Studies of aqueous U(VI)–thiosalicylate complex formation via UV–Vis absorption spectrophotometry, TRLFS and potentiometry

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ABSTRACT

The formation of U(VI)–thiosalicylate (TSal) complexes in aqueous solutions ($I = 0.1$ M) was investigated over a wide range of pH values (from 3 to 9) using UV–Vis absorption and time-resolved luminescence spectroscopy, as well as by a potentiometric technique. It is demonstrated that the formation of U(VI)–TSal complexes, including monodentate, bidentate and ternary complexes, is responsible for the enhanced solubility of U(VI) and the strong U(VI)-luminescence quenching effects by TSal. In this study the stability constants of the complexes as well as two pK_a values of TSal ($pK_{a1} = 3.76 \pm 0.05$; $pK_{a2} = 8.33 \pm 0.07$) are provided. The spectrophotometric analysis confirms the presence of both 1:1 and 1:2 (U(VI):TSal) charge-transfer complexes ($\log \beta_{101} = 7.59 \pm 0.04$ and $\log \beta_{102} = 13.67 \pm 0.09$). In luminescence quenching studies, mixed (dynamic and static) quenching processes are observed. The dynamic quenching for UO_2^{2+} is attributed to bimolecular excited-state processes by both the acidic and monobasic forms of TSal, i.e., H_2TSal and $HTSal^-$. The static quenching processes are explained by the formation of non-radiative ground-state complexes: $UO_2(HTSal)^+$ ($\log \beta_{111} = 12.11 \pm 0.09$) at pH 3.0; $UO_2(OH)(TSal)^-$ and $UO_2(OH)_2(TSal)^{2-}$ ($\log \beta_{1-11} = 3.9 \pm 0.1$ and $\log \beta_{1-21} = -3.8 \pm 0.1$, respectively) at a higher pH. In particular, the formation of the latter ternary species is found to be responsible for the strong static quenching of hydroxo-uranyl species, i.e. $(UO_2)_2(OH)_2^{2+}$ and $(UO_2)_3(OH)_5^+$.

1. Introduction

A fundamental understanding of the interaction between natural ligands and radionuclides, e.g. actinide metal ions, is required to predict the migration processes from potential contamination sites into groundwater environments and biosystems [1]. Important natural complexing ligands include polyelectrolytic macromolecules (e.g. humic and fulvic acids) that possess various ionizable functional groups, or protein species containing specific sites that interact with metal ions [1,2]. Therefore, typical functionalities such as carboxyl, hydroxyl or nitrogen/sulfur-containing groups have been studied to understand the metal complexing behaviors of natural ligands [3–10].

A sulfhydryl group (–SH, thiol) is a reduced forms of sulfur functionality that can bind heavy metal ions, including actinide ions. As compared to carboxyl and phenolic OH groups, it appears less abundantly in natural ligands. The sulfur content in humic acids is lower than 2 wt.%, depending on the origin of the acids [11], and cysteine is the only unit amino acid possessing a sulfhydryl group. However, sulfur-containing functional groups play an important role in binding certain metal ions. In particular, soft and borderline metals, e.g. Hg^{2+}, Cd^{2+}, Pb^{2+} and Zn^{2+}, based on Pearson's theory [12], exhibit high affinity to a soft sulfhydryl group. Therefore, the cysteinyl active sites of enzymes, such as some peroxidases, can be deformed or blocked by these metal ions [13]. In humic substances, the thiol moiety is also considered as a complexing site for metals such as Zn and Hg [14,15]. Another study using X-ray photoelectron spectroscopy and time-resolved laser-induced fluorescence spectroscopy (TRLFS) demonstrated that increasing the sulfur content of synthetic humic acids leads to an increase in their U(VI) loading capacity, owing to the involvement of the reduced sulfur functionality on the metal binding [5].

Salicylate derivatives have been studied as a dual functional model ligand. Previous studies show that either –OH or –COOH, or both, can participate in binding U(VI) in a pH-dependent manner [3,16–19]. In contrast, few studies have investigated the complex formation of U(VI) with thiol-containing ligands, such as cysteine or thiosalicylate (TSal) [4,10,20,21]. Early studies using potentiometry reported 1:1 uranyl–cysteine complex formation, with the main involvement of amino and carboxyl groups for coordination [20,21]. Recent studies led by Günther et al. using TRLFS and UV–Vis absorption spectroscopy specified two types of 1:1 complexes occurring at different pH levels [4]. Interestingly, these complexes are reported as non-luminescent species. For TSal, in contrast, the involvement of a thiol group (–SH) was reported for

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complex formation of both 1:1 and 1:2 uranyl-ligand species [20]. As a structural analogy of –OH, –SH is expected to form a 5- or 6-membered ring structure through concerted binding with an adjacent functional group, as previously suggested for α-hydroxy-carboxylic acid and salicylate [3,9]. Both functional groups (–SH and –COOH) in TSal are deprotonated at different pH levels. However, as shown in Table 1, the literature values of TSal pK_a are not in good agreement with each other [22–24], likely owing to the susceptibility toward air-oxidation and the slow dissolution rate in an aqueous medium. Thus, the equilibrium constants are often obtained in aqueous-organic solvent mixtures.

In this study, the complexation equilibria of a U(VI)–TSal system are examined in detail using UV–Vis absorption spectrophotometry, TRLFS and potentiometry. In particular, the methods of U(VI)-luminescence (LM) quenching analysis by TRLFS and potentiometry were selected since all the U(VI)–TSal complexes were identified as non-luminescent species. The changes of UV–Vis absorption and LM quenching, dependent on the ligand concentration, are monitored and analyzed primarily using commercial data fitting programs. The stability constants of the involved complex species are calculated based on the literature values of the stability constants for various hydroxo-uranyl species, as well as the pK_a values of the TSal, re-evaluated in this study. Applying a Stern–Volmer analysis, the LM quenching mechanisms of UO_2^{2+}, $(UO_2)_2(OH)_2^{2+}$ and $(UO_2)_3(OH)_5^+$ are also discussed.

2. Experimental

2.1. Preparation of sample solutions

A stock solution of uranium(VI) perchlorate and various aqueous solutions containing UO_2^{2+} were prepared as described in earlier work [3]. Thiosalicylic acid (H_2TSal) (Sigma–Aldrich, St. Louis, MO) was used as received. All procedures required for the sample preparation were done in an Ar-filled glove box. Aqueous TSal stock solutions (~pH 5) were prepared freshly through an overnight dissolution process prior to each test. For a test at a given pH (e.g., 3.0, 4.6 or 5.2), each solution was prepared in a batch-wise manner to make the final pH and ionic strength constant (I = 0.1 M, $NaClO_4$). Each spectroscopic measurement was carried out in three hours after the preparation of the sample at room temperature, 26 ± 1 °C. Details of the general procedures are described in the aforementioned study [3].

For solubility tests, a series of U(VI)–TSal mixtures was prepared by keeping the total U(VI) concentration constant at 2 mM.

The concentrations of TSal added were varied from 0.1 to 4.0 mM in test samples. Over a 3-day equilibration period in an Ar-filled glove box, the solution pH was daily checked and adjusted to 8.1 ± 0.1 (I = 0.1 M, $NaClO_4$). Finally, the solid precipitates formed were removed using syringe filters (0.2-μm pore size) and then the total uranium concentration dissolved in the filtrate was determined by ICP-AES (inductively coupled plasma-atomic emission spectroscopy) analysis, which was conducted by the Radiochemical Analysis Laboratory in the Korea Atomic Energy Research Institute (RAL-KAERI).

2.2. Measurement of UV–Vis absorption and analysis

Absorbance measurements were carried out using a dual-beam UV–Vis spectrophotometer (CARY 3E, Varian, Palo Alto, CA) and all spectra were baseline-corrected against a blank (0.1 M $NaClO_4$) solution. The spectra were collected between 200 and 700 nm. For the determination of the equilibrium constants, the absorbance changes were analyzed in the wavelength range 400–600 nm.

To determine the pK_a of TSal, the TSal concentration was set to 200 or 80 μM. Each sample solution was prepared separately with a different final pH and subjected to the absorption measurement. To determine the complex formation constants of the 1:1 and 1:2 U(VI)–TSal species, the ligand concentration was varied (from 0 to 10 mM) at fixed levels of U(VI) concentration. At a low U(VI) concentration (10 μM with 5 μM–4 mM of TSal), a liquid-waveguide capillary cell (LWCC) setup was used, as reported earlier by the authors [25]. Analysis of the spectrophotometric data was carried out primarily using commercial SUPERQUAD programs (HypSpec® and HySS2009®, Protonic Software, Leeds, UK [26]). The stability constants ($\log \beta$ at 0.1 M $NaClO_4$) of the hydroxo-uranyl species used in this study are −5.63, −12.75, −20.83, −6.22, −13.1, −17.20, −2.6 and −32.7 for the 1:1, 1:2, 1:3, 2:2, 3:4, 3:5, 2:1 and 3:7 species, respectively [27].

2.3. Time-resolved laser-induced fluorescence spectroscopy (TRLFS)

A pulsed Nd:YAG laser (Surelite II, Continuum, Santa Clara, CA) operating at 355 nm with a third harmonic generator was used as the excitation source for the U(VI) species at a repetition rate of 20 Hz and an average pulse energy of 2.8 mJ. To avoid the effect of photodecomposition, i.e. the accumulation of decomposed products, a flow-through system was constructed, as illustrated in Fig. S1. An optimal flow rate of 2.5 mL/min was chosen for the selected quartz cell dimensions (cell volume 450 μL). The LM

Table 1
Equilibrium constants measured using spectroscopic methods.

Species	Conditions	Constants		Refs.
		pK_{a1} ($H_2TSal/HTSal^-$)	pK_{a2} ($HTSal^-/TSal^{2-}$)	
H_2TSal	I = 0.1 M ($NaClO_4$) 26 °C	3.72 ± 0.01[a]	8.38 ± 0.04[a]	this work
		3.80 ± 0.04[b]	8.28 ± 0.05[b]	this work
		(avg. 3.76 ± 0.05)[*]	(avg. 8.33 ± 0.07)[*]	
	–	4.04	9.08	[24]
	I = ~0.04 M, 23 °C	3.5	8.9	[22]
	I = 0.05 M, 17 °C in 50% ethanol	3.3	9.7	[23]
$UO_2(TSal)^0$	I = 0.1 M, 26 °C	$\log \beta_{101}$ (=$\log K_{101}$)	7.59 ± 0.04[a]	this work
	I = 0.1 M, 30 °C in 50% dioxane	$\log K'_{101}$	4.60 [b]	[20]
$UO_2(TSal)_2^{2-}$	same as above	$\log \beta_{102}$ ($\log K_{102}$)	13.67 ± 0.09 (6.1 ± 0.1)[a]	this work
		$\log K'_{102}$	3.90 [b]	[20]
$UO_2(HTSal)^+$	I = 0.1 M ($NaClO_4$), 26 °C	$\log \beta_{111}$	12.11 ± 0.09[c]	this work

Note that pK_a, $\log \beta$, $\log K$ and $\log K'$ denote logarithmic forms of acid dissociation constants, stability constants, step-wise stability constants and conditional equilibrium constants, respectively.
[a] UV–Vis spectrophotometry.
[b] Potentiometry.
[c] TRLFS.
[*] pK_a values used for calculating other stability constants in this study.