

EPR Investigation on a Quantitative Analysis of Eu(II) and Eu(III) in LiCl/KCl Eutectic Molten Salt

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EPR spectroscopic technique was applied for a quantitative analysis of Eu(II) for a speciation of europium in a LiCl-KCl eutectic melt. By adopting the first absorption line of each isotopes (^{151}Eu and ^{153}Eu), a calibration plot was obtained. The calibration of the EPR intensity shows a good linearity according to the amount of Eu(II). The EPR intensity was identified to increase proportionally with a decrease of the attenuation parameter for EPR microwave power. The fluorescence technique was used qualitatively to find whether either of Eu(II) or Eu(III) ions exists in a molten salt sample. The ICP-AES technique was also adopted to determine the total concentration of europium in the sample, since EPR is only sensitive for detecting the Eu(II) ion. The extent of the reduction of Eu(III) in the LiCl-KCl eutectic melt at 723 K was determined by using this technique.

Key Words : EPR, Eu speciation, Eutectic molten salt, Quantitative analysis

Introduction

Application of a pyrochemical process is an active option for reprocessing spent nuclear fuels. In this pyrochemical process, molten salt based electrochemical processes have been proposed as a promising method in which actinides are separated and recycled from lanthanides in molten chlorides.^{1,2} Although the oxides of actinides and lanthanides were sparingly soluble in molten salts, the solubility of the europium oxides was identified to be several orders of a magnitude higher than that of the other lanthanide oxides in LiCl-KCl eutectic melts at 723 K, according to our previous work.³ In that paper, some portion of the Eu(III) ions were found to be reduced to Eu(II) in the LiCl-KCl eutectic melts at 723 K. However, detailed information such as the extent of an europium reduction or its mechanism are not known yet due to the lack of investigation. The spectroscopic techniques such as absorption and fluorescence were not easily obtained for accurate measurement of europium species in a molten salt. Establishing the redox behavior of lanthanide ions in molten chlorides will provide important information to enhance the separation efficiency in electro-refining and electrowinning processes.

In this work, electron paramagnetic resonance (EPR) technique was applied to the quantitative analysis of Eu(II) and Eu(III) in LiCl-KCl eutectic melts. The ICP-AES technique was also adopted to analyze the total concentration of europium, since EPR is only sensitive for a detection of the Eu(II) ion.

Experimental Section

Sample preparation. The LiCl-KCl eutectic (41.5 mole% KCl) mixture was prepared from lithium chloride (99.9+%, Aldrich) and potassium chloride (99+%, Aldrich). EuCl_2 and EuCl_3 were obtained from Alfa Aesar Co. Ltd. (99.99% purity). All the sample preparations for the experiments with

the dried salts were carried out inside a glovebox under a purified Ar atmosphere. The oxygen and H_2O level in the glovebox was maintained to be less than 2 ppm. The EuCl_2 or EuCl_3 dissolved in the molten salt was equilibrated at 723 K for 10 hours with a frequent stirring. The molten salt sample was solidified at room temperature and then transferred into a quartz tube for an EPR measurement. For the solid fluorescence measurement, the molten salt sample was ground into a fine powder and transferred into the triangular spectroscopic cell and capped with a plastic film to prevent an air contact. After the EPR measurement, the molten salt sample was diluted with 5 mL of water for an analysis of the total amount of europium by using the ICP-AES.

Instrumental method of the EPR spectrometry. The EPR spectra of the sample in the LiCl-KCl matrix were recorded at room temperature on a Bruker EMX spectrometer at an X-band frequency with a 100 kHz field modulation. A modulation amplitude of 5 G, microwave power attenuation of 5 to 15 dB and a sweep width of 300 G were used. Typical value of the receiver gain was 6.32×10^3 . The modulation amplitude and microwave power settings were chosen such that neither an over-modulation nor a saturation occurred. All the instrumental parameters except for the receiver gain were kept as the same for all the experimental series. The samples were taken from the molten LiCl-KCl eutectic melt and cooled to room temperature (hereafter referred as molten salt sample otherwise being stated). EPR measurements were carried out with about 50 mg of each sample inserted into a quartz tube and sealed to prevent it from contacting with air. The magnetic field was scanned four times in the range of 3300 to 3600 G, and swept at a rate of 15 G/sec.

Results and Discussion

Solid fluorescence spectroscopy study of the Eu molten salt. The europium ions (Eu(II) and Eu(III)) showed a

luminescence that strongly depends on its valence state. The fluorescence spectrum of Eu(II) exhibited a strong band centered at 430 nm, while Eu(III) exhibited several sharp lines ranging from 520 to 720 nm, which are associated with the transitions from the excited 5D_1 and 5D_0 levels to the 7F_J level.⁴⁻⁶ Therefore, a fluorescence spectroscopy can be used to simultaneously identify the presence of Eu(II) and Eu(III) in a solid state. The fluorescence spectra of the LiCl-KCl eutectic molten salt samples were measured with various concentration of Eu(III). Since the fluorescence intensity did not provide a good linearity against the Eu(III) concentration, it does not seem to be an adequate method for a quantitative analysis of Eu(II) and Eu(III) in a LiCl-KCl eutectic molten salt. Even though this fluorescence technique is not good for the quantitative analysis, it can be a very useful tool to establish whether either of Eu(II) or Eu(III) ions exist in a molten salt sample

Optimization of the EPR for a quantitative analysis.

The Eu^{2+} is EPR active since it shows a paramagnetic property with an electron configuration of $4f^7$ and $^8S_{7/2}$ ground levels.⁷⁻⁹ A typical EPR spectrum of Eu^{2+} dissolved in a LiCl-KCl matrix at room temperature exhibits a well-resolved hyperfine structure with 12 absorption lines centered at a g factor ~ 1.989 as shown in Figure 1. These 12 absorption lines contribute to the two magnetically non-equivalent pairs of europium ions, the ^{151}Eu (47.82% abundance) and ^{153}Eu (52.18% abundance) isotopes, respectively. Since the ^{151}Eu and ^{153}Eu nucleus have a different magnetic property, it causes a different hyperfine splitting. From an analysis of the observed EPR spectrum, the hyperfine splitting constant of ^{151}Eu was evaluated to be ~ 33.4 gauss and ^{153}Eu to be ~ 14.8 gauss. Bruker WIN-EPR and Simfonia programs were used for spectrum simulation and analyzing the EPR results.³ Each of eight absorption lines in the central area were slightly overlapped or close to each other when compared to the first or the last absorption line. Therefore, the first absorption line was chosen for a quantitative analysis throughout this experimental work.

One of the major factors affecting a quantitative analysis is

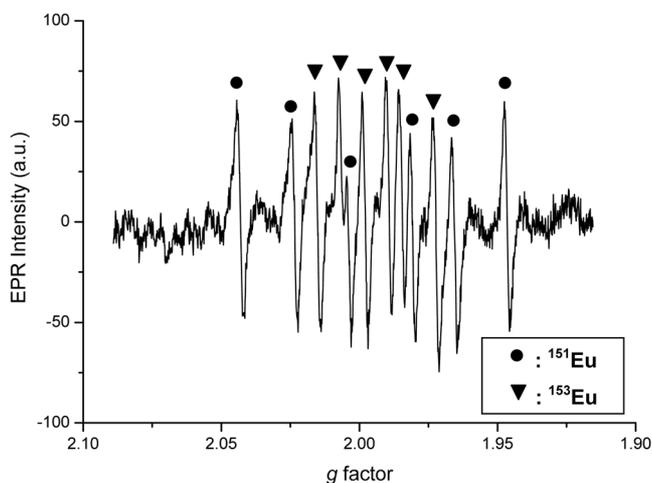


Figure 1. Typical EPR spectrum of Eu(II) in the LiCl-KCl eutectic melts at room temperature.

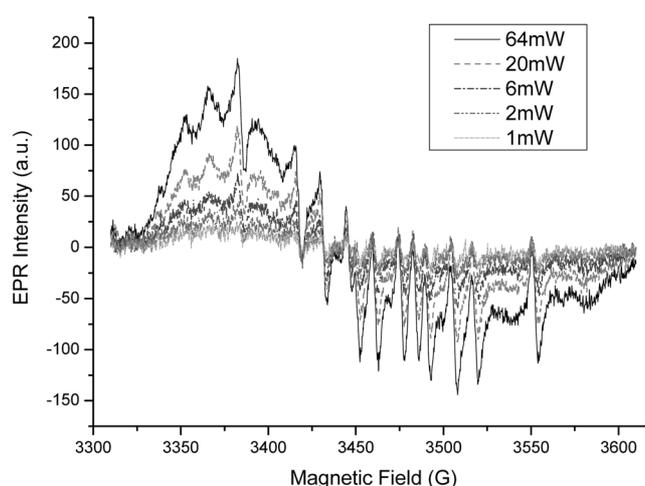


Figure 2. EPR spectrum of the Eu(II) molten salt sample with various microwave power.

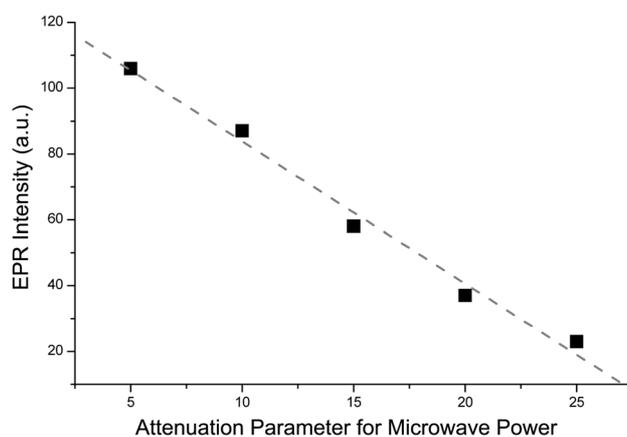


Figure 3. Plot of the EPR intensity of the first absorption line against the attenuation parameter for microwave power.

a power saturation of the absorption lines. Figure 2 shows the EPR spectrum of a Eu(II) molten salt sample obtained by changing the microwave power from 1 to 64 mW. Plotting the EPR intensity of the first absorption line versus the attenuation parameter which is corresponding to the microwave power value provided a good linearity as shown in Figure 3. The attenuation value of 15 was used in this work for the weight range of Eu(II) between 1 and 25 μg .

Analysis of the reduction of Eu(III) to Eu(II) in a LiCl-KCl molten salt system. The fluorescence spectrum of the europium molten salts showed a distinct reduction from Eu(III) to Eu(II) in the LiCl-KCl eutectic molten salts at 723 K, as reported in the previous work.³ The Eu(III) ion, which was added as an initial material, was spontaneously reduced to Eu(II) to some extent.^{10,11} It is well-known that Eu(III) is chemically reduced in a molten salt media according to the following reaction:^{12,13}



However, quantitative information on this reduction has not been reported yet. The EPR technique established in this work was applied to evaluate the thermodynamics for reduction of Eu(III) in a LiCl-KCl eutectic melt at 723 K.

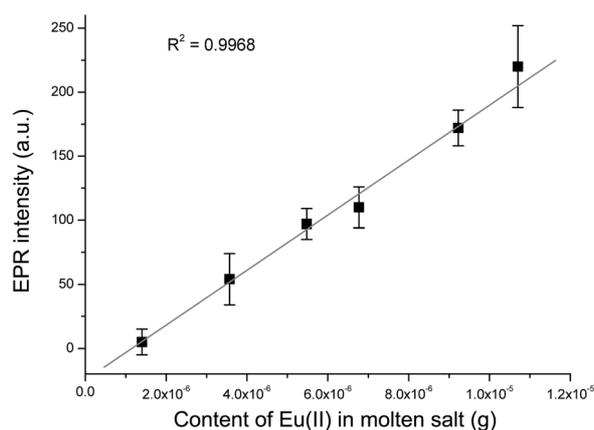


Figure 4. Standard calibration curve for the Eu(II) based on EPR study.

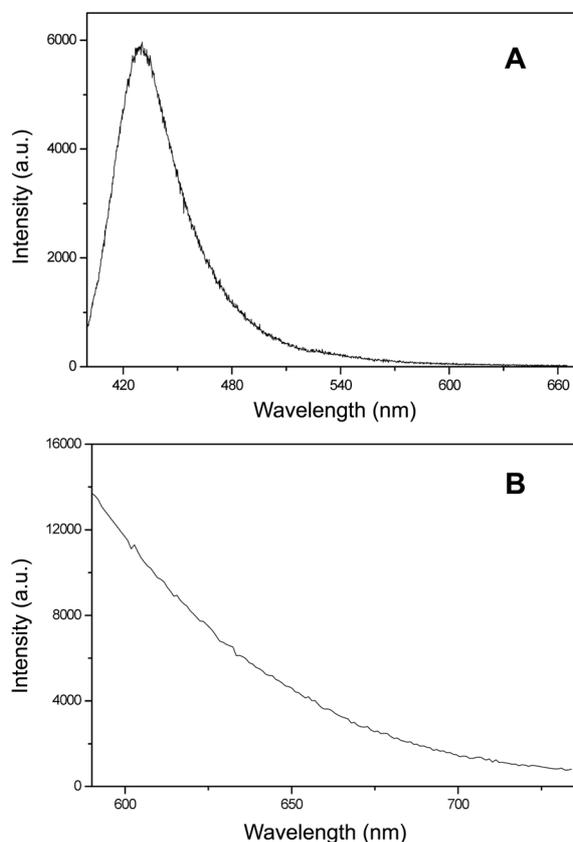


Figure 5. Fluorescence spectra of the europium molten salt sample where the Eu(II) was added into the LiCl-KCl eutectic molten salt at 723 K as an initial material. (A: Eu(II), B: Eu(III))

Figure 4 shows a good calibration curve of the EPR intensity vs. Eu(II) with a correlation coefficient ($R^2 = 0.9968$), in which the samples for a calibration were made by adding a known amount of Eu(II) chloride into a LiCl-KCl eutectic molten salt at 723 K.

On the contrary that the Eu(III) ion added as a initial material was spontaneously reduced to Eu(II) to some extent, an oxidation of Eu(II) was not observed when Eu(II) was added into a LiCl-KCl eutectic molten salt at 723 K as an initial material. The fluorescence spectrum of europium

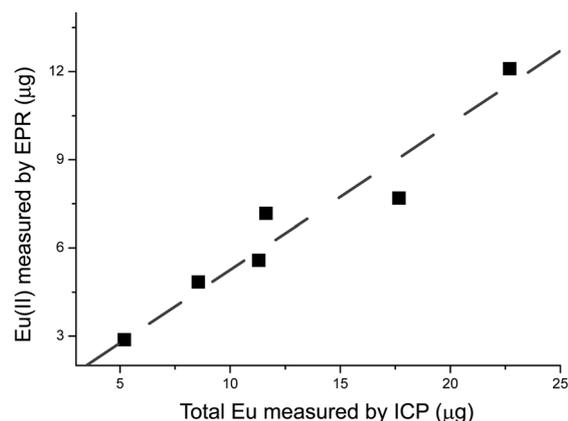


Figure 6. Plot of the amount of Eu(II) in the LiCl-KCl eutectic melts versus the total amount of europium measured by ICP.

molten salt sample was shown in Figure 5. The strong band of Eu(II) was shown centered at 430 nm, but the fluorescence peaks of Eu(III) ($\lambda_{\max} = 600-700$ nm) were not observed. This strongly suggests that an oxidation reaction of Eu(II) did not occur and further implies that the Eu(II) species are quite stable in a LiCl-KCl eutectic media to be used as an calibration standard unlike most of the divalent species of the other lanthanide elements.

The evaluation results of the redox behavior of Eu(III) in a LiCl-KCl eutectic melt is shown in Figure 6. It was observed that approximately 50 percent of the Eu(III) was reduced to Eu(II) in the eutectic melt melt at 723 K. As a conclusion, it can be said that the EPR spectroscopic method can be used to measure the content of Eu(II) in solid matrices as a fast and non-destructive analytical method.

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