation, redox state and solubility of uranium will be presented in this contribution, discussed in the context of the presence/absence of ternary species, and evaluated as an analog for An(IV) actinides.
Figure 1. Uranium-EDTA absorption spectra as a function of [EDTA] in 0.5 M HCl. Isobestic points are clearly seen at a number of wavelengths indicating the formation of one EDTA complex (presumably the neutral U-EDTA complex).

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Impact of EDTA on the solubility and redox behaviour of uranium in dilute to concentrated NaCl solutions

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Introduction

Uranium typically comprises the largest inventory in treated TRU and HLW radioactive waste and is the main component of spent fuel. Understanding its chemistry is important in its own merit as well as being potentially useful as an analog of the An(VI) and An(IV) actinides.

- Most relevant oxidation states of U:
  - U(IV): forms sparingly soluble hydroxy oxides (UO2(OH)2).
  - EDTA is a strong complexing ligand used for decontamination purposes in nuclear reactors.

This work aims at evaluating the impact of EDTA on the solubility and redox phenomena of U(IV) and U(VI) in the presence of EDTA.

Summary and Outlook

- U(VI) and U(IV) complexation with EDTA
- U(VI): UO2-edta2-, UO2(Hedta)- and (UO2)2-edta(aq) species selected in NEA-TDB.[2]
- U(IV): [EDTA] clearly indicate the formation of single EDTA complex
- Spectroscopic measurements as a function of [EDTA] indicate the formation of single EDTA complex
- Significant increase in U(VI) solubility with increasing [EDTA] at 6 ≤ pHm ≤ 9
- Precipitation observed at pHm < 4, hinting towards (UO2)-EDTA(s)
- Filtration results show that no colloids (>5 nm) are present in the system
- Sample re-acidification results show that the higher-pH complex is reversible and no U(VI) is present
- Changes in the higher-pH absorption spectra suggest the presence of ternary species

References


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