Electronic Absorption Spectra of U(IV) in Molten LiCl-SrCl₂ and CsCl-SrCl₂

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Electronic absorption spectra of tetravalent uranium in LiCl and CsCl were measured. Redox potentials of U⁴⁺/U³⁺ and U³⁺/U⁰ couples were estimated by cyclic voltammetry. By adding SrCl₂ into the melts, changes in absorption spectra and cyclic voltammograms were seen. The effect of the coexisted Sr²⁺ on the coordination circumstance of uranium ions was discussed.

Key Words : Molten Salt, Uranium, Absorption Spectrometry, Cyclic Voltammetry

1 Introduction

Pyrometallurgical reprocessing is a candidate for the future spent nuclear fuel reprocessing.¹⁾ Uranium, plutonium, and transuranic elements in a molten alkali chloride are recovered in an electrowinning process. Because of the low solubility of actinide oxides in the melt, the process needs a pretreatment to reduce the oxides to metals. The direct use of the oxides has been demonstrated by employing a Li metal reductant in the molten LiCl, while an electrochemical reduction process with LiCl or CaCl₂ has been found to be more efficient.¹⁾

Knowledge of the behavior of uranium ions in the molten LiCl is essential for these processes. UV/Vis/NIR spectrophotometry is a useful analytical technique for characterizing chemical species and their behavior in molten salts. By using this technique, we have studied the formation of U(IV) oxychloride²⁾ and the redox behavior of U(IV) and U(III) in molten chlorides.³⁾ In this study, the change in the absorption spectrum of U(IV) in the molten LiCl was studied by adding SrCl₂. Strontium is one of the major fission product elements. An alkali molten chloride containing Sr may show a different chemical property when compared to that of the pure one. Hence, the binary system LiCl-SrCl₂ is of interest. For a further comparison, another binary system CsCl-SrCl₂ was also studied.

2 Experimental

Anhydrous uranium tetrachloride was synthesized by reacting UO₂ with carbon tetrachloride under an inert atmosphere. The CCl₄/N₂ mixed gas obtained by bubbling N₂ gas through CCl₄ was introduced to the reaction tube and reacted with UO₂ at 723 K for 20 hours. Then anhydrous UCl₄ particles were obtained by the subsequent heat treatment of the above sample at 693 K for 40 hours in the same atmosphere. The product identified

as UCl₄ by XRD analysis was used in the present study. Anhydrous LiCl, CsCl, SrCl₂, and NdCl₃ (99.99% purity) were products of Anderson Physics Laboratory Engineered Materials.

All the experiments were carried out in a glove box filled with dry argon where humidity and oxygen impurity was continuously kept less than 1 ppm. The details of our experimental apparatus and the procedure for absorbance measurements can be seen elsewhere.^{4,5)} The temperature of the sample during the experiment was controlled to the desired value (973 K) within ± 3 K. Absorbance measurements (UV/Vis/NIR spectrometer, V-570, JASCO) were performed with various compositions of binary systems, LiCl-SrCl₂ and CsCl-SrCl₂, containing 0.01-0.02 mol dm⁻³ (M) UCl₄. Absorption spectra of a lanthanide, Nd, in these molten chlorides were also measured for comparison.

Then, the electrodes were put into the molten chloride sample to measure the cyclic voltammogram. A pyrographite-coated graphite rod (Tokai Carbon Co., Ltd.) of 3 mm diameter was used as both working and counter electrodes. A Ag|Ag⁺ electrode was used as a reference electrode.^{3,6)} The electrochemical measurement system Hz-5000 (Hokuto Denko Co., Ltd.) was used for the cyclic voltammetry.

3 Results and Discussion

Absorption spectra of U(IV) in the LiCl-SrCl₂ mixtures are shown in Fig. 1. A large absorbance at the UV region is due to the Laporte forbidden transition (5f²-5f6d transition). At a wavenumber 8,673 cm⁻¹, a specific transition band (5f²-5f² transition) can be seen. By comparing with the crystallographic data of U(IV) compounds,^{7,8)} this transition was assigned to be the ³F₃-³F₄ ← ³H₄ transition. The molar absorptivity of this transition was determined to be $\epsilon = 19.6 \text{ M}^{-1} \text{ cm}^{-1}$. This value is

Fig. 1 Absorption spectra of U(IV) in LiCl-SrCl₂ mixtures.

Fig. 2 Absorption spectra of U(IV) in CsCl-SrCl₂ mixtures.

consistent with a reported value, $\epsilon = 18.75 \text{ M}^{-1} \text{ cm}^{-1}$ for U(IV) in the LiCl-KCl eutectic at 723 K.⁹⁾ According to a report,⁸⁾ small peaks on the shoulder of the $5f^2-5f6d$ transition would be the $1I_6 \leftarrow 3H_4$ transition. The absorbance of U(IV) at this region increased with the SrCl₂ content. This increase may be correlated with the coordination circumstance change of UCl₆²⁻, which is the major species of U(IV) in chloride melts.

Absorption spectra of U(IV) in CsCl-SrCl₂ mixtures are shown in Fig. 2. A similar increase at the higher wavenumber region can be seen. A prominent point of this figure is about the peaks marked as X, Y, and Z. The absorption peak Y can be seen clearly in both Figs. 1 and 2. The peaks X and Z are clear in Fig. 2, while the intensities of these are very small in Fig. 1. This is because the coordination circumstance of U(IV) in LiCl is different from that in CsCl. The symmetry of LnCl₆³⁻ (Ln: lanthanides) in CsCl is considered to possess octahedral symmetry (O_h), while by adding cations with strong polarizing power like Li⁺, the octahedral symmetry is distorted.^{10,11)} This may be adapted to our UCl₆²⁻ case. Actually, it has been reported that the peaks X and Z can be found for UCl₆²⁻ with octahedral symmetry.^{9,12)}

In order to discuss the coordination circumstance change, we evaluated the oscillator strength for the results shown in Figs. 1 and 2. Absorption bands X and Y were analyzed by dividing the raw spectrum into simple Gaussian functions. Background of each spectrum was treated as a shoulder of Gaussian function whose peak was set $> 25,000 \text{ cm}^{-1}$. The oscillator strength can

Fig. 3 Ratio of oscillator strengths of U(IV) absorption peaks X and Y.

Table 1 Redox potentials of U⁴⁺/U³⁺ and U³⁺/U⁰ couples.

	$E(\text{U}^{4+}/\text{U}^{3+})^a$ /mV	$E(\text{U}^{3+}/\text{U}^0)^a$ /mV
LiCl	-131	-1477
LiCl + SrCl ₂ ^b	-131	-1478
CsCl	-97.5	-1137
CsCl + SrCl ₂ ^c	-107	-1077

^a Errors are estimated to be $\pm 5 \text{ mV}$.

^b [Li] : [Sr] = 88.9 : 11.1

^c [Cs] : [Sr] = 78.6 : 21.4

be defined as Eq. 1,

$$f = 4.319 \times 10^{-9} \frac{9n}{(n^2 + 2)^2} \int \epsilon(v) dv \quad (1)$$

where $\epsilon(v)$ is the molar absorptivity at energy $v(\text{cm}^{-1})$ and n is the refractive index of the solvent medium. The n value of eutectic was estimated by a linear interpolation between the n values of LiCl¹³⁾ and SrCl₂.¹⁴⁾ From the determined f values, we evaluated the ratio of f 's for peaks X and Y (Fig. 3). By adding SrCl₂ into LiCl, f_X/f_Y increased. This suggests that the octahedral symmetry of UCl₆²⁻ improved. An opposite trend can be seen in the CsCl-SrCl₂ mixtures. Adding SrCl₂ into CsCl would result in a distortion of the symmetry.

Cyclic voltammograms were obtained for U(IV) in LiCl, CsCl, a LiCl-SrCl₂ mixture, and a CsCl-SrCl₂ mixture. The redox potentials of U⁴⁺/U³⁺ and U³⁺/U⁰ couples were evaluated (Table 1). For LiCl-SrCl₂ system, neither $E(\text{U}^{4+}/\text{U}^{3+})$ nor $E(\text{U}^{3+}/\text{U}^0)$ changed by adding Sr²⁺. The coordination circumstance change for uranium complexes in the LiCl-SrCl₂ system was less sensitive by cyclic voltammetry. For CsCl-SrCl₂ system, we found shifts in $E(\text{U}^{4+}/\text{U}^{3+})$ and $E(\text{U}^{3+}/\text{U}^0)$.

The change in the octahedral symmetry of UCl₆³⁻, which is the major species of U(III) in chloride melts is of interest. As an alternative, the change in absorption spectra of Nd(III) in LiCl and CsCl was checked by adding SrCl₂. The electric dipole transition between f orbitals that show abnormal variations in intensity are classified as hypersensitive transitions.¹⁵⁾ These varia-

Fig. 4 Oscillator strengths of a Nd(III) hypersensitive transition.

tions are attributed to the action of an inhomogeneous electromagnetic field from the surrounding medium. The hypersensitive transition of Nd(III), ${}^4G_{5/2}, {}^2G_{7/2} \leftarrow {}^4I_{9/2}$, can be seen in the visible region (~ 590 nm). In our previous study,¹¹⁾ we characterized the coordination circumstance of NdCl_6^{3-} in various chloride melts by focusing on the hypersensitive transition. The same treatment was performed in this study. The f value of the hypersensitive transition of Nd(III) is shown in Fig. 4, in which the increase of f means the distortion of the octahedral symmetry of NdCl_6^{3-} . The f value decreased with the increase of Sr content. The decrease was clearer for the CsCl-SrCl₂ system. This suggests that the octahedral symmetry of NdCl_6^{3-} is improved by adding Sr^{2+} into the CsCl. This may be applicable to the U(III) case.

4 Conclusion

This work demonstrates the effect of coexisted Sr^{2+} in the alkali chloride melts on the coordination circumstance of uranium ions. The effect was smaller for LiCl compared to CsCl. The absorption spectra suggested that, by adding SrCl₂ into CsCl, the octahedral symmetry

of UCl_6^{3-} is improved but that of UCl_6^{2-} is distorted.

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