

# Spectrophotometric and Potentiometric Study on Complexation of Thorium(IV) with Benzoate in Aqueous Solution

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Understanding the chemical behavior of actinides in natural waters is of utmost interest in the field of nuclear engineering and environmental chemistry, since the thermochemical properties are essential to accurately assess the migration of the long-lived radionuclides into the biosphere released from a geological disposal repository for radioactive waste. The deep geological environment generally provides a reducing condition, and actinides exist primarily in the tetravalent oxidation state. However, most of actinides, such as uranium, neptunium, and plutonium, appear to be stable in higher oxidation states under ambient conditions. Thus, thorium in the tetravalent state and with an ionic radius similar to other actinides has been extensively utilized as a chemical homologue for other tetravalent actinides. Furthermore, the solubility, species distribution, and sorption characteristics of actinides are intrinsically controlled by complexations with inorganic/organic ligands, which are ubiquitous in natural aqueous systems. In particular, aromatic carboxyl moieties are abundant in natural organic macromolecules and are mainly responsible for binding with actinides in natural waters. The complexation of actinides with intricate organic macromolecules can be simulated quantitatively using the thermochemical data of simple actinide complexes with model ligands [1]. In this framework, we aimed to reliably generate the stability constants of thorium complexes with benzoate, the simplest model ligand of aromatic carboxyl functionalities, by means of UV-vis spectrophotometry and potentiometry in order to expand the current thermochemical database of tetravalent actinides to be developed for safe radioactive waste management.

To reduce the uncertainties of the resulting thermochemical data of thorium benzoates, the experiments were conducted under acidic conditions ( $\text{pH} < 2$ ) to avoid the influence of complicated thorium(IV) hydrolysis reactions at  $T = 25 \pm 2$  °C and  $I = 0.1$  M  $\text{H}/\text{NaClO}_4$ . Table 1 summarizes the resulting stability constants of thorium benzoate complexes, and Figure 1 shows the determined molar absorptivities of relevant chemical species.  $\text{Th}^{4+}$  has a stronger binding affinity to the benzoate anion than  $\text{UO}_2^{2+}$  [2], which is generally explained by the effective electric charge of metal cations.

[1] T. Sasaki, et al. (2015), *Radiochim. Acta* 103, 411-421.

[2] S. Choi, J.-I. Yun (2019), *Polyhedron* 161, 120-125.

Table 1. Stability constants of thorium benzoate complexes in molarity scale.

Experimental method	$\log \beta(\text{ThBen})$ (1:1 complex)	$\log \beta(\text{ThBenz})$ (1:2 complex)	$[\text{Ben}]_{\text{total}}/[\text{Th}]_{\text{total}}$
Potentiometry	$3.94 \pm 0.01$	$7.97 \pm 0.04$	0 ~ 1.78
UV-vis spectrophotometry	$3.65 \pm 0.35$	-	0.04 ~ 0.08

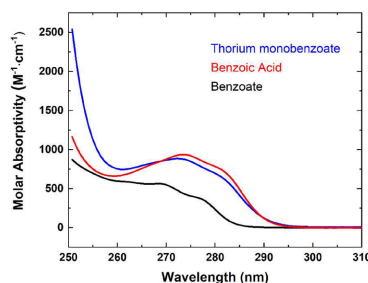


Figure 1. Molar absorptivities of thorium monobenzoate, benzoic acid, and benzoate species.