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Comparison of the spectroscopic characteristics of uranium status when U(III) in LiCl-KCl eutectic melt is leached out with water and ionic liquid

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ABSTRACT

The physicochemical properties of U(III) in molten salt in contact with ionic liquid and water were investigated to obtain better understandable information on the long-term storage of waste salt remaining from pyrochemical processing. UCl_3 in LiCl-KCl eutectic melt was added into appropriate room-temperature ionic liquid and water, and determination of the oxidation state of uranium (U) in LiCl-KCl eutectic melt was achieved using spectroscopic methods. The addition of UCl_3 in LiCl-KCl eutectic melt into the ionic liquid provided the same absorption spectrum as that obtained from the solvation of UCl_3 by LiCl-KCl eutectic melt at 450 °C except for much less absorption peak intensities. The room-temperature ionic liquid of 1-hexyl-3-methyl-imidazolium chloride (HMICl) used in this research did not cause any oxidation or reduction of the U(III), as the other reported ionic liquids did. The U(III) in LiCl-KCl eutectic melt was stable in an HMICl ionic liquid and unstable in water.

1. Introduction

Molten salt is a high-temperature stable (in some cases, stable up to a temperature of 950 °C), corrosive, less-volatile, and viscous medium [1–3]. The most interesting application of this technology in the nuclear energy industry is a molten salt based pyrochemical processing technique, which is regarded as one of the promising options for a future spent nuclear fuel management concept.

As a type of spent nuclear fuel treatment, the pyrochemical process is well known for its non-proliferation of the nuclear fuel cycles (the final product is a mixture of transuranic, and there is no signal of separated pure plutonium obtained in the pyrochemical processing), separation of long-term radioactive nuclides during processing, the recovery of uranium for re-use as a nuclear fuel, and a significant volume-reduction of high level waste [4]. Through an electrorefining step of the pyrochemical processing, uranium ions (existing as 3+ ion) dissolved in LiCl-KCl eutectic melt at 450 °C are recovered as pure uranium metal at a cathode using an electrochemical method, and the remaining U(III) in the LiCl-KCl eutectic melt goes to salt waste after an electrowinning step of the pyrochemical process. After the complete pyrochemical processing, a remaining small amount of salt waste, apart from the salt for recycling, will be stored long term and is composed of some actinide and lanthanide species (mainly existing as 3+ ions) dissolved in molten salt.

In this study, we investigate the behavior of U(III) dissolved in LiCl-KCl eutectic melt, especially when U(III) in LiCl-KCl eutectic melt is leached out with room-temperature ionic liquid, as compared to water, to obtain better understandable information for long-term waste-salt storage. The physicochemical properties of U(III) in LiCl-KCl eutectic melt in contact with ionic liquid or water were investigated spectroscopically based on the absorption and luminescence characteristics.

Actually, U(III) compounds are not stable under common conditions and are difficult to be synthesized under normal processes except when using a radiation technique [5] or when existing as high-temperature melting metal halogen based glasses or crystals [6,7]. Therefore, studies on the possible leaching of U(III) into the environment during long-term storage are pretty much limited. However, it is known that U(III) in molten salt can be stable, and the absorption studies of U(III) in LiCl-KCl eutectic melt was previously reported [8,9]. Nevertheless, to the best of our knowledge, spectroscopic studies of U(III) in molten salt in contact with ionic liquid or water have yet to be reported. An ionic liquid system, which is similar to the environment of a slushy micelle system in ground water migration, was considered as a medium for a convenient bench-scale experiment.

2. Experimental

For the fundamental spectroscopic study described herein, U(III) was converted from uranium metal using convenient chemical syntheses through a well-known method [10]. The U(III) in LiCl-KCl eutectic melt can be prepared, as shown in equation below, from the reaction of uranium metal (0.371 g; 1.56 mmole) with cadmium chloride (0.429 g;

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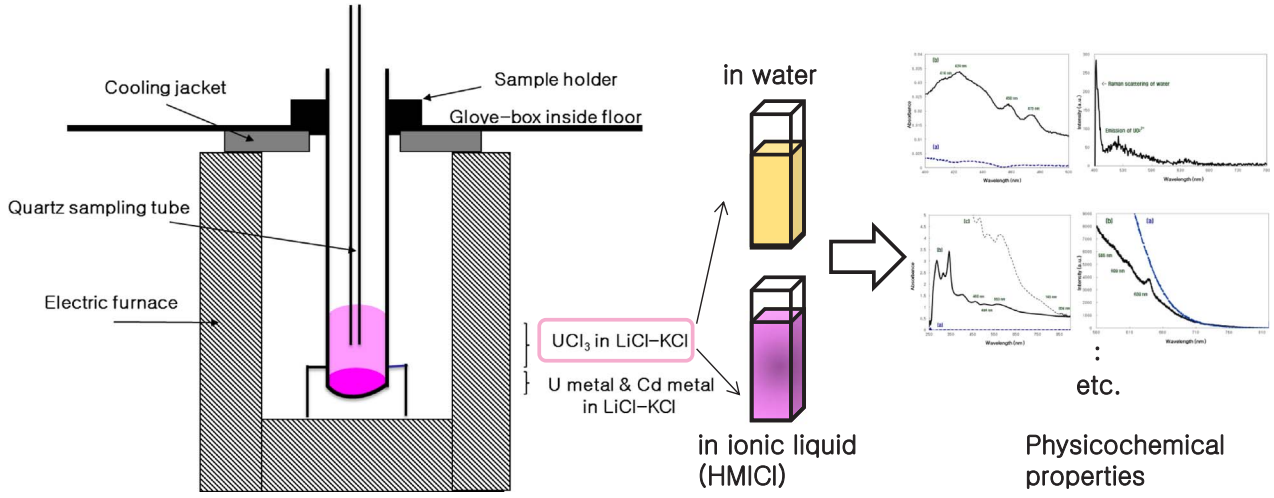

Scheme 1. Schematic diagram of preparation of UCl_3 in LiCl-KCl eutectic melt at 450 °C and experiment of this research [U(III) in molten salt in contact with ionic liquid (similar to the environment of a slushy micelle system in a ground water migration) and water].

3.12 mmole, 99.99% purity, Aldrich) in a LiCl-KCl mixture [30 g, 44 wt % LiCl, from A.R. grade of LiCl (Aldrich) and KCl (Aldrich)] at 450 °C in an Ar-atmosphere glove box [11–13].

$$2U\ (metal) + 3CdCl_2 \rightarrow 2UCl_3 + 3Cd\ (metal) \quad (1)$$

The reaction was performed in a 2-cm diameter quartz tube, and some part of the product was taken using a capillary tube from the center of the reaction tube at 450 °C. The densities of $CdCl_2$ and Cd are 3.37 and 7.32 respectively, and they are not soluble with each other at 450 °C. Therefore, Cd metal will sink to the bottom of the quartz tube after a reaction, whereas $CdCl_2$ in LiCl-KCl eutectic salt reacts with U metal to produce UCl_3 in the middle of the tube. The part taken was cooled down in a glove box at room temperature and then ground to powder for spectroscopic tests. The sample preparation and process of this research are simply drawn in Scheme 1.

One gram of the sample was diluted into 4 mL of water. The sample was very soluble in water but was not well soluble into room-temperature ionic liquid [1-hexyl-3-methyl-imidazolium chloride (HMICl), $C_{10}H_{19}ClN_2$, Chem. Tech. Research Incorp. (C-TRI), > 99.0% assay]. When 1 g of the sample is diluted by 8 g of ionic liquid, the salt can be homogeneously dispersed in the ionic liquid but not dissolved completely. The mixture was used directly after shaking vigorously without filtering or taking a decant for the spectroscopic measurements.

A fluorescence spectrometer (Model FL900CD) was used to obtain the emission and excitation spectra. Absorption spectra were recorded on a Cary 3E UV–Vis Spectrophotometer (Varian, EL 95123037).

3. Results and discussion

LiCl-KCl eutectic melt containing about 1.2 wt% of UCl_3 was prepared by melting U metal, $CdCl_2$, and LiCl-KCl mixture together at 450 °C as mentioned in the experiment section. The absorption spectrum of the UCl_3 in LiCl-KCl eutectic melt mixed in HMICl ionic liquid was obtained at room temperature after a baseline correction with LiCl-KCl eutectic melt mixed in HMICl ionic liquid, not including UCl_3. As shown in Fig. 1, the spectrum of U(III) in LiCl-KCl eutectic melt mixed in HMICl ionic liquid presents absorption within the region of 450–600 nm, which is the same as the shape and position of U(III) in LiCl-KCl eutectic at 450 °C in the sample preparation and that reported in [9]. The two absorption spectra are very comparable with each other because Cl ions are the only possible complexing anionic species in the mixing system. Transitions of $5f^3$-$5f^26d^1$ in U(III) are not forbidden and parity-allowed as free dipole radiation, and thus the characteristic $5f^3$-$5f^26d^1$ band from about 553 nm and others at shorter than this

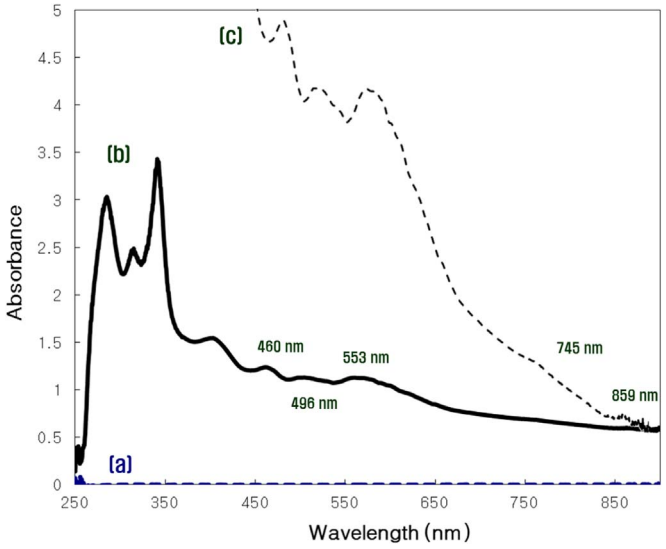

Fig. 1. Absorption spectra of (a) baseline, (b) UCl_3 in LiCl-KCl eutectic melt mixed in HMICl ionic liquid, and (c) enlarged spectrum of (b), after baseline correction with LiCl-KCl eutectic melt mixed in HMICl ionic liquid not including UCl_3.

wavelength were observed as predicted from the reported absorption spectrum of a non-diluted UCl_3 polycrystalline sample [14]. Partial f-f bands are reported to be superimposed on the f-d bands, as mentioned in [15]. In addition, it is unfortunate that the partial overlapping of known U(III) and U(IV) UV absorptions in this area makes it difficult to achieve 100% U(III) stability without oxidation to U(IV) in the room-temperature ionic liquid [16]. The other $5f^3$-$5f^3$ absorption bands for U(III) at a longer wavelength were much weaker than those of mixed $5f^3$-$5f^26d^1$ and $5f^3$-$5f^3$ or beyond of our absorption spectral measurement region [6,9].

However, the overall observed intensities of the absorption bands in Fig. 1 are weaker than those from U(III)-LiCl-KCl eutectic melt at 450 °C prepared from U metal with $CdCl_2$ in a LiCl-KCl mixture, as mentioned in the Experimental section. The high-temperature absorption was measured in the middle of the quartz cell *in situ* and on-line by using a specially designed absorption measurement furnace in a glove box [9,12]. The solubility of U(III) in LiCl-KCl eutectic melt into the HMICl ionic liquid at room temperature is low, and the addition of an HMICl ionic liquid into the UCl_3 in LiCl-KCl eutectic melt has no significant effect on the absorption spectrum of U(III) with respect to the van der Waals or hydrogen interactions through the C-H···Cl between the ionic