

Study of the Eu^{2+} and Eu^{3+} coexist in LiCl-KCl Eutectic Melt by Spectrophotometry and Electrochemistry Method

Tack-Jin Kim, Akihiro Uehara*, Toshiyuki Fujii*, Hajimu Yamana*, Do-Hee Ahn, Han-Soo Lee

Korea Atomic Energy Research Institute 150 Deokjin-Dong, Yuseong, Daejeon 305-353, Korea,

*Research Reactor Institute, Kyoto University, Asashiro Nishi, Kumatori, Sennan, Osaka 590-0494, Japan

ktj@kaeri.re.kr

1. Introduction

Molten salt based pyrochemical process receives attention as a possible separation technique for future reprocessing of spent nuclear fuel [1-2]. In order to ensure the pyrochemical process, it is necessary to understand the chemical behavior of lanthanides in the molten salt. Though most of lanthanides in molten salts take trivalent states, Eu, Sm, and Yb are possible to take divalent states under reducing conditions, and Eu(II) is the most stable among them. The redox potential of the $\text{Eu}^{2+}|\text{Eu}^{3+}$ couple has been reported for various chloride melts [3-4]. Those reports suggest the existence of Eu(II) in the chloride systems. In electrochemical analysis with molten salts, yttria stabilized zirconia membrane electrodes (YSZME) are largely used as an activity indicator of oxide anion, O^{2-} [5]. In the present study, the effect of the coexisted Eu^{2+} on the potentiometric titration of Eu^{3+} was examined.

2. Experimental and Results

2.1 Sample Preparation

Anhydrous LiCl-KCl eutectic and EuCl_3 (99.99% purity) were purchased from Aldrich-APL LLC. Anhydrous EuCl_2 (99.99% purity) and Na_2CO_3 (99.999% purity) were products of Aldrich. The reference electrode and counter electrode were consisted of a closed-end Pyrex glass tube. As a working electrode, a pyro-graphite rod and Pt wire were used. Alumina crucible was used at the titration experiment. The pO^{2-} indicator electrode

was a tube of yttria-stabilized zirconia filled with LiCl-KCl containing Na_2CO_3 and AgCl. An Ar gas was ventilated through the melt during the titration experiments. The electrochemical study was performed with a measurement system, Hz-3000. Electronic absorption spectra were measured by using a spectrophotometer, JASCO V-570. The concentration of Eu was determined by ICP-AES. The chemical composition of precipitants was analyzed by X-ray diffraction analysis. All the sample preparations, absorption spectrometry, and electrochemistry, were carried out in a glove box under a purified argon atmosphere.

2.2 Determination of the ratio of concentrations $[\text{Eu}^{2+}]/[\text{Eu}^{3+}]$ in the LiCl-KCl eutectic

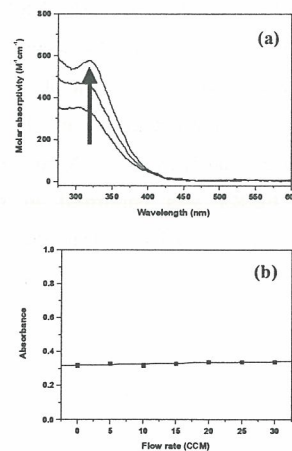


Fig. 1. (a) Change of absorption spectrum of europium ions with argon bubbling in the LiCl-KCl eutectic melt at 773K. (b) Plot of absorbance vs. argon flow rate in the LiCl-KCl eutectic melt at 773K.

The spectrum of Eu^{3+} was measured after oxidation Eu^{2+} completely to Eu^{3+} by controlled potential electrolysis. As the time passed, the spectrum of Eu^{3+} was increased. At last the intensity of absorption spectrum was same as initial absorption spectrum of EuCl_3 . It means that the same ratio of Eu^{2+} always coexisted with Eu^{3+} when EuCl_3 was dissolved in the LiCl-KCl eutectic melt at 773K. In order to confirm the relation of argon gas and ratio of $\text{Eu}^{2+}/\text{Eu}^{3+}$, argon gas was bubbled into the solution of Eu^{3+} . While argon gas passes through the melt, as shown in Figure 3-(a), there is the rapid increase of absorption spectrum intensity. When the intensity of absorption spectrum became constant, we did change argon gas flow rate to confirm the relation of argon gas flow rate and absorption spectrum intensity. As shown in Figure 3-(b), the intensity of absorption spectrum did not change. It means that the ratio of Eu^{2+} is not controlled by argon gas flow rate.

2.3 Potentiometric titration of Eu^{3+} with O^{2-} in LiCl-KCl eutectic melts at 773K

In order to determine $[\text{Eu}^{3+}]$ dissolved in the melt (the ratio of $[\text{Eu}^{2+}]/[\text{Eu}^{3+}]$), potentiometric titration of Eu in the LiCl-KCl eutectic at 773K was performed by adding Na_2CO_3 into the melt. The YSZ electrode was used after the calibration. As shown in Figure 2, it has only one equivalent point at $x < 1$ ($x = [\text{O}^{2-}]_{\text{added}}/[\text{Eu}^{3+}]_{\text{total}}$). Precipitations at the end of experiment were analyzed by X-ray diffraction spectrometry. EuOCl was confirmed in the XRD pattern. This result indicates that the Eu^{3+} was precipitated with O^{2-} according to the following reaction ;



The formation of EuOCl in the LiCl-KCl eutectic at 773K was observed at the theoretical equivalent point $x = 1$ [5]. Our result showed smaller equivalent point than the theoretical value. This difference could be explained based on the result for

ratio of $[\text{Eu}^{2+}]/[\text{Eu}^{3+}]$. Some percentage of Eu^{2+} always exists when EuCl_3 was dissolved in the LiCl-KCl eutectic at 773K under argon atmosphere.

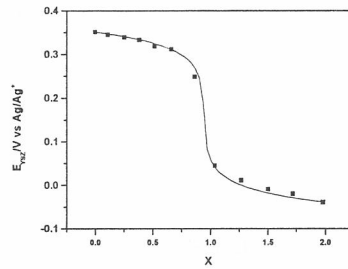


Fig. 2. Experimental potentiometric titration of a EuCl_3 in the LiCl-KCl eutectic with O^{2-} ions at 773K.

3. Conclusion

The spectrophotometry and electrochemistry method could be used to measure the ratio of $[\text{Eu}^{2+}]/[\text{Eu}^{3+}]$ efficiently. The existence of the europium divalent in the LiCl-KCl- EuCl_3 solution has been demonstrated by potentiometric titration method with YSZ electrode and Pt wire as a working electrode.

4. References

[1] H.P. Nawada, K. Fukuda, J. Phys. Chem. Solids 66 (2005) 647
 [2] K. Uozomi, M. Iizuka, T. Kato, T. Inoue, O. Shirai, T. Iwai, Y. Arai, J. Nucl. Mater. 325 (2004) 34
 [3] A. Uehara, O. Shirai, T. Nagai, T. Fujii, H. Yamana, Z. Naturforsch. 62a (2007) 191-196.
 [4] S.A. Kuznetsov, L. Rycerz, M. Gaune-Escard, J. Nuclear Materials 344 (2005) 152-157
 [5] M.R. Bermejo, F. de la Rosa, Y. Castrillejo, E. Barrada, J. Electroanal. Chem. 603(2007) 81-95