Communication

Separation Factor of Americium from Cerium in Molten Chloride - Liquid Gallium Reductive Extraction System

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The distribution coefficients of Am and Ce were measured in the eutectic LiCl-KCl/liquid Ga system at 773K. By using ZrCl₄ as the oxide ion scavenger in order to avoid the formation of such oxychlorides as MOₓ₋ₓ₋₂ₓ, the effect of oxide ion concentration was well controlled on the distribution coefficients of Am and Ce. The separation factor between Am and Ce was then obtained to be about 100. By comparing the present value with the other experimental and the predicted ones, it was confirmed that the Ga system was more selective than the Bi and Cd system.

Key Words : Reductive Extraction, Actinides, Lanthanides, Separation Factor

1 Introduction

Reductive extraction, which uses molten salt and liquid metal as solvents, is expected to be useful for the separation and recovery of minor actinides (MAs), as seen in a proposed pyrometallurgical partitioning method. In this method, a reductive extraction process is combined with an electrochemical process, and used for the separation and recovery of MAs. Because of the high radiation resistance of the solvents, it is expected to reduce the quantity of the radioactive secondary waste and to downscale the size of requisite processing equipment. Extensive efforts are thus being devoted to develop such a process with higher separation and recovery of MAs.

Recently, Conocar et al. reported that the separation factors of Pu and Am from Ce and Sm were very high in the system of LiF-AlF₃/Al-Cu. In addition, by measuring the electromotive force of Pu and Ce, Laplace et al. reported that the separation factors of these elements depended on the liquid metals and that solvent metals were ordered from the least selective to the most selective one as Al > Ga > Bi > Zn > Cd. It is thus interesting to compare the separation factors in different reductive extraction systems.

In the present study, the separation factors of Am from Ce were measured in the LiCl-KCl/Ga system at 773 K, which were expected to be higher as above. By considering possible formation of such soluble compounds as AmO⁺ in LiCl-KCl, which was reported by Lambertin et al., the effect of oxide ions on the separation factors of Am from Ce was discussed.

2 Experimental

Table 1 shows the experimental conditions for the measurement of the distribution coefficients of Am and Ce. Eutectic LiCl-KCl was obtained from the APL Engineered Materials Inc., Ga and Ce metals from Nilaco Corporation, Ce (III) standard solution from Wako Pure Chemical Industry, Ltd., GaCl₃ with a purity of 99.9% from Nacalai Tesque Co and radioactive tracers of Am-241 and Ce-139 from the Isotope Products Laboratories (IPL). These radioactive tracers in a nitric acid medium were transformed to their fluorides with known amounts of Ce by using a hydrofluoric acid solution. The reductant Li (Nacalai Tesque Co.) was prepared in the form of a Li-Ga alloy (3 wt% Li) for ease of addition into the Ga phase. LiCl-KCl-ZrCl₃ mixtures (10.95 wt% Zr) were prepared by heating a sealed quartz tube containing eutectic LiCl-KCl and ZrCl₃ (a purity of 99.9%, obtained from Anderson Physics Laboratory) in order to avoid vaporization of ZrCl₃ subliming above 573 K. Other reagents used were of reagent grade, obtained from Nacalai Tesque Co.

In a typical experiment, known amounts of LiCl-KCl

Table 1 Experimental conditions.

<table>
<thead>
<tr>
<th>Run No.</th>
<th>Temp. (K)</th>
<th>Solvent weight (g)</th>
<th>Solute weight (mg)</th>
<th>Tracer (kBq)</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>LiCl-KCl</td>
<td>Ga</td>
<td>ZrCl₃</td>
<td>Ce</td>
</tr>
<tr>
<td>1</td>
<td>773</td>
<td>25</td>
<td>35</td>
<td>-</td>
</tr>
<tr>
<td>2</td>
<td>773</td>
<td>25</td>
<td>35</td>
<td>60</td>
</tr>
<tr>
<td>3</td>
<td>773</td>
<td>25</td>
<td>35</td>
<td>66</td>
</tr>
</tbody>
</table>
and Ga were loaded in an alumina crucible (SSA-S, \( \phi = 2.4 \) cm) together with small amounts of solutes, as shown in Table 1. The system was then heated to 773 K (\( \pm 5 \) K) and the equilibrium distributions were controlled by adding small amounts of Li-Ga alloy and/or GaCl\(_3\). After attainment of equilibrium, samples were taken from each phase by using a syringe and quartz tube, and were then subjected to gamma-ray spectroscopy. In some cases, the lithium concentration in the gallium phase was also measured by atomic absorption spectrometry. All experiments with high purity reagents were performed in a glove box under argon atmosphere containing <0.5 ppm of O\(_2\) and <0.2 ppm of H\(_2\)O.

### 3 Results and Discussion

#### 3.1 Mechanism of equilibrium distributions

When a metal halide MCl\(_n\) (M: actinide and lanthanide, \( n \): ionic valence) is reduced by a reducing agent Li to its metal state M, the equilibrium distribution of M is expressed as

\[
\text{MCl}_n + n\text{Li} \leftrightarrow n\text{LiCl} + \text{M},
\]

and its equilibrium constant \( K_{\text{M:Li}} \) is given by

\[
K_{\text{M:Li}} = \frac{a(\text{LiCl})^n a(\text{M})}{a(\text{MCl}_n) a(\text{Li})^n} = \frac{\gamma(\text{LiCl})^n \gamma(\text{M})}{\gamma(\text{MCl}_n) \gamma(\text{Li})^n X(\text{LiCl}) X(\text{M})}. \tag{2}
\]

where \( a \) represents the activity, \( X \) the concentration (molar fraction), and \( \gamma \) the activity coefficient of each component denoted in the brackets. Then, we obtain the following relation

\[
\log D_M = n \log D_{\text{Li}} + \log K_{\text{M:Li}} \tag{3}
\]

where \( D_M \) and \( D_{\text{Li}} \) are the distribution coefficients defined by \( D_{\text{Li}} = X(\text{Li})/X(\text{LiCl}) \) and \( D_M = X(\text{M})/X(\text{MCl}_n) \), respectively, and \( K_{\text{M:Li}} \) the apparent equilibrium constant of reaction (1). In the presence of Ce instead of Li, reaction (1) is replaced by

\[
\text{MCl}_n + (n/3)\text{Ce} \leftrightarrow (n/3)\text{CeCl}_3 + \text{M}, \tag{4}
\]

and the following relation is obtained.

\[
\log D_M = (n/3) \log D_{\text{Ce}} + \log K_{\text{M:Ce}}, \tag{5}
\]

where \( K_{\text{M:Ce}} \) is the apparent equilibrium constant of reaction (4). The separation factor between the two solute elements M and Ce is then given by \( S_{\text{M:Ce}} = D_M/D_{\text{Ce}} \).

By taking into account the effect of oxide ions as impurities and the formation of oxychlorides as indicated in the literature\(^8\), the following reaction should be considered in addition to Eq.(4).

\[
\text{MCl}_n + O^{2-} \leftrightarrow \text{MO}^{(n-2)+} \tag{6}
\]

Then, the next relation is obtained instead of Eq. (5),

\[
\log D_M = (n/3) \log D_{\text{Ce}} + \log K_{\text{M:Ce}} + \log K (\text{MO}^{(n-2)+}) - \log (K(\text{MO}^{(n-2)+}) + X(\text{O}^{2-})), \tag{7}
\]

where \( K(\text{MO}^{(n-2)+}) \) is the dissociation constant of \( \text{MO}^{(n-2)+} \).

#### 3.2 Distribution coefficients of Am and Ce

Table 2 summarizes the distribution coefficients obtained in the present study, and in Fig. 1, the log \( D_M \) values for Am are plotted as a function of the log \( D_{\text{Ce}} \) values. Some scatters in the values are observed, partially due to the low counting and to the incompletely corrected self-shielding of the 59 keV radiations for Am.

In the first run of this experiment, the separation factor of Am and Ce was obtained to be about 60. This value seems not so high compared with those reported in the other systems such as the LiCl-KCl/Bi at 773 K.\(^1\) For one of the reasons, it may be considered that a small amount of water is introduced to the system with incompletely dried solutes and that such oxychlorides as \( \text{MO}^{(n-2)+} \) are formed to affect the distribution coefficients. In fact, it was observed that the mass balance of Am and Ce was low (about 30\%) in the run No.1, possibly due to the formation and precipitation of their oxychlorides and/or oxides, as observed for uranium in the literature\(^1\). By

![Fig. 1](image-url) Distribution coefficients of Am as a function of that of Ce in the LiCl-KCl/Ga system at 773 K. Dashed and solid lines represent the least squares fitting results of the data of Run No. 1 and 2 to Eqs. (5) and (7), respectively.
Table 3  Relationships for distribution coefficients.

<table>
<thead>
<tr>
<th>M</th>
<th>log $D_M = (n/3) \log D_{Cl} + \log K_{M/Cl}$</th>
<th>log $D_M = (n/3) \log D_{Cl,0}$</th>
<th>log $D_M = n \log D_{Cl}$</th>
</tr>
</thead>
<tbody>
<tr>
<td>Ce</td>
<td>log (KMO$^{+3}$) - log (KMO$^{+3}$ + X$(O^2)$)</td>
<td>3 - 1.80 ± 0.05$^e$</td>
<td>3 - 2.00 ± 0.02$^a$</td>
</tr>
<tr>
<td>Am</td>
<td>3</td>
<td>3</td>
<td>17.42 ± 0.56$^e$</td>
</tr>
</tbody>
</table>

$^e$ Run No.1.  $^a$ Run No.2.  $^c$ Run No.3.  $^d$ Calculated from log $K_{Ce/Li}$ (Run No.3) and log $K_{M/Cl}$ (Run No.2).

correlated with the ionic radii of metal ions possibly due to complex formation. In the liquid metal phase, on the other hand, the excess enthalpies were explained with the Miedema’s atomistic model$^{30}$ and the excess entropies were with the vibrational entropy$^{30}$ due to alloy formation.

Using these correlations and models, some missing values of the excess thermodynamic quantities were evaluated, and the separation factors of MA’s from lanthanides were calculated in different reductive extraction system of Al, Bi, Cd, and Ga. As shown in Fig. 2, the present result is found to be consistent with the predicted separation factors$^{11}$ together with the experimentally obtained values.$^{2,7}$

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References


Fig. 2 Comparison of the separation factors of Am from Ce obtained in the systems using the salt phase of (a) LiCl-KCl at 773 K (calculated)$^{26}$ (b) LiCl-KCl at 773 K (experimental)$^{23}$ (c) NaCl-KCl at 1073 K (experimental)$^{27}$ and (d) LiF-AlF₃ at 1103 K (experimental).$^{25}$

assuming the formation of CeOCl, the molality scale concentration of the oxide ion ([O$^-$]) may be obtained to be larger than 10⁻⁶ by taking the literature value of the solubility products $K_d(CeOCl)=[Ce^{3+}][O^2^-]=10^{-7.43}$ with the present Ce$^{3+}$ concentration of [Ce$^{3+}$] = 10⁻⁴. In this condition, the distribution coefficients of Am are thus expressed by Eq. (7).

On the other hand, in the second run, ZrCl₄ was added to the molten salts phase as the oxide ion scavenger in order to avoid the formation of oxochlorides, and the separation factor of Am and Ce was obtained to be about 100. In this case, the mass balance of Am and Ce was kept high (about 100%). Considering the formation of zirconium oxochloride and/or oxide, the [O⁻] value was obtained to be 10⁻⁵ to 10⁻⁸ by taking the literature value of $K_f(ZrOCl)=[Zr^{4+}][O^2^-]=10^{-11.3}$ and $K_f(ZrO_2)=[Zr^{4+}][O^2^-]=10^{-16.8}$ with the present Zr$^{4+}$ concentration of [Zr$^{4+}$] = 10⁻⁵ to 10⁻⁸. In this condition, the distribution coefficient of Am is expressed as Eq. (5). The results with and without the oxide ion scavengers were thus fitted to Eqs. (5) and (7), respectively, and the parameters were obtained as summarized in Table 3.

3.3 Comparison of the separation factors to those obtained in the different reductive extraction systems

In Fig. 2, the present result is compared with the experimental values in the different reductive extraction systems.$^{1,2,7}$ In parallel with the present experiment, some predictions of the distribution coefficients were performed for reductive extraction of MA’s.$^{8}$ The excess enthalpies and entropies of actinide and lanthanide trichlorides in molten chloride phase were found to be

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