



On the covalency of U(III)–Cl, U(IV)–Cl bonding in a LiCl–KCl eutectic melt at 450 °C: Spectroscopic evidences from their 5*f*–6*d* and 5*f*–5*f* electronic transitions



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ABSTRACT

UV–VIS spectra of uranium ions provided information not only on the electronic state of U(III)–Cl and U(IV)–Cl species, but also on the metal–ligand bonding properties. The 5*f*–6*d* transition lines in the electronic absorption spectra of U(III) and U(IV) provided key information on the covalent bonding properties of U(III)–Cl and U(IV)–Cl complexes. The position and intensities of 5*f*–6*d* and 5*f*–5*f* transitions varied depending on the oxidation state and bonding properties. The 5*f*–6*d* transitions of U(III) ion occur at a lower energy of as low as the 400–600 nm range with decreased intensity. However, U(IV) ions occur at the much higher ~250 nm range. The 5*f*–6*d*/5*f*–5*f* intensity ratio indicated the degree of covalency. The U(III)–Cl species exhibited stronger covalent bonding than the U(IV)–Cl. This means that U(III)–Cl bonding is stronger than U(IV)–Cl species. Compared with uranium ions, Eu(II) ion showed no measurable covalent bonding under the same conditions, which means that Eu(II)–Cl bonding is predominantly ionic in nature. The bond strength (covalency) was evaluated in the order of U(III)–Cl > U(IV)–Cl ≫ Eu(II)–Cl. The reduction rate of U(IV) is ~4 times faster than that of the oxidation of U(III), indicating that U(III)–Cl is more stable than U(IV)–Cl species. The UV–VIS spectral analysis method may also be effective in investigating the bonding properties of neptunium and plutonium ions with chloride ligands in molten salt media.

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1. Introduction

Ionic melts have recently become an attractive reaction media in many fields [1,2]. Molten salt based electrochemical processes, so called pyroprocessing, have been proposed as a new option for the advanced spent nuclear fuel cycle [3]. The actinide ion–solvent interactions in a high temperature molten salt are a less explored research field based on nonaqueous coordination chemistry that is of growing interest in the nuclear field. Studies of chloride complexes of trivalent lanthanides and actinides have received growing attention recently because of their implications in the long term safety of high level nuclear waste and pyrochemical processing of spent nuclear fuel.

The understanding and the interpretation of the metal–halide chemical bond in terms of covalency and ionic interaction are fundamental in *f*-element chemistry. Some fundamental questions for actinide ions in a high concentrated chloride solution are such as to what extent the bonding is ionic or covalent and what the nature of the metal–ligand interaction is [4]. Knowledge on the electronic states and the nature of metal–ligand bonding in molten salt media is essential for understanding

their optical, and electrochemical properties. Electronic absorption spectra may provide detailed information on the oxidation state of the ions as well as on the nature of their electronic state and chemical bonding. Several studies have been reported over the past decades on the electronic absorption spectra of uranium ion species in high temperature molten salt media [5–7]. In our previous paper, we reported the visible range electronic absorption spectra of [U^{III}Cl₆]^{3–} and [U^{IV}Cl₆]^{2–} species [hereafter denoted [U^{III}Cl₆]^{3–} and [U^{IV}Cl₆]^{2–} species as U(III)–Cl, U(IV)–Cl, respectively] in a LiCl–KCl eutectic melt at 450 °C [8].

While studying the chemical behavior of actinide ions in the chloride based molten salt, we recognized the importance of the 5*f*–6*d* transitions of the actinide ions in interpreting the bonding properties of the An–Cl complexes. We aimed to explain the nature of chemical bonding in the U(III)–Cl and U(IV)–Cl complexes in the high temperature alkali chloride melt by focusing on interpretation of their electronic absorption spectra. To achieve the goal, one needs both 5*f*–6*d* and 5*f*–5*f* transition measurements for each uranium ion species. However, few attempts have been successful to measure the 5*f*–6*d* transitions of the U(IV)–Cl and to interpret the spectra with respect to the chemical bonding point of view. Here, we report the spectroscopic evidence of covalent bond formation in the U(III)–Cl and U(IV)–Cl species in a LiCl–KCl eutectic melt at 450 °C.

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2. Experimental

All experiments were carried out in a controlled glove box system. The inert atmosphere was maintained by purging with purified Ar gas to avoid exposure to oxygen and water. The O₂ and H₂O levels were maintained at less than 1 ppm. The electrochemical/spectroscopic integrated measurement units interfaced with a glove box–furnace system were designed and set up for spectro and electrochemical measurements simultaneously in high temperature molten salt media. The experimental details of the spectro-electrochemical measurement are described in our recent paper [7,8].

The spectro-electrochemical measurement system interfaced with controlled glove box is shown schematically in Fig. 1. A rectangular quartz cell (path length: 1 cm) attached to a 350-mm long quartz tube (o.d.: 10 mm) is placed at the center of the electric furnace. The light source beam generated by a deuterium–halogen lamp (Ocean Optics Inc.) was guided into and out of the sample chamber using an optical fiber cable.

The U(III) ion species was prepared by anodic dissolution of metallic uranium by wiring to working electrode, and the U(IV) species by oxidation reaction of the U(III) species. Another way of producing the U(III) species is by chemical method such as by reacting uranium metal with CdCl₂. However, in this case it is difficult to get well resolved spectra because the reaction product species interfere in the UV region. In our study, anodic dissolution method was the best way to produce spectroscopically pure U(III) ion species.

3. Results and discussions

In the 1960s, Shiloh reported the evolution of the UV–VIS spectra of several actinides as a function of chloride concentration up to ~12 M/L in a concentrated lithium chloride aqueous solution [9–11], indicating the significant effect of chloride ion on the actinide metal–chloride complexation as chloride ion concentration increases. Recently, Allen reported the EXAFS studies for U(IV) ions under the similar experimental conditions of Shiloh's work [12]. Their results agreed each other with an indication of U(IV)–Cl bond formation. The chloride based alkali metal molten salts serves as a solvent with ~25 M chloride concentrations. Although electronic absorption spectra of the uranium ions in the chloride melt were reported previously by several research groups [6,8,13–16], the in-depth interpretation of the spectra with respect to their electronic state and bonding is very limited. Recently, some spectral analysis results were

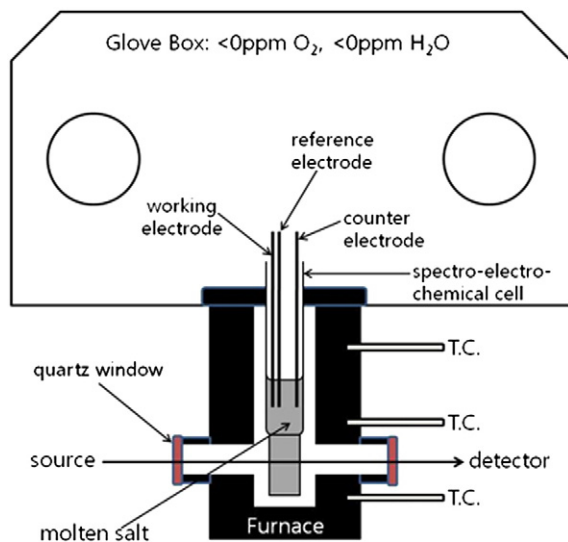


Fig. 1. Schematic diagram of spectro-electrochemical measurement system interfaced with glove for studying electrochemical reaction of uranium species in high temperature molten salt media.

reported for U(III) ion diluted in several crystal lattices. Systematic studies of U(III) ions in the well-defined solid phase have been made to explain the 5*f*–6*d* transitions [17–20], which has shed lights on the interpretation of the observed spectra in our experiments. Our observation of the UV–VIS spectra of U(III) can be interpreted based on those recent studies.

Actinides (5*f* electrons) and lanthanides (4*f* electrons) exhibit different electronic transition patterns from the other elements. In general, two types of electronic transitions are expected in 5*f*-block ions in vacuum UV (VUV) to the near infrared energy range. The first is intra-configurational transitions occurring within 5*f*–5*f* levels. They are forbidden to a first order by the parity conservation rule. They appear in the spectra as very weak and narrow lines. The second is inter-configurational transitions. They are called 5*f*–6*d* transitions and are La Porte-allowed. Consequently, they are much more intense (with molar absorption coefficient > 10³) than 5*f*–5*f* transitions.

3.1. Measurements of the 5*f*–6*d* and 5*f*–5*f* transition lines of the U(III) and U(IV) ions in a LiCl–KCl at 450 °C

Fig. 2-a shows the electronic absorption spectrum of U(III) species obtained from the anodic dissolution reaction U metal in a LiCl–KCl at 450 °C. This method provides the purest form of U(III) ion species. It consists of two main peaks in the wavelength range of 400–600 nm which are mainly attributable to the inter-configurational 5*f*³–5*f*²6*d*¹ (5*f*–6*d*) transitions of U(III) ion with 5*f*³ electronic configuration. The spectrum agrees well with that of recent reports under similar

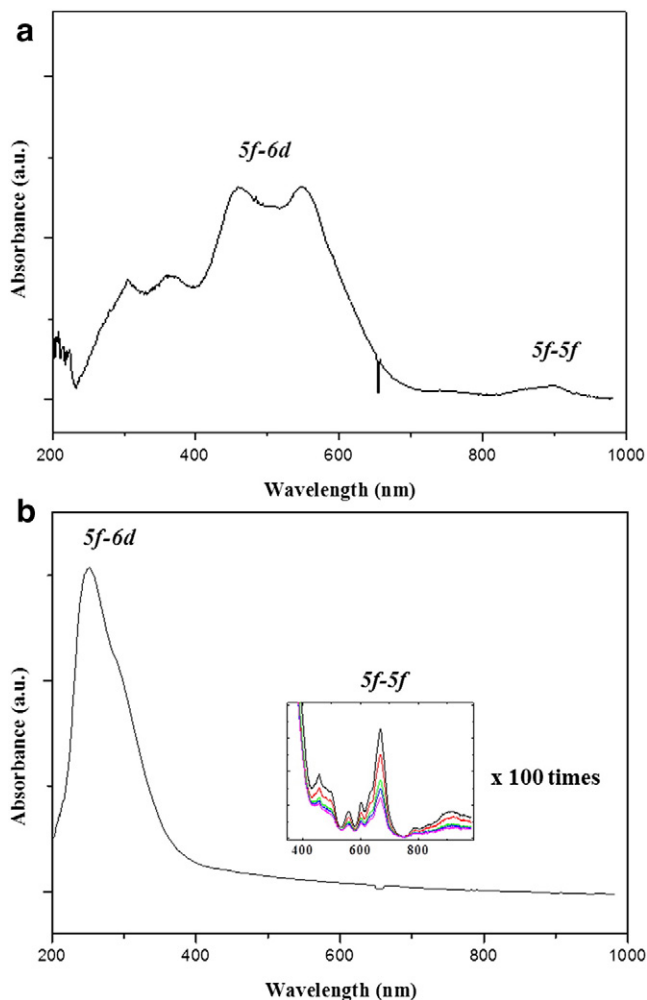


Fig. 2. a. Electronic absorption spectra of the U(III) ion in a LiCl–KCl eutectic melt at 450 °C. b. Electronic absorption spectra of the U(IV) ion in a LiCl–KCl eutectic melt at 450 °C.

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